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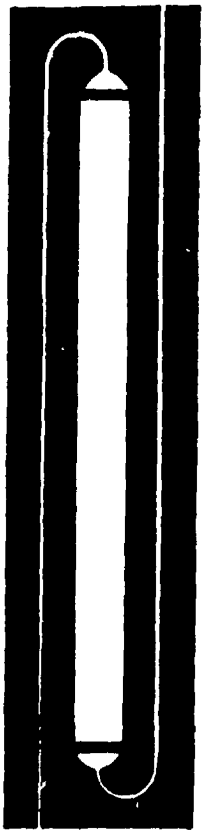
5th SYMPOSIUM ON ION EXCHANGE



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ABSTRACTS

AT THE LAKE BALATON
(HUNGARY)

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5th SYMPOSIUM ON ION EXCHANGE

ABSTRACTS

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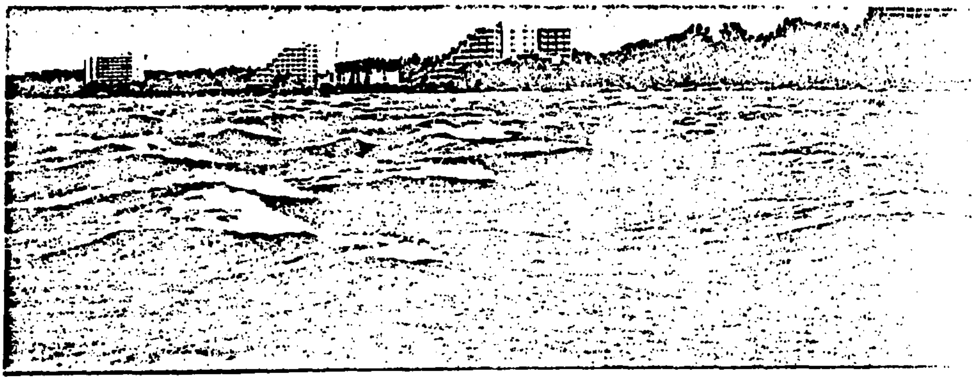

Edited by

P. HAJÓS Ph.D. and A. MARTON Ph.D.

University of Veszprém

Institute of Analytical Chemistry

HUNGARY

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THEORY OF ION EXCHANGE

ION-EXCHANGE; ION-CHROMATOGRAPHY, PHASE TRANSFER CATALYSIS AND CATALYZED RING OPENING POLYMERIZATION USING CROSS LINKED MACROCYCLIC POLYETHERS

E. Blasius and K.-P. Janzen

Fachrichtung Anorganische Analytik und Radiochemie, Universität des Saarlandes, 6600 Saarbrücken, FRG

Introduction

In the course of this lecture altemps will be made to present not only our experimental results but also the problems in using cross linked macrocyclic polyethers in ion-exchange, ion-chromatography, phase transfer catalysis and ring opening polymerizations.

Experimental

Monomeric macrocyclic polyethers can be converted to organic and inorganic matrices by several different methods: condensation, copolymerization and substitution reactions. The ability to form host guest complexes with inorganic salts and organic molecules offers a wide range of analytical and preparative applications.

Results and Discussion

About 60 mono- and bicyclic polyethers have successfully been build into polymers in our laboratory. Condensation resins and copolymers allow the separation of cations, anions and organic compounds. Unfortunately gel kinetic, swelling and low rigidity counteract rapid chromatographic separations. The best way using macrocyclic polyethers for fast separations (ion-chromatography) is the immobilisation on inorganic supports. Silica gel coated or modified by cyclic polyethers is used. Separations of cations, anions and organic compounds are possible in less then 15 min. Electrolyte free solvents (water or methanol) are eluents.

For phase transfer catalysis the condensation resin with dibenzo-18-crown-6 as anchor group is the best. It catalyses substitution oxidation, reduction, dichlorcarbene and ring opening polymerization reactions. The highest yield in phase transfer catalysis are up to 95%. For the ring opening polymerization the yields are nearly 80%.

ION-EXCHANGE, THERMAL STABILITY AND SORPTION STUDIES OF FAUJASITES WITH DIFFERENT Si/Al RATIOS

C-Y Li[1] and **L.V.C. Rees**[2]

1. Research Institute of Petroleum Processing,
   PO Box 914, Beijing, China.

2. Physical Chemistry Laboratories,
   Imperial College of Science & Technology, London, SW7 2AY, England.

Introduction

Dealuminated faujasites are very important cracking catalysts in petroleum refining. In this paper an attempt is made to obtain a better understanding of the location of cations as a function of Si/Al ratio and of some of the physical properties of these ion exchanged materials.

Experimental

Faujasites with Si/Al ratios of 1.23, 2 and 2.8 were obtained by hydrothermal synthesis of the appropriate gels. Using the sample with Si/Al ratio of 2.8 as starting material two dealuminated samples were prepared by slow extraction of Al with e.d.t.a. to give Si/Al ratios of 3.8 and 4.5. A third sample was dealuminated by treatment with $SiCl_4$ vapour at 420°C to give a Si/Al ratio of 7.0.

All samples were converted to their Na^+ forms, tagged with ^{22}Na, and ion-exchange followed by radiochemical analysis of either/and solution and solid phases.

Results and Discussion

Cs^+, NH_4, Ca^{2+} and La^{3+} exchange isotherms of the Na^+ form of the faujasites have been determined predominantly at 25°C but to a lesser extent at 65°C and 80°C. Linear correlations have been found between the number of framework Al atoms per unit cell and the number of Cs^+ ions sited in the supercages and in the small cavities. NH_4^+, Ca^{2+} and La^{3+} behaved differently showing somewhat different curved relationships in each case.

The thermal stabilities of the Na^+ and some of the above cation exchanged forms were determined. The thermal stability of low Si/Al ratio faujasites were found to be more sensitive to the cationic form and the degree of exchange than the high Si/Al ratio samples.

Thermogravimetric studies of water sorbed in the various cationic forms of the above faujasites showed that the number of water molecules per unit cell increased linearly with decrease in the Si/Al ratio. Ethanol and n-hexane demonstrated subtle differences from water in the Na-faujasites as a function of Si/Al ratio.

I.R. SPECTROSCOPIC AND THERMODYNAMIC DETERMINATION OF HYDRATION OF TRANSITIONAL METALLIC IONS IN SULFONIC ION-EXCHANGE RESINS.

N. Vesituluta*, M. Muzzi, A. Jenard and H.D. Hurwitz

Laboratoire de Thermodynamique Electrochimique, Faculté des Sciences,
Université Libre de Bruxelles, Bruxelles, Belgium.

We endeavour to show in this work that combined spectroscopic approaches and thermodynamic investigations provide valuable means of assessing various aspects of ionic interaction and hydration of Co^{2+}, Ni^{2+} and Cu^{2+} ions in sulfonic ion-exchange resins (Dowex 50W). These resins are taken at various degrees of cross linking (2, 4, 8 and 12% D.V.B.). In each case, comparison is made with the behaviour of the resins in their Na^+ form, and in some cases all the alkaline and alkaline-earth ion sequences are considered.

I. I.R. Spectroscopic Measurements

Experimental

The KBr pellets contain about 2 to 5% in weight of resins. Karl-Fisher titration and gravimetric determination are used to measure the water content of the resin. The water is removed by drying the pellet and keeping it under an ambient water free atmosphere in the I.R. sampling compartment. No ionic exchange between KBr and the resin is observed. The integrated absorbance of the band at 1415 cm^{-1} corresponding to the para-substituted benzene ring is directly proportional to the resin exchange capacity and serves as an internal reference.

Results and Discussion

(a) In situ determination of adsorption isotherms of water

In the presence of alkaline and of alkaline earth counter-ions, and for small numbers of water molecules per site ($\bar{n} \leqslant 5$), as afforded by the experimental technique, we ascertain the existence of a linear relationship between the integrated absorbance of the OH bending absorption band at about 1640 cm^{-1} and the amount of water per site ($\bar{n}$). The slope of this line decreases with an increasing degree of cross-linking of the resin. The linear relationship does not hold in the case of transition metal ions due to formation of coordinated complexes with water. The more stable the aqueous complex, the larger the deviation from the linear relationship. In the presence of alkaline and alkaline earth counterions, the linear relationship provides an easy way of deriving water absorption isotherms.

(b) Competitive effects between counter-ion hydration and counter-ion-SO_3^- interaction

The splitting around 1200 cm^{-1} of the antisymmetrical stretching vibration corresponding to the sulfonate groups is directly proportional to the interaction strength between the counter-ion and the polyanion. The water content of the polyelectrolyte influences this interaction which is independent of the degree of cross-linking at small amounts of water. The stretching vibration of the OH groups, corresponding to the water involved in ionic hydration, is found between 2000 and 3800 cm^{-1}. It allows the estimate of the strength of cation-water bonding and it reveals particularly the influence of the Jahn-Teller effect with Cu^{2+}.

II. Thermodynamic Measurements

Experimental

The ion-exchange resins are put in different homoionic (Na^+, Co^{2+}, Ni^{2+}, Cu^{2+}) and heteroionic (Na^+-Co^{2+}, Na^+-Na^{2+}, Na^+-Cu^{2+}) forms. Their water content is fixed by means of equilibration of the dry resins with wet atmospheres under isopiestic conditions at different temperatures (± 0.05°C) for periods lasting from 7 days to 40 days depending on the system.

Results and Discussion

The free energy of sorption of water is evaluated from the sorption isotherms according to the expression :

$$F = -RT \int_0^x \bar{n} \frac{dx}{x} + \bar{n}\, RT \ln x$$

where x is the relative water pressure ($x = p/p_c$).
The enthalpy of sorption of water is computed by graphical integration of the isosteric heat. The isosteric heat itself is derived from the temperature dependence of the free energy.
A treatment of these results allows the estimate of (a) the dissociation enthalpy of ionic pairs;

(b) the average integral enthalpy of hydration per water molecule in the first and second hydration sheet;

(c) the partial molar entropy of hydration of the cations.

These data indicate that the water molecules, first absorbed in the resin, contribute to the disrupture of the ionic pairs. The further absorbed water molecules are used to complete the first hydration sheet of the cation, which contains about 6 molecules for Cu^{2+} and Ni^{2+}, somewhat more for Co^{2+}, and 2.5 water molecules in the case of Na^+.

We have used some N.M.R. investigation with D_2O as the solvent, in absence of outside water, in order to check the existence of a first and second hydration sheet of these counter-ions.

A NEW EQUATION FOR THE CALCULATION OF THE THERMODYNAMIC ION EXCHANGE EQUILIBRIUM CONSTANTS

Marton, A. - Inczédy, J.

Department of Analytical Chemistry, University of Veszprém,
H-8201 Veszprém, Hungary

Thermodynamic equilibrium constant of the ion exchange reaction

$$nRA + B^{n\pm} \rightleftharpoons R_nB + nA^{\pm} \qquad 1$$

can be defined by the equation

$$K^T = \frac{\bar{a}_B \cdot a_A^n}{\bar{a}_A^n \cdot a_B} = \frac{\bar{x}_B \cdot a_A^n}{\bar{x}_A^n \cdot a_B} \cdot \frac{\bar{f}_B}{\bar{f}_A^n} = K' \cdot \frac{\bar{f}_B}{\bar{f}_A^n} \qquad 2$$

where a and x are the activity and the equivalent fraction, $\bar{f}$ is the resin phase activity coefficient of the component given and K' is the experimentally accessible selectivity coefficient. If the exchange reaction is considered as a formation of a mixture of concentrated electrolyte solutions then the excess free energy of the ion exchanger phase can be approximated as

$$\Delta \bar{G}^E = RT \cdot \bar{x}_A \cdot \bar{x}_B [\bar{g}_0 + \bar{g}_1(\bar{x}_A - \bar{x}_B)] \qquad 3$$

where $\bar{g}_0$ and $\bar{g}_1$ are parameters characterising the electrostatic interactions between the components of the mixed electrolyte solution of a given ionic strength. Equation (3) was, in fact, derived by Friedman [1] for the calculation of the excess free energy change of the formation of a two component mixture of highly concentrated electrolyte solutions.

By making use of the above function equations can be derived for the calculation of the thermodynamic equilibrium constant (K^T) of the ion exchange reactions. Contrary to the generally used equations the derived relationships contain parameters characteristic for the behaviour of the concentrated electrolyte solutions of the resin phase. With these parameters the ln $K'-\bar{x}_B$ functions are described in an adequate way. The derived equations can always be used for the calculation of K^T whenewer the experimentally obtained ln $K'-\bar{x}_B$ functions can be approximated by a linear or a quadratic polynomials.

The lecture will be concerned: with the discussion of the equations corresponding to those limiting cases when $\bar{g}_1 > 0$, $\bar{g}_1 < 0$, $\bar{g}_o = 0$, $\bar{g}_1 = 0$ and $\bar{g}_o = \bar{g}_1 = 0$; with the relationship between our equation and the Gaines-Thomas as well as the Högfeldt equation; with the relative importance of the $\bar{g}_o$ and $\bar{g}_1$ parameters and finally; with the dependence of $\bar{g}_o$ as a function of the resin crosslinking and the size of the exchanging $B^{n\pm}$ ion.

1. Friedman, H.L.: Ionic Solution Theory, Interscience New York, 1962, p. 225.

Respective Influence of Thermodynamical and Diffusional Phenomena on the Saturation Rate of Ion Exchange Resins

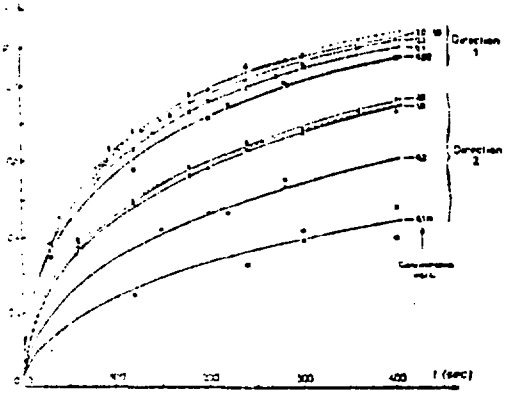
R.M. NICOUD, D. SCHWEICH
Laboratoire des Sciences du Génie Chimique
C.N.R.S.-E.N.S.I.C., 1 rue Grandville, 54000 Nancy, France

Introduction

Numerous kinetic investigations have shown that the parameters determined with the classical ion exchange kinetic models greatly depend on the experimental conditions (normality, exchange direction). Our goal consists in showing that the equilibrium properties of the resin-solution system must be taken into account to model the saturation curves.

Experimental Support

J.A. DODDS and D. TONDEUR (1) have obtained the following saturation curves for the Ca/Na exchange process by the shallow bed technique :



direction 1
Ca+Res-Na = Res-Ca+Na

direction 2
Res-Ca+Na = Ca+Res-Na

At a given normality, the exchange rate is higher when the divalent ion is entering. The influence of normality is very low for direction 1 whereas it is very important for direction 2.

Classical Interpretation

At a given high normality No, the difference between direction 1 and 2 is attributed to internal kinetic limitation. This is modeled with the Nernst-Planck model, assuming the grain is an homogeneous medium where total Donnan exclusion prevails. All the cations having their own diffusion coefficients are supposed to be mobile. This model doesn't explicitely take the selectivity into account.

The influence of the normality is attributed to an external kinetic limitation. HELLFERICH (2) has given a criterion allowing the estimation of the rate determining step.

Shortcomings

Though the Nernst-Planck model is able to fit the experimental curves obtained at high normality, some paradoxes remain :

- contrarily to the observations in bulk solution, this model leads to diffusion coefficients of divalent ions 10 to 15 times lower than the diffusion coefficient of monovalent ions. This result can't be explained by sterical effects.

- in the high concentration range where the model explains the experimental results, the total Donnan exclusion assumption is not valid.
- this model assumes an electrical potential gradient and electroneutrality. These two assumptions are incompatible with the POISSON equation.
- what diffusion coefficient must be used in the HELLFERICH criterion ?

Propositions

The influence of the valencies on the diffusion coefficient is explicitely attributed to the selectivity. Two limiting models are proposed :

1. The normality of the solution and the exchange capacity of the resin N̄ are of the same order of magnitude : Donnan exclusion is ignored. The model relies on the following assumptions :

- the grain is a porous two phase medium
- the normality of the liquid filling the pores equals the external normality
- thermodynamic equilibrium is reached between the cations contained in the pores and the cations fixed on the matrix
- the fixed cations are not involved in the diffusional process
- all the cations have the same diffusion coefficient
- external limitation is neglected.

This model gives the difference in the saturation rates with a single diffusion coefficient, but is doesn't give the asymetrical influence of the normality.

2. The normality No is lower than N̄, the anions are completely excluded : This model takes into account the competition between external and internal diffusion. The assumptions are :

- the interface between the resin and the solution behaves as a selective membrane. The resin compartment is supposed to be an homogeneous phase at the normality N̄. The thermodynamic equilibrium is reached at the interface.
- all the cations contained in the grain are mobile with the same diffusion coefficient.

This model gives the asymetrical influence of the normality, when the equilibrium is modeled with a mass action law. The influence of the direction is given when external limitation is not negligible.

Conclusion

The two models show that the sensitivity of the saturation curves to the normality and exchange direction can be explained by the selectivity and Donnan exclusion, with a single mean diffusion coefficient. Since selectivity and Donnan exclusion can be measured easily, this would allow to extrapolate laboratory kinetic data to industrial situations where other hydrodynamic conditions prevail. However, a more sophisticated approach should be developped to take into account partial Donnan exclusion.

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THO-06

ION EXCHANGE EQUILIBRIA OF ALKALI METAL IONS/HYDROGEN IONS ON TITANIUM(IV) AND TIN(IV) ANTIMONATES

M. Abe[1], R. Chitrakar[1] and N. Furuki[2]

1. Department of Chemistry, Faculty of Science, Tokyo Institute of Technology, 2-12-1, Ookayama, Meguro-ku, Tokyo 152, Japan

2. Mitsubishi Chemical Co. Ltd., Kurosaki, Yahata, Kita-kyushu 806, Japan

Introduction

Some of the synthetic inorganic ion exchangers exhibit an extremely high selectivity for certain elements or group of elements. Both of titanium(IV) antimonate(TiSbA) and tin(IV) antimonate (SnSbA) behave as cation exchangers with good stability of most of chemical reagents. These antimonates showed an unusual selectivity for alkali metal ions; $Na^+ < K^+ < Rb^+ < Li^+ < Cs^+$ on TiSbA, and $Na^+ < K^+ < Rb^+ < Cs^+ \ll Li^+$ on SnSbA(1). This behavior can be applied to the removal of Li^+ from seawater and hydrothermal water(2). It is of considerable interest that these exchangers show an extremely high selectivity for lithium ions while a normal sequence of selectivities for alkaline earth metal ions; $Mg^{2+} < Ca^{2+} < Sr^{2+} < Ba^{2+}$(3). The selectivity of alkali metal ions on the SnSbA depends strongly on their concentrations, as reported previously(1).

This paper describes a study of the ion-exchange equilibria of the system of alkali metal ions/H^+ over various exchanging compositions at an ionic strength of 0.1, from which the appropriate thermodynamic data may be derived, in order to interpret the selectivity of these exchangers.

Experimental

TiSbA or SnSbA was prepared by hydrolysis of a mixed solution of titanium(IV) or tin(IV) chloride and antimony(V) chloride at 60-80 °C, and then followed by washing and drying. The samples were ground and sieved to 100-200 mesh size. Identification and characterization of SnSbA was carried out by powder X-ray diffraction analysis with a JEOL X-ray diffractometer Model, JDX-7E, with Ni-filter Cu Kα radiation, and thermal analysis with a Rigaku Denki thermoflex Model 8001.

Ion exchange equilibria: In the forward reaction, the SnSbA (0.10g) in H^+ form was immersed in 10.0 ml of a mixed solution of varying ratio of alkali metal nitrate/ nitric acid in a sealed glass tube with intermittent shaking at 30 ± 0.5, 45 ± 0.5 and 60 ± 1°C. In the reverse reaction, ion-exchanged SnSbA corresponding in weight to 0.10g of the SnSbA in its H^+ form was immersed in 10.0 ml of a mixed solution with the same ionic strength. The concentration of metal ions and H^+ in the solid and solution phases were deduced from the change between initial and equilibrated concentration of metal ions in supernatant solution.

The thermodynamic equilibrium constant can be evaluated by using the simplified Gaines-Thomas equation by assuming that the change of water content in the exchanger and the entrance of anion from the solution phase are negligible. The thermodynamic values, ΔG°, ΔH° and ΔS°, were calculated in the usual way.

Results and Discussion

The exchangers obtained were identified by X-ray diffraction analysis, thermal analysis and IR spectra. The results agree well with those of our previous works(3,4). The crystallite size of the SnSbA was found to be 41 Å by using the Scherrer's equation from a plane (110). The empirical formula calculated by the chemical analysis was found to be $TiO_2 \cdot 0.32Sb_2O_5 \cdot 1.61H_2O$ and $SnO_2 \cdot 0.94Sb_2O_5 \cdot 4.95H_2O$ for samples used, respectively.

The isotherms for the reverse exchange reaction are performed at 30 °C and can be plotted on the curves of the forward reaction. Thus, reversible exchange reactions are established and no hysteresis effect is observed throughout the entire range studied. The plot of $\ln K_H^M$ vs $\bar{X}_M$, which is referred to as a Kielland plot, can be approximated to two straight lines with a break point at different equivalent fractions. The break points of the $\bar{X}_M$ are found to be 0.04 for Li^+ and 0.14 for other alkali metal ions on SnSbA, indicating the presence of two different exchange sites. The similar behavior can be observed on the TiSbA. The sequence of the values of $(\ln K_H^M)_{\bar{X}_M \to 0}$ is the same as that of the selectivity of for alkali metal ions in micro-amounts. The $\ln K_H^M$ increases rapidly with decreasing $\bar{X}_{Li}$ lower than the inflection point. The results of $\ln K_H^M$ vs $\bar{X}_M$ suggest that there are present specific sites where Li^+ can be accepted but other alkali metal ions can not enter. The selectivity sequences in a 0.1M alkali metal salt solution showed $Na^+ < Cs^+ < K^+ < Rb^+ < Li^+$ on TiSbA and $Cs^+ < Rb^+ < K^+ < Na^+ < Li^+$ on SnSbA, respectively. In order to interpret the selectivities in the infinitesimal concentration of alkali metal ions, hypothetical equilibrium constant in logarithm scale at 25 °C, $(\ln K_H^M)_{\bar{X}_M \to 0}$, was evaluated by extrapolating to "zero loading" of the metal ions. From these values the hypothetical thermodynamic data was calculated by usual way.

The high selectivity coefficient of Li^+ can be interpreted in the terms of both contributions of a highly positive value of $(\Delta S^\circ_{ex})_{\bar{X} \to 0}$ and a positive value of $(\Delta H^\circ_{ex})_{\bar{X}_M \to 0}$. The entropy producing process for Li^+/H^+ may be due to net transfer of some water molecules from exchanger to the solution phase.

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[illegible] WAY TO REPRESENT METAL-RESIN COMPLEX EQUILIBRIA

J. Szabacka

Department of Analytical Chemistry, University of
Veszprem, Hungary

Introduction

In evaluating the stability constants of metal-resin complex equilibria the difficulty lies in the lack of expressions describing the equilibrium hydrogen and metal ion concentrations in the resin phase (1).

These equilibrium concentrations can be calculated from experimentally measurable quantities by taking into account that the complex forming reaction is always accompanied by an ion exchange process (2). This accompanying process has to be postulated because the complexation of the metal ion is, in fact, an uptake of ν positive charges, which should be compensated by a simultaneously occuring ion exchange process to preserve the electroneutrality of both phases.

The metal ion concentration in the resin phase can be calculated by the equation:

$$(M^{\nu+}) = [M^{\nu+}]\left(\frac{(G)}{[G]}\right)^{\pm\nu}$$

where $(M^{\nu+})$ and $[M^{\nu+}]$ are the molalities of the metal ions in the resin and the solution phases, respectively, (G) and $[G]$ are the molalities of the ions which take part in the ion exchange process.

The sign of the exponent is

+, when a cation exchange and

–, when an anion exchange preserves the electroneutrality.

For the calculation of the hydrogen ion concentration the c
equation holds ($\gamma = 1$).

Experimental

The chelating resin used in this study was commercially available from the firm Reanal (Budapest, Hungary) under the trade name Ligandex-E. In this resin the ethylene-diamine-triacetic acid active groups are covalently bound to a lightly cross-linked styrene-divinyl benzene matrix.

To obtain equilibrium data static batch experiments were made. In the resin phase the molalities of the species were referred to the water content of the resin, determined according to (3).

The stability constants of the different metal-resin complexes were calculated and compared to those of the N-benzyl-ethylene-diamine-triacetic acid which is the water soluble monomer of the resinous active groups.

The suggested way of calculation is justified by the reasonable agreement between the metal stability constants of the anchored and that of the water soluble ligands.

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THO-08

REACTION IN ION EXCHANGERS. APPARENT STABILITY CONSTANTS OF COMPLEXES IN RELATION WITH SALTING-IN/OUT EFFECTS .

M.Métayer, D.Langevin, B.Pollet, M.Hankaoui and M.Labbé.
UA 500, Faculté des Sciences et des Techniques, Université de ROUEN, F-76130 Mont-Saint-Aignan.

In ion exchange resins , many examples of formation of products ST^z , $S_mT_n^{nz}$ by fixation of the non ionic compound S on a counter ion T^z are known .Often S is a ligand and T^z a complexing ion. Coupled with diffusion, these reactions can facilitate extraction or transport of the permeant S through ion exchange membranes. Somes examples are found in the literature but quantitative relations between measured fluxes and typical properties of ion-exchange materials are not usually shown.

We have already modelled facilitated extraction of dissolved ammonia ($S=NH_3$) through cation exchange membrane using H^+ as carrier. Distribution of ammonia between membrane and solution (salting-in/out effect) and H^+/NH_4^+ on exchange isotherm are taken into consideration. Facilitated extraction and transport have now been extended to other systems through a) cation ($S=NH_3$ and $T^z=Ag^+$ with ion exchanger in $Ag^+ + NH_4^+$ form) and b) anion ($S=CH_3CO_2H$ and $T^z=OH^-$, S=boric acid and $T^z=OH^-$ (*) ,borate and polyborate ions) exchange membranes .

Prior to modelling of these facilitated extractions and transports, the purpose of this paper is to study in various ion exchange membranes a) distribution of substrate NH_3 and isotherms for the NH_4^+/Ag^+ or $NH_4^+/Ag(NH_3)_n^+$ exchange (cation exchangers)
b) distribution of acetic or boric acids, isotherms for the acetate or borate/OH^- exchange and formation of polyborates (anion exchangers). In particular a relation between salting-in/out effects and apparent stability constants of complexes (NH_3 and ammines, boric acid and polyborate ions),is shown.

For example, with ammonia, Nafion membranes exhibit a salting-in effect which stabilizes ammonia-silver complexes in ion exchangers. Equilibria with $NH_4^+ + Ag^+ + NH_3$ mixing show an NH_4^+/Ag^+ selectivity inversion (selectivity in favour of NH_4^+ when $pNH_3 > 4$, in favour of $Ag^+ + Ag(NH_3)_n^+$ when $pNH_3 < 3$).

Proposed interpretations are corroborated by complementary membrane conductivity measurements.

(*) In these particular cases,the products are formed with elimination of a molecule of water.

THEORY OF DIFFUSION ION EXCHANGE KINETICS IN COMPLEXING ION EXCHANGERS

A.I.Kalinitchev, T.D.Semenovskaya and E.V.Kolotinskaya

Institute of Physical Chemistry, Moscow, USSR

Introduction

The Helfferich-Tunitsky approach using one differential mass balance equation in which ion fluxes are described by the Nernst-Plank relation is not applicable for the ion exchange kinetics accompanied by diffusion of coions (Y) into grain and formation of weakly dissociating compounds between counter ions (B,A) and fixed groups (R) of exchanger.

Our intraparticle diffusion kinetic model (1.),(2.) describes sorption system with two degrees of freedom and takes into account the equlibrium of association reaction (complex formation). The influence of crossing interference kinetic effects on ion interdiffusion process is characterized in the model by mutual dependences of diffusion fluxes of i,j-components. The diffusion fluxes of B,A,Y- ions in this model are characterized by the generilized Fick relation, where the effective diffusion coefficients D_{ij} depend on the concentrations of counterions and coion. The kinetic process is described in the model by the system of two nonlinear diffusion-type equations in partial derivatives.

The computerized analyses of the diffusion process allow to come to important conclusions about influence of various parameters of the model on the ion exchange kinetics accompanied by complex formation. The following parameters of the model were used - the individual diffusion coefficients of ions (D_B, D_A, D_Y); the dissociation constants (K_{RB}, K_{RA}) of complexes RB,RA; the concentration of fixed exchange groups (a_0); the concentration of a solution (C_0).

The influence of exchange selectivity (K_{RA}/K_{RB}) and ions mobility (D_B, D_A, D_Y) on the ion exchange kinetics in complexing ion exchanger have beeh discussed. The theoretical deductions have been verfied experimentally.

Experimental

Experiments have been performed in two directions in accordance with the theoretical analyses. The kinetic dependence $F(t)$ was measured in a thin ionite layer and concentration distributions of free (C_i) and bound (a_{RB}, a_{RA}) ions in spherical particle were studied by using a spherical particle sector model. The model comprised a cone made up of separate rings and filled with fine-ground swollen ionite.

The effect of the ratio of the individual diffusion coefficients and of the exchange selectivity on the kinetic dependences in carboxylic (KB-4) and vinylpyridinecarboxylic (VPC) ionites for hydrogen-metall and metall-metall exchanges has been studied for a large number of the real ion exchange systems.

Results and Discussion

The concentration profiles ($(C_B, a_{RR}, C_A, a_{RA}, C_Y$) in ionite particle depend on the correlation of D_A/D_B factor and of K_{RA}/K_{RR} factor. The selectivity factor (K_{RA}/K_{RB}) determines the form of exchange isotherm in ionite for weakly dissociating complexes ($K_{Ri}/C_0 \ll 1$). In presented model the kinetic process accompanied by association is characterized by both D_A/D_B and K_{RA}/K_{RB} factors. This result on one side is in contrast with physical sorption kinetics (where only the form of isotherm determines concentration profiles of sorbate in grain) on the other with kinetics of usual ion exchange (where the concentration profiles C_i and the rate of the exchange are determined by D_A/D_B factor).

The sharp concentration profiles C_B, a_{RB} of the entering ion B in particle are formed if both factors promote sharpening of concentration front, i.e. if the relations $D_A/D_B > 1$ and $K_{RA}/K_{RB} > 1$ hold. It is shown that the exchange rate doesn' depend on the value of the D_Y diffusion coefficient in the investigated region of parameters.

The results of the theoretical analyses determine the limits of the approximate analytical solution presented in our paper (1.), i.e. it is suitable for quantitative estimation of the exchange rate for the case of convex isotherm of entering B-ion ($K_{RA}/K_{RB} > 1$) and if the relation $D_A/D_B \geqslant 1$ holds.

The distributions of C_i, a_{Ri} concentrations in the spherical particle sector model confirm the conclusions of theoretical analyses and the adequacy of the proposed theoretical model.

It is shown that for nonideal ion exchange systems a distorted view of the role of external and intraparticle diffusion factors results from applying the Helfferich-Tunitsky criterion since the diffusion coefficients of the criterion can vary significantly while the direction of ion exchange alters. These results are not taken into account previously for ion exchange in complex forming and weakly dissociating macroporouos ionites where the presence of free and bound ions don't exclude. It is shown that the very slow exchange rate in particle of macroporous ionite may be explained only by the influence of ion transfer.

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ThP-01

PROPERTIES OF Zr(IV) AND Hf(IV) IONS ON DOWEX 50-CATION EXCHANGER : AN EQUILIBRIUM AND PROTON-NMR STUDY

W. D'Olieslager and D. Comeyne

Katholieke Universiteit Leuven, Laboratorium voor Radiochemie,
Celestijnenlaan 200G, B-3030 Heverlee, Belgium

Introduction

Zirconium and Hafnium are strongly absorbed on sulphonated polystyrene resins (Dowex 50 W). The unusual high selectivity at high loading of the resin contrasts with a very slow exchange rate. A proton NMR study indicates that both Zr(IV) and Hf(IV) ions are almost completely dehydrated in the cation exchange resin.

Results and Discussion

It was shown by saturation of Dowex 50 cation exchanger that zirconium and hafnium are absorbed as divalent ions (e.g. $Zr(OH)_2^{2+}$ or a polymeric form). The selectivity constants of the exchange $Zr(IV)/H^+$ and $Hf(IV)/H^+$ were obtained from batch equilibration experiments. The concentration equilibrium constants, corrected for the activity coefficients in the aqueous phase (1), increase by a factor of 10^6 with increasing loading of the ion exchanger as is shown for Zr(IV) in fig. 1.

The thermodynamic equilibrium constant (K_a) was calculated using the method of Gaines and Thomas (2) to correct for the activity coefficients in the resin phase :

$$\ln K_a = -1 + \int_0^1 \ln K_c . d\, \beta_H$$

with β_H the equivalent fraction of H^+ ions in the ion exchanger. The results, summarized in the table indicate that the large decrease of ΔG^o is due to a very large increase of the entropy (ΔS^o) since ΔH^o is positive. The values of ΔH^o and ΔS^o are much larger than the data for other di- and trivalent ions as reported in the literature, they are consistent with a mechanism that involves the dehydration of these metal ions in the ion exchanger.

Table

	K_a (298 K)	ΔG^o(kJ/mole)	ΔH^o(kJ/mole)	ΔS^o(J/mol.K)
$Zr(IV)/H^+$	7,8 10^3 ($\pm$ 0,2)	- 22,2	41	212
$Hf(IV)/H^+$	5,1 10^3 ($\pm$ 0,2)	- 21,1	32	178

Proton NMR-spectra of Dowex 50, in the H^+-form or saturated with metal ions, show two resonance peaks. The chemical shift (δ) of the peak due to hydration water of the cation depends on the electric field strength of the cation ($Z/(R+a)$) in the resin as shown in fig. 2. The data agree well with these in aqueous solution (the solid line in the figure) except for Zr(IV) and Hf(IV). The effective hydration number (h) of the different cations was obtained from the temperature dependence of the chemical shift (3). The values thus obtained for the cations in the resin phase generally agree well with the data in the literature; the hydration number of Zr(IV) and Hf(IV) however are very small ($0 \leqslant h < 0,4$) and support the conclusion drawn from the thermodynamic data.

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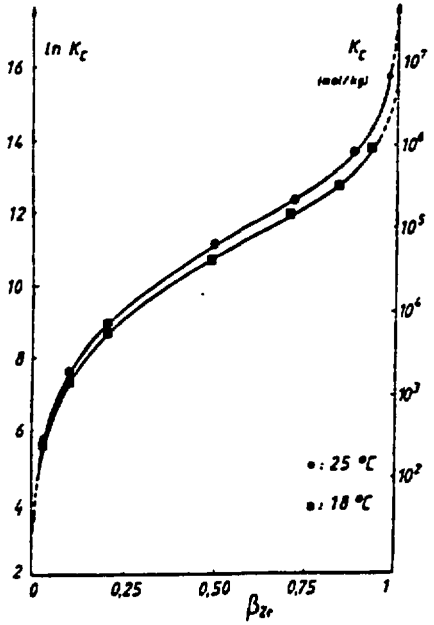

Fig: 1

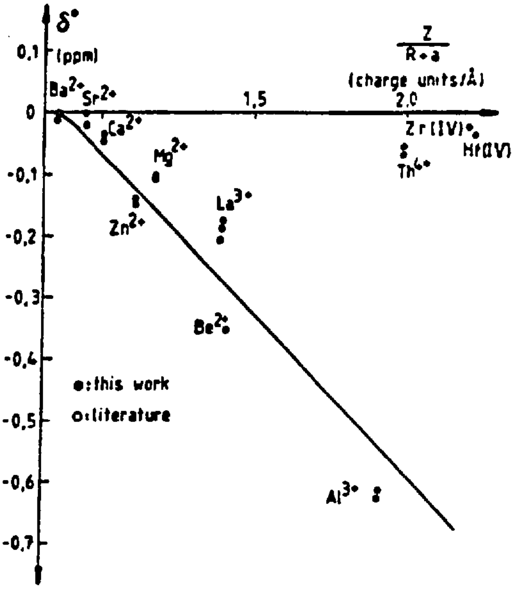

Fig: 2

Fig. 1 : Selectivity constants of Zr(IV) on Dowex 50 Wx8, corrected for activity coefficients in the aqueous phase, as a function of the equivalent fraction in the resin (β_{Zr}).

Fig. 2 : Proton chemical shift of metal ions in Dowex 50 Wx8 as a function of the electric field parameter (Z/(R+a)); the full line is the correlation obtained in aqueous solutions.

STUDY OF EQUILIBRIA IN A THREE PHASE SYSTEM CONTAINING ION EXCHANGE RESIN, ELECTROLYTE SOLUTION AND GAS

Marton, A. - Inczedy, J.

Department of Analytical Chemistry
University of Veszprém, H-8201 Veszprém, Hungary

The removal of nitrate ions from drinking water can efficiently be carried out on a HCO_3^--form anion exchange resin. The process is economic only if the above resin is available (the spent resin can be regenerated) at a reasonable cost. According to our experiments an economic regeneration can be achived if the spent resin is first converted into OH^--form then to HCO_3^--form by a treatment with carbon dioxide gas [1].

The lecture is concerned with the derivation of the equations used for the quantitative description of the equilibria in a three phase system containing $ROH_{(s)}/KHCO_{3(l)}/CO_{2(g)}$. The presented system of equations are also used to calculate the equilibrium composition of the solution and resin phases as a function of the pressure of the carbon dioxide gas. The theoretically calculated and the experimentally obtained degrees of resin converions ($\overline{x}_{HCO_3^-}$) are in a good agreement. From kinetic point of view, the concentration of the $KHCO_3$ solution and the pressure of the CO_2 gas seems to play an important role.

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THP-03

THERMODYNAMIC DATA FOR SOME ANION EXCHANGE REACTIONS

Marton, A. - Inczédy, J.

Department of Analytical Chemistry
University of Veszprém, H-8201 Veszprém, Hungary

For a considerable group of cation exchange reactions there is a well known linear relationship between e.g. the ΔG^o values and the reciprocal crystallographic radius of the cations. A similar, generally experienced relationship does not exist, however, for a larger set of different anion exchange reactions. When the ln K^T or the ΔG^o values are plotted against either the crystallographic or the hydrated anionic radius the obtained functions do not show any easily understandable relationship.

Thermochemical parameters (K^T, ΔG^o, ΔH^o and ΔS^o) for the anion exchange reaction

$$RA + B^- \rightleftharpoons RB + A^-$$

were determined by static equilibrium and precision calorimetric measurements at 25 °C. ($A^- = Cl^-$; $B^- = ClO_4^-$, I^-, Br^-, NO_3^-, HCO_3^-, ClO_3^-, BrO_3^-, IO_3^- and OH^-).

It has been found that for the above mentioned exchange reactions the ΔG^o and ΔH^o values show a well defined linear relationship as a function of the so called thermochemical radii of the exchanging B^- ions. These latter parameters were calculated for the anions interested by the Kapustinskii equation using relaiable values of the lattice energies.

The experienced linear relationship suggests that inside the resin the concentration is so high that the electrostatic circumstances, as it were, preplays the situation prevailing in a solid crystalline phase.

THP-04

THE INFLUENCE OF PRE-ADSORBED MOISTURE ON EQUILIBRIUM AND THERMODYNAMICS OF HYDRATION OF ANION EXCHANGE RESINS

B.M.Katz, G.M.Shekhaleeva, F.B.Sherman

Odessa State University Physics Research
Institute, Odessa, USSR

Introduction

At present, a wealth of experimental data concerning water vapor sorption (hydration isotherms) by ion-exchange resins has been accumulated using sorption, spectral and other techniques. Hydration isotherms are usually interpreted assuming that the initial resin samples are pre-dried in vacuum at a temperature that keeps their structure intact with the water having been removed. It is common knowledge that thermolabile anionites dried under such conditions still retain 2 to 4 percent of firmly bound residual water. Conditions for obtaining absolutely dry anionites without changing their structure during deamination and degradation remain to be elucidated, and that is why some aspects of determination of pre-adsorbed (residual) moisture (H) call for systematic investigation.

There is also lack of data on the relationship between H values and sample pre-treatment conditions, the characteristics of the polymer matrix and the nature of the ionogenic groups in ion-exchange resins.

Results and Discussion

An aquametric micro technique is proposed for measuring the pre-adsorbed (residual) moisture (H_n) and equilibrium moisture content (H) in macroporous weakly basic anionites and their gel analogues directly in the course of derivation of isotherms of water vapor sorption in a vacuum system, using a modified McBain balance.

The absolute values of H and H_n were determined by direct titration of a weighed sample of the anionite with a Fischer reagent after equilibrium hydration had been achieved at different relative water pressure (p/p_s). The paper shows the relationship between the H_n value and the sample pre-treatment conditions, characteristics of polymer matrix (basicity and porocity) and the nature of the ionogenic groups in ion-exchange resins. It has been established that in terms of the BET theory hydration parameters and specific anionite surface depend largely on the H_n value. For instance, in the case of strongly bases anionites AB-I7I and AB-I7-8 which contain quaternary ammonium groups, the degree of hydration in the BET region may be larger of effective capacity (h) of the BET monolayer, the value of h being apparent. It is shown that the specific surface calculated for water (S_{H_2O}) from aquametric isoterms using the BET equation obviously corresponds to the actual hydrophilic surface as compared to the S_{H_2O} value calculated from gravimetric isotherms.

DIELECTRIC RELAXATION IN ZEOLITES

Szász, Á. - Sayed Sabet Abd El Rehim - Liszi, J.

Department of Analytical Chemistry, University of Veszprém,
H-8201 Veszprém, POB 158.

Dielectric studies have been made over the range of 200 Hz to 1 MHz and 260 K to 298 K in Na^+, K^+, Rb^+, Cs^+, NH_4^+ and $CH_3NH_3^+$ forms of synthetic Linde A-type zeolite. Ion exchange was carried out via batch method, the degree of exchange was not complete in several cases. The water content of the samples was controlled by standardized drying. Permittivity and loss factor were measured in suspensions of zeolite in paraffine oil.

The relaxation process was described by the Kirkwood-Fuoss-relation and the distribution parameters (β and ω_{max}) were determined. Arrhenius activation energy of the process was calculated from the temperature dependence of ω_{max}. Comparison of the effective dipole moment and that of derived from the Onsager' theory indicates relaxation of water in the investigated dispersion region.

A set of results are given in Figs. 1 and 2.

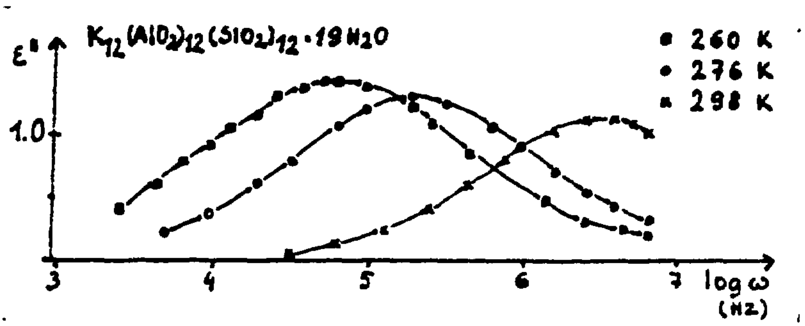

Fig. 1.

The imaginary part of the permittivity as a function of frequency and temperature.

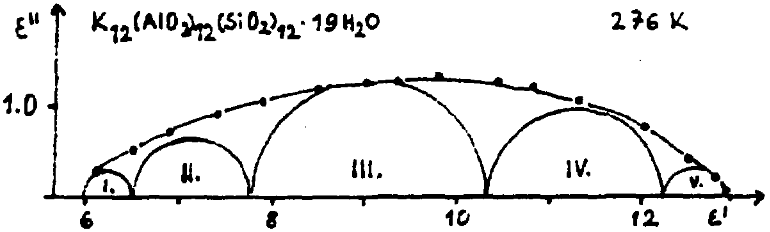

Fig. 2.

Cole-Cole plot for the K^+ form zeolite. The semicircles indicate Debye dispersions.

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THP-06

Separation of Exchange and Adsorption Processes in ^{45}Ca-bentonite/^{54}Mn^{2+} System

J. Kónya[1] and Á. Hargitai Tóth[2]

[1] Isotope Laboratory of Kossuth Lajos University, Debrecen, Hungary

[2] Chemistry Department of Bessenyei György Teacher's Training College, Nyíregyháza, Hungary

Introduction

It is important to determine at the thermodinamic and kinetic evaluation of the parameters of ion exchange processes whether the reaction partners take part only in exchange or in other processes as well. In this work a theoretical interpretation is made for the separation of the ion exchange and other processes which are explained as adsorption processes. Our method is used for the exchange of mono- and bivalent cations[1]. In this work the surface processes between ^{45}Ca-bentonite and ^{54}Mn^{2+} are examined.

Experimental

Both the amount of ^{54}Mn^{2+} joint to the surface and the amount of ^{45}Ca^{2+} got into the solution are measured in order to decide whether the results of the theoretical calculation give a close picture to the reality. It is easyly carried out when we use radioactive ^{45}Ca-bentonite and ^{54}Mn^{2+} ions. 50 mg ^{45}Ca-bentonite is added to 20 cm^3 destilled water or to $CaCl_2$ solution is pipetted to the system at 0, 25 or 40 °C. After attaining the equilibrium the phases are separated and the activity of ^{45}Ca and ^{54}Mn as well as pH are measured. The amount of the adsorbed Mn can be calculated from the experiment as the difference between the amount of Mn joint to the surface and the amount Ca got into the solution.

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Results and Discussions

The sorption of Mn^{2+} ions can be described by an isotherm of Langmuir type:

$$\frac{c_{Mn}}{Ad\text{-}Mn} = \frac{1}{V}\,\frac{y}{x}\left(\frac{1}{\xi} + \frac{1}{z}\right)\left\{ c_{Mn^{2+}} + K\left[f\left(c_{Ca}\right)\right]\right\} \qquad /1/$$

c_{Mn} is the concentration in the solution, Ad-Mn is the amount of Mn joint to the surface, V is the volume of the solution, y and x are the activities of ^{54}Mn in the solution or on the surface respectively /as a part of the total activity/, ξ and z are the numbers of the active places of the exchange and adsorption, $K\left[f(c_{Ca})\right]$ is as follows:

$$K\left[f\left(c_{Ca}\right)\right] = K^{o}_{Mn}\left(1 + \frac{c_{Ca}}{K^{o}_{Ca}} \right) \qquad /2/$$

K^{o}_{Mn} and K^{o}_{Ca} are the solubility of the pure Mn-bentonite and Ca-bentonite. When we write down the Langmuir's equation of the exchange and the adsorption separately and take into consideration the law of mass action, the Equ. 1 has the following form:

$$\frac{Ad\text{-}Mn}{c_{Mn}}\left(1 + \frac{c_{Ca}}{K\left[f\left(c_{Mn}\right)\right]}\right) = z\,\frac{1}{c_{Mn} + K\left[f\left(c_{Ca}\right)\right]} +$$

$$+ K_{s} Ad\text{-}Ca\,\frac{1}{K\left[f\left(c_{Mn}\right)\right]} \qquad /3/$$

K_s is the selectivity coefficient. From the slope the number of the active places of the adsorption can be calculated. The theoretically and experimentally determined amounts of the adsorbed Mn are in a relatively good agreement.

ThP-07

STUDY OF KINETICS OF ION EXCHANGE IN TERNARY SYSTEM $Na^+ - Co^{2+} - Ni^{2+}$

J. Plicka, K. Štamberg, J. Cabicar, V. Spěváčková
Technical University of Prague, Faculty of Nuclear
Science and Physical Engineering,
115 19 Prague 1, Břehova 7, Czechoslovakia

Introduction

In the present work we have studied the behaviour of two components with very close properties (i.e. Co^{2+}, Ni^{2+}) in ternary system under unstationary conditions. The verification of the kinetic model based on equations of nonequilibrium thermodynamics was performed.

Experimental

The equilibrium and kinetic experiments were studied on the model system $Na^+ - Co^{2+} - Ni^{2+}$ - strong acidic cation exchanger OSTION KS 08. In each type of experiments binary and ternary ion exchanges ($\overline{Na}^+ - Co^{2+}$, $\overline{Na}^+ - Ni^{2+}$, $\overline{Ni}^{2+} - Co^{2+}$, $\overline{Na}^+ - Co^{2+} - Ni^{2+}$ respective - the bar denotes the initial form of ion exchanger) were studied. The initial composition of the solution for all kinetic experiments was 0.095 M $Co(NO_3)_2$ + 0.005 M $Ni(NO_3)_2$.

Kinetic Model

The Stefan-Maxwell equations were used for description of difusion of counterions in ion exchanger particle (rate controlling step). Using the assumptions generally acceptable for ion exchange on strong acidic cation exchanger (1) we obtained the following relations for difusional fluxes N_i of counterions in ternary system :

$$- N_1 = D_{11}\nabla C_1 + D_{12}\nabla C_2$$
$$- N_2 = D_{21}\nabla C_1 + D_{22}\nabla C_2$$

where the coefficients D_{ij} $(i,j = 1,2)$ depend on Stefan-Maxwell coefficients, charges and concentrations of all components in system.

Results and Discusion

The nine Stefan-Maxwell coefficients necessary for calculations of kinetics of ternary ion exchange were obtained from (i) the results of above mentioned binary ion exchanges, (ii) isotope exchange $\overline{Na}^+ - {}^{22}Na^+$ (2), (iii) literature data (3). The comparison of calculated kinetic curves with experimental ones are in good agreement. All realized experiments as well as all calculations confirmed that the ratio of nickel and cobalt is not constant during ternary ion exchange.

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THE KINETICS OF AMMONIA SORPTION ON CATION EXCHANGE RESIN IN Cu^{2+}-FORM

E.M.Katz, L.M.Kutovaya, V.Ya.Altshul
Odessa State University Physics Research Institute,
Odessa, USSR

Introduction

Studies of ammonia sorption on cation exchange resins are of interest because they are used for removal of ammonia from gaseous mixtures. A variety of processes exists where diffusion in porous resins is of interest too.

Experimental

Investigation was carried by means of vacuum adsorptional apparatus with McBain-Bakr's scales. The equilibrium sorption was measured at 298K, the pressure range was from 0 to I50 Torr, kinetics - at 2, 8 and 30 Torr. We used cation exchange resin KU-23 (IO, I5 and 30% cross-linking) in which the matrix was a copolymer of styrene and divinylbenzene and the ionized groups were sulphonate groups.

Results and Discussion

The sorption isotherms of ammonia by Cu^{2+}-form resin are shown in Figure I. They all have identical form which is

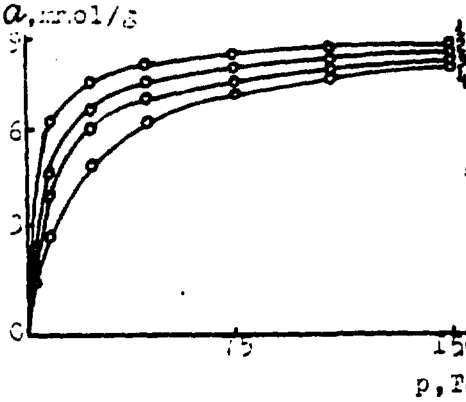

Fig.I. The sorption isotherms:
I-IO/60; 2-IO/IOO; 3-I5/IOO;
4-30/I50.

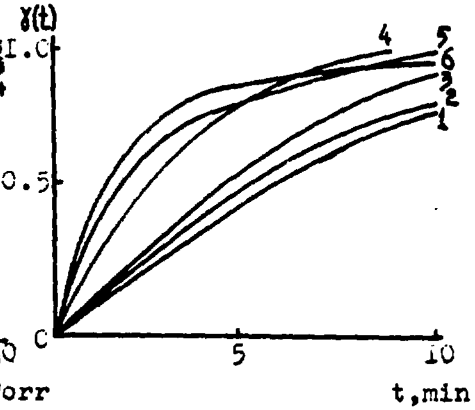

Fig.2. The kinetic curves.
I5/IOO: I-2;2-8;3-30 Torr
30/IOO: 4-2;5-8;6-30 Torr

analogous to Langmuir isotherm. The equilibrium sorption depends on the level of copper in sorbent only and doesn't depend on the cross-linking percentage.

For studies of sorption kinetics of ammonia we used I5/IOO and 30/IOO resin modifications. They had identical equilibrium sorption and differed only in cross-linking percentage. The kinetic curves $\gamma(t)$ are shown in Figure 2. It is obvious that the increase of pressure produces only the change of the process rate, but doesn't influence the character of the process in case of I5/IOO resin. But in case of 30/IOO resin the character of the process is changed at the final stage.

Table

Resin	p, Torr	$D_a/R_a^2\cdot IO^4$ s^{-I}	$D_i/R_i^2\cdot IO^4$ s^{-I}	$D_a\cdot IO^7$ cm^2/s	$D_i\cdot IO^{I4}$ cm^2/s
I5/IOO	2	2.54	2.29	2.52	2.29
	8	2.60	2.6I	2.76	2.6I
	30	4.II	3.65	4.08	3.85
30/IOO	2	4.53	451	4.40	45I
	8	7.98	69.3	7.92	69.3
	30	9.46	6.36	9.39	6.36

Values of kinetic parameters derived from the equations in "biporous" model (I) are listed in the table. Simbols are those as in (I). The kinetic curves and values of parameters permit to make the following conclusions. Diffusion in the transport pores is the limiting process at the initial stage. Diffusion in the micropores is the limiting process at the final stage. The pressure increase leads to the increase of the diffusion coefficient D_a. Diffusion into micropores doesn't contribute significantly to the equilibrium sorption provided the pressure is small. If the pressure is increasing the sorption kinetics of ammonia in case of 30/IOO resin has two stages. A first stage is observed during which only macropores sorption occurs followed by a much slower second stage during which macropore sorption is at equilibrium and only micropore sorption occurs.

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THP-09

ION-EXCHANGE MODELLING IN CONTAMINATED GROUNDWATER

L.Sovadina[1], P.Konosavskij[1] and I.Landa[2]

1. Mining Academy , Department of Hydrogeology
   Leningrad, Soviet Union

2. Geofond Praha
   Praha, Czechoslovakia

Introduction

Prognostic estimation of contaminants /pollutants/ in groundwaters is based on following systems of differential equations

$$n\frac{\partial Ca}{\partial t}+v\frac{\partial Ca}{\partial x}-D\frac{\partial^2 Ca}{\partial x^2}=0$$

$$\bar{n}\frac{\partial C_1}{\partial t}+v\frac{\partial C_1}{\partial x}-D\frac{\partial C_1}{\partial x^2}-\frac{C_1}{Ca^2}\bar{b}\frac{\partial Ca}{\partial t}=0 \qquad (1)$$

$$\bar{n}=n\frac{\bar{b}}{Ca}\;;\;\bar{b}=f(Q_v,K_{12},C_1,Ca)$$

where n-porosity;Ca,C_1-anion ;cation concentration;t-time, $\bar{b}$-coefficient;D-coefficient of diffusion. The equations express migration phenomena including an effect of both diffusion and ion-exchange.

Experimental

The exact analytical solution of the equation(1)does not exist at present. Therefore, the methods of mathematical modelling are applied in solving it. Variation methods in modifications of the method of finite elements /F.E./ or the method of finite differences /F.D./ are usually applied. The method of F.E. can be used when computers with comparatively large operational memory and speed are available..An advantage of the method of F.D. lies in better understanding of the physical analogies of starting equations, while the method of F.E. and even the Galerkin´s method are suitable for simple physical interpretations.

Our contribution summarizes our experience with the solution of the equation(1) by the method of F.D. using the integral-iterative Samarsij´s approach.We identify and explain some anomalous phenomena in ion-exchange discussed already by A.J.Valocchi et al./1981/. Algorithm of the solution of the basic equation (1) is verified by several test studies. Conditions of the optimum solution are defined. The conditions improved the method of modelling of ion-exchange generally in case of contaminated groundwater.

The results are demonstrated by the figures and tables.

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ION EXCHANGE MATERIALS

MO-01.

SYNTHESIS, STRUCTURE AND PROPERTIES OF NEW FIBROUS ION EXCHANGERS

V.S. Soldatov, A.A. Shunkevich, and G.I. Sergeev

Institute of Physico-Organic Chemistry of the Byelorussian Academy of Sciences, Minsk USSR.

Ion exchange fibrous materials open new technological possibilities in gas and liquid purification, preparative chromatography, extraction of valuable compounds from gaseous and aqueous media. Their main advantages compared to industrial granulous ion exchange resins are: a high rate of an ion exchange process (caused by a small diameter of monofilaments ranging from 3 to 50 mcm), a low and easily controlled resistance of the ion exchange filters to the flow of liquids and gases, the possibility of using in various physical forms such as column filters, conveyer belts, thin layers, etc. A small diameter and a uniform fibre thickness provide good chromatographic characteristics of these materials. Natural elasticity of the fibres permits retaining the integrity of an ion exchanger layer. It also provides constant geometric dimensions of the filtering layer in the column independently of the swelling of the ion exchanger in different ionic forms. The resistance of the filters to the flows can be easily controlled by density and the way of material packing.

The synthesis, structure, physico-chemical, mechanical and sorption properties of different new types of ion exchange fibrous materials (registered trade mark "FIBAN") are discussed in the lecture. They are represented by strong-base and strong acidic ion exchangers analogous to the spread granulous resins, carboxylic ion exchange fibres, weak and medium base anion exchangers with imidazoline functional groups, polyampholites and a number of special functionalized fibres. The applicability of these materials was illustrated by several examples such as removal of acidic impurities from air (SO_2, H_2S, etc.), removal of heavy metals from aqueous media (Hg, Pd, Cu, Cr(VI), etc.), chromatographic separation of alkali metals, halogenides, heavy metals, amino acids.

The studies performed show a high efficiency of fibrous ion exchangers of the FIBAN type.

110-02

SEPARATION OF PROTEINS BY HIGH-POROUS HYDROPHILIC ION EXCHANGERS

Takaharu ITAGAKI, Eiji MIYATA and Hiroshi KUSANO

Research Center of Mitsubishi Chemical Industries Ltd.,
Yokohama, JAPAN

INTRODUCTION

Separation and purification of various proteins by SEPABEADS® FP Series (Mitsubishi Chemical Industries) have been studied. SEPABEADS FP Series are based on a spherical hydrophilic high-porous polymer of vinyl-type monomers and have many advantages over conventional polysaccharide- or styrene-based ion-exchangers. SEPABEADS FP Series carrying various functional groups are suitable for chromatographic separation and purification of biological substances especially in large-scale, industrial processes.

EXPERIMENTAL

SEPABEADS FP Series used in this work are listed in Table I. The adsorption capacity for proteins was determined in batch processes. Protein concentration was determined photometrically (UV 280 nm).

RESULTS and DISCUSSION

As preparative chromatographic packings, SEPABEADS showed advantageous basic properties such as:

(1) Low irreversible protein adsorption.
(2) High stability against acids and alkalis (0.5 N HCl or NaOH at 40° C) as well as organic solvents.
(3) Stable swollen volume independent of pH and salt concentration (<10 %).
(4) Low compressibility due to high mechanical stability and low pressure drop (P=0.9 kg/cm^2·m-bed at LV:5 m/hr).

The type of pendant functional groups as well as the pore size distribution was found to be effective for a number of applications. For example, SEPABEADS FP-DA (diethylamino type) is most commonly used as a weakly basic anion-exchanger. Fig. 1 shows the effect of the pore size of FP-DA on adsorption capacity for proteins, indicating that size exclusion separation of proteins is easily accomplished by selecting

SEPABEADS of the appropriate pore size. Replacement of diethylamino group with other types of amino group caused a marked change in binding strength between the target proteins and the amino group (Fig. 2). As described above, SEPABEADS FP Series based on a high-porous hydrophilic rigid polymer can be easily adapted to preparative- or even industrial-scale separations of proteins. Further application data will be presented in the session.

Table I. Chromatographic packing materials.

	Functional Group	Pore Size (70-100Å)	(300-500Å)	(1000-2000Å)
SEPABEADS				
FP-HG	-OH	FP-HG20	FP-HG13	FP-HG05
FP-DA	$-N(C_2H_5)_2$	FP-DA20	FP-DA13	FP-DA05
FP-HA	$-NH(CH_2)_6NH_2$	FP-HA20	FP-HA13	FP-HA05
FP-CM	$-CH_2COOH$	FP-CM20	FP-CM13	FP-CM05
FP-BL	Cibacron Blue 3G-A		FP-BL13	
FP-OT	$-O(CH_2)_8H$		FP-OT13	
FP-ZA	$-NHCH_2-C_6H_5$		FP-ZA13	FP-ZA05
FP-CL	$-N(CH_2COOH)_2$	FP-CL20	FP-CL13	

Standard particle size : 120μm in diameter.

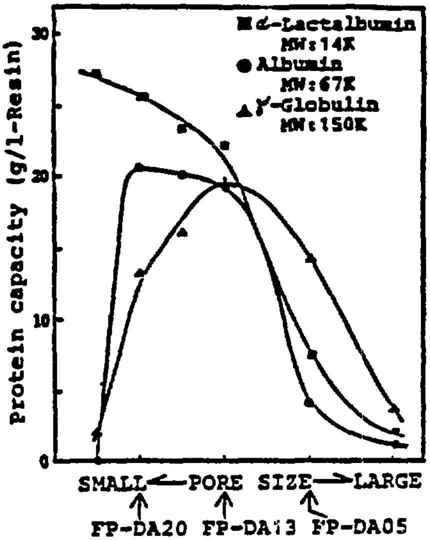


Fig.1 Pore size of FP-DA vs. protein capacity (in 0.1M Tris-HCl buffer of pH 7.50 at 10°C)

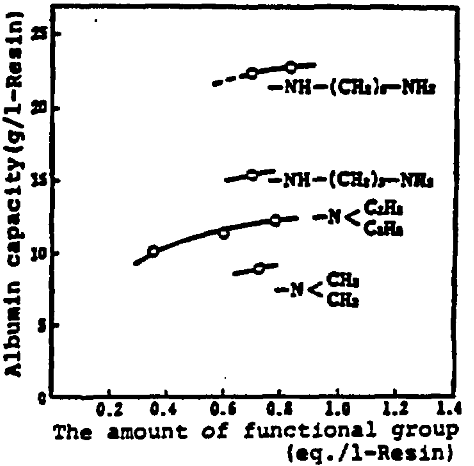


Fig.2 Functional group vs. Albumin capacity (in 0.1M Tris-HCl buffer of pH 7.50 at 10°C)

MO-03

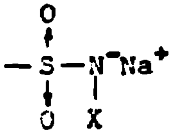
MONO- AND DIHALOGEN-DERIVATIVES OF POLY/ST-CO-DVB/SULFONAMIDE

R.Bogoczek and E.Kociołek-Balawejder

Technological Institute of Chemical and Food Industry,
Academy of Economics, Wrocław, Poland

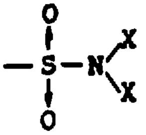
Introduction

In this work, novel reactive resins, which are halogen derivatives of macroporous poly/St-co-DVB/sulfonamide characterized by the following functional groups, are presented(1,2) :



$-\mathrm{SO_2}-\mathrm{N^-Na^+}(\mathrm{X})$

X=Cl,Br,I



$-\mathrm{SO_2}-\mathrm{NX_2}$

where X means Cl, Br, I, and the nitrogen atom with the halogen atoms are bound covalently, and the halogen atom is at the +1 degree of oxidation.

Experimental

In the experiments a macroporous poly/St-co-DVB/sulfonamide resin /SAR/ has been used. It was obtained as the result of following reactions:

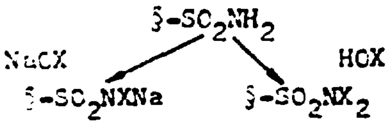
$$\S\text{-}SO_3H \xrightarrow{PCl_5\text{-}POCl_3} \S\text{-}SO_2Cl \xrightarrow{NH_3\ aq.} \S\text{-}SO_2NH_2$$

where § - means a macroporous St-co-DVB matrix.

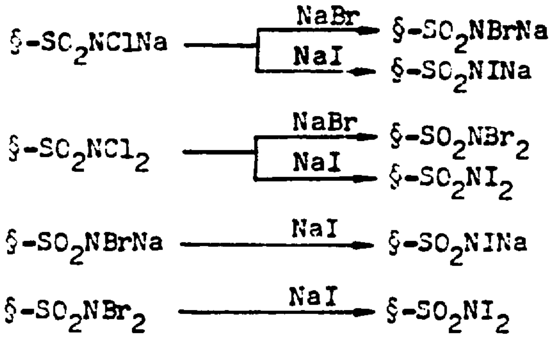
A commercial sulfonate cation-exchange resin WOFATIT KS-10 /produced by Chemiekombinat Bitterfeld, GDR/ was used as starting material. This resin is a macroporous styrene- ca. 20% divinylbenzene copolymer.

The halogen derivatives of this copolymeric sulfonamide were obtained in two different ways:

A - by the reaction of SAR with NaOCl, NaOBr and NaOI to obtain monohalogen derivatives
- by the reaction of SAR with NaOCl, NaOBr and NaOI in an aqueous acetic acid medium to obtain N,N-dihalogen derivatives:



B - by the reaction of the appropriate halogen derivatives of SAR with the aqueous solution of alcaline metal bromides or iodides according to the following reaction:



$$§\text{-}SO_2NClNa \xrightarrow{NaBr} §\text{-}SO_2NBrNa \qquad §\text{-}SO_2NClNa \xrightarrow{NaI} §\text{-}SO_2NINa$$

$$§\text{-}SO_2NCl_2 \xrightarrow{NaBr} §\text{-}SO_2NBr_2 \qquad §\text{-}SO_2NCl_2 \xrightarrow{NaI} §\text{-}SO_2NI_2$$

$$§\text{-}SO_2NBrNa \xrightarrow{NaI} §\text{-}SO_2NINa$$

$$§\text{-}SO_2NBr_2 \xrightarrow{NaI} §\text{-}SO_2NI_2$$

Results and Discussion

By means of two different synthesis routes a number of novel comparatively stable products which contained active chlorine or bromine or iodine in their functional groups have been obtained. Except for the N,N-diiodo-poly/St-co-DVB/sulfonamide these resins were obtained in high yield /i.e. uniformity of functional groups/reaching 85-100%. The obtained products show different intensity of the following properties:

- cation-exchanging /only the N-monohalogeno derivatives/
- disinfecting /in contact with water or aqueous solutions/
- oxidative / in aqueous media/
- halogenating /in contact with aromatic or aliphatic compounds/

The application of the obtained chemical active resins can be as follows:

- generally, in such sciences as microbiology, biochemistry, biotechnology, medicine, pharmacy
- particulary, in carrying out processes like organic and inorganic synthesis /both in halogenation and oxidation/, sterilisation of solutions, stopping and preventing fermentation, water processing.

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EXCHANGE MECHANISM OF ALKALINE IONS ON ZINC FERROCYANIDES

C. LOOS-NESKOVIC [1] and M. Fedoroff [2]

1. Laboratoire d'Analyse par Activation P. Sue
   C. E. N. Saclay, 91191 Gif sur Yvette, France

2. Centre d'Etudes de Chimie Metallurgique
   15, rue Georges Urbain, 94400 Vitry, France

Insoluble ferrocyanides can be used as fixators for a number of elements. They have been already involved in the decontamination of caesium from radioactive liquid wastes. We have limited our study to two types of zinc ferrocyanides which show a great affinity for Cs+ ions. This work was devoted to the understanding of the fixation mechanisms of alkaline ions in order to determine the optimal recovery conditions.

This aim was achieved through the study of the influence of the ferrocyanide composition and structure, a determination of the kinetics and capacity, a study of the modification of the solid at each step of the ion fixation involving the use of different methods: radioactive tracers, atomic absorption, X-ray diffraction, potentiometric measurements. In order to model the experimental kinetics, we have studied the self diffusion of sodium in a sodium-zinc ferrocyanide.

The studied products have been prepared by various ways: direct precipitation with sodium or potassium ferrocyanide and various Zn:Fe ratios; precipitation with ferrocyanidric acid obtained by exchange on a cationic resin in presence or not of an alkaline salt (Na+, K+). All products were analysed for their composition by several methods. Compositions close to definite formulae were obtained. The mixed ferrocyanides belong to the $M'_2Zn_3/Fe(CN)_6/_2, xH_2O$ series (M'=H, Na, K, Cs) with a rhomboedric structure $R\bar{3}c$. Pure zinc ferrocyanide, $Zn_2Fe(CN)_6, xH_2O$ has a trigonal structure. The macroscopic porosity of $Na_2Zn_3/Fe(CN)_6/_2$ seems to be similar to molecular sieve 4A.

The kinetic of sodium self-diffusion in this product has been studied. The ferrocyanide, labelled with the ^{22}Na isotope, was placed in an inactive sodium chloride solution, and the activity of the solution was quoted in function of time. The equilibrium was reached within 20 minutes. The experimental results were compared to different theoretical models: Boyd's law related to diffusion into particles or diffusion through a bounding liquid film. The sodium self-diffusion seems to be controlled by the speed of passage through the surface barrier. The high self-diffusion coefficient in the solid is related to the ionic conductivity measurements and explained by the partial occupancy of the possible Na sites in the crystal structure.

The study of Na^+-H^+ exchange on this product was performed by potentiometric method correlated to tracer measurements. H^+ fixation is a slower phenomenon and the speed of the reaction seems to be bound to H^+ diffusion into the particles.

Kinetics and capacity measurements of caesium were achieved by using radioactive ^{134}Cs isotope. Atomic absorption spectroscopy was used for the determination of the elements found in solution after exchange. The absorption on $Zn_2Fe(CN)_6$ needs more than 70h, while on $M^I_2Zn_3/Fe(CN)_6/_2$ the absorption is achieved within an hour. The capacity does not exceed 1.6 Cs atom per one Fe atom in the first product. The expected $Cs_2ZnFe(CN)_6$ formula was not achieved. The capacity is limited to one Cs atom per Fe atom in the second product. The kinetic experimental curves of caesium fixation cannot be related to a single mathematical model. Caesium is partly retained by cationic exchange with the alkaline or zinc ions and partly by molecular adsorption of a caesium salt.

The results about the kinetic studies let us predict that mixed alkaline-zinc ferrocyanides are the most efficient products towards caesium decontamination in liquid radioactive wastes. Until now, their use was limited because they could not be produced under a convenient form for liquid chromatography columns. We have found a new preparation procedure leading to large particles (mean grain size: 0.25mm) and a patent has been deposited on this subject.

MO-05

TITANIUM HEXACYANOFERRATE/PHENOLSULPHONIC RESIN - A NEW COMPOSITE ION EXCHANGER SELECTIVE TO CAESIUM IONS

J.Narbutt, B.Bartoś and A.Bilewicz

Department of Radiochemistry, Institute of Nuclear Chemistry and Technology, 03-195 Warsaw, Poland

Introduction

The advantage of inorganic ion exchangers - high selectivity to given ions - is generally accompanied by some drawbacks, mainly slow kinetics of ion exchange and poor mechanical properties. Various attempts were made to improve these characteristics (1). Titanium hexacyanoferrate (TCF) synthesized under special conditions (2) proved to be a very efficient sorbent of caesium ions from aqueous solutions, even in the presence of competing potassium and ammonium ions in considerable concentrations (3). However, some of the properties of pure TCF limited its practical applications.

Experimental

Powdered TCF was implanted into a matrix of a phenolsulphonic resin in the course of polycondensation (4). Sorption of $^{137}Cs^+$ from aqueous solutions containing competing cations of various concentrations was studied using the sorbent samples comprising 23 % TCF.

Results and Discussion

Various samples of the composite sorbent were synthesized, comprizing up to 45 % TCF. The spherical shape and good mechanical properties of the sorbent grains are determined by the respective properties of the resin matrix - they are much better for practical purposes than those of pure TCF grains.

The affinity of the composite sorbent towards caesium ions in the range of NH_4^+ concentrations 0.01 - 5 mol/dm^3 is about two orders of magnitude higher than that of sulphonic resin, Dowex 50Wx12, and more than one order higher than that of phenolsulphonic resin (the matrix). The distribution coefficients of Cs^+ on the composite sorbent are as follows: $K_d \geqslant 10^5$ cm^3/g at $[NH_4^+] < 0.01$ mol/dm^3, $K_d \approx 10^4$ at $[NH_4^+] = 0.1$ mol/dm^3 etc. The rate of Cs^+ sorption on the composite sorbent is much greater than that on pure TCF, which is obviously due to a larger surface area of fine grained TCF particles in the porous matrix.

Another important improvement of the sorbent properties is due to the decreased solubility of TCF implanted into the matrix. The leakage of $Fe(CN)_6^{4-}$ to the purified aqueous solutions falls from ca. 10^{-5} mol/dm^3 for pure TCF to less than 10^{-6} mol/dm^3 for the composite sorbent.

The composite TCF/phenolsulphonic resin produced from cheap and easily available materials is thus a convenient sorbent for efficient removing radiocaesium from acidic and neutral solutions which must not be contaminated with other ions. 25000 sorbent-bed volumes of the simulated primary coolant of a nuclear reactor (WWER-440), containing K^+ and NH_4^+ in millimolar concentrations, were purified that way from carrier free ^{137}Cs with the decontamination factor greater than 200 (3). Other possible applications of the composite sorbents in radiochemistry and nuclear technology are discussed.

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110-06

INTERCALATION OF AROMATIC COMPOUNDS INTO ZIRCONIUM PHOSPHATE TYPE MATRIX

L. Szirtes and J. Környei
Institute of Isotopes of the Hungarian Academy of Sciences, Budapest, Hungary

It is known that these types of intercalation complexes could have importance in labeling of the aromatic ring compounds. Thus these complexes could have interest in radiochemical practice. However the aromatic compounds with ring formation could not be directly intercalated in zirconium phosphate type matrix because of we tried to obtaine them with various methods.

For the preparation of above mentioned complexes we have got good results with the following methods:

/i/ intercalation into alfa-zirconium phosphate via its ethanole complex;

/ii/ intercalation into alfa-zirconium phosphate and its derivatives after defoliation of their layered structure.

We collected here the results /XRD and thermoanalytical investigations/ concerning alfa-zirconium phosphate, zirconium-/carboxy ethane phosphonate/ and zirconium carboxy ethane phosphonate-phosphate containing m-amino-phenol, m-amino-benzoic acide and m-amino-hippuric acide.

MIXED INSOLUBLE ACID SALTS OF TETRAVALENT METALS - III
CRYSTALLINE MIXED HAFNIUM-TITANIUM PHOSPHATES

S.K. Shakshooki, J. Kowalczyk, S. Khalil, O. Azabi and N. Naqvi
Department of Chemistry, Al-Fateh University, Tripoli, Libya, SPLAJ

Introduction

Amorphous and crystalline forms of ZrP and TiP have been intensively investigated (1). Only crystalline hafnium acid phosphate (HfP) has been reported (2,3), but has not been studied much in detail. HfP and HfTiP in the amorphous form have been prepared and investigated in this laboratory (4). Crystalline HfP and HfTiP have now been prepared both by refluxing the gels and by Hf method. X-ray diffractogram shows these compounds to be homogeneous in the α-ZrP crystalline form. Exchange capacity for these ion-exchangers have been evaluated by pH-titration combined with radio-isotope tracer technique for Na^+, K^+, Rb^+ and Cs^+ ions (5).

Experimental

(i) Gel-reflux method for a typical compound: 74ml of 0.5M $TiCl_4$ in 6M acetic acid was mixed with 430ml of 0.32M of $HfCl_4$ in 4.5M acetic acid and this mixture was added to 400ml of 12% w/v H_3PO_4. The gel was aged in the mother liquor for 5 days which was filtered and washed to pH 1.5. The filter cake was redispersed in 10M H_3PO_4 and refluxed for 120hrs. Crystalline material thus obtained was characterized by chemical analysis, thermal analysis and X-ray which showed that the compound conforms to the formula $Hf_{0.78}Ti_{0.22}(HPO_4)_2.H_2O$. A similar method was employed for the preparation of compounds 2, 5, and 7 Table 1.

(ii) HF-method: Conditions set by earlier workers (6) for the preparation of ZrP and TiP were not found suitable for the best recovery of the mixed HfTiP or ZrTiP (4). Typical preparation: To 200ml of 8.1M H_3PO_4 was added a mixture of 30ml of 1.0M $TiCl_4$ in 2M HF and 20ml of 0.5M of $HfCl_4$ in 3.0M HF kept at 60C° for 1-2 days. The formula found is: $Hf_{0.78}Ti_{0.22}(HPO_4)_2.H_2O$. Rest of the compounds shown in Table 1 were prepared by the same method.

Results and Discussion

[illegible] of the final products from the HF-source is [illegible] that the Hf:Ti ratio as used in the original mix[illegible] in favour of Hf even when large excess of Ti is used. Similar behaviour was observed for ZrTiP (4). The composition of the refluxed samples does not change. X-ray diffractograms show that the mixed HfTiP are in α-ZrP crystalline form. Exchange capacities for these ion-exchangers for Na^+, K^+, Rb^+ and Cs^+ are given in Table 1. (R = reflux)

Table 1. Exchange capacities mmol/g at pH=5.5

No.	Composition		Method				
	Hf	Ti		Na^+	K^+	Rb^+	Cs^+
1	1	0	HF	3.55	3.83	2.29	1.73
2	1	0	R	3.77	4.50	2.29	0.62
3	0.78	0.22	HF	2.82	4.10	2.54	0.89
4	0.78	0.22	R	2.55	4.30	2.54	0.98
5	0.61	0.39	R	2.52	4.10	1.27	0.50
6	0.32	0.68	HF	4.18	4.20	1.78	0.48
7	0.40	0.60	R	4.29	4.30	1.53	0.48

In samples 1-5 the selectivity sequence is: K>Na>Rb>Cs but for samples 6 and 7 the sequence is K = Na>Rb>Cs. This also shows that materials prepared from both reflux and HF-method, the exchange capacity of Na increases with the increase of Ti in the ion-exchanger.

Acknowledgement to L. Szirtes, Institute of Isotope. Budapest.
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POLYPODAND ION-EXCHANGERS. A HIGHLY SELECTIVE AND CAPACITIVE STRUCTURE FOR MERCURY

M. Lauth and Ph. Gramain

Institut Charles Sadron (CRM-EAHP) CNRS-ULP Strasbourg
6, rue Boussingault, 67083 Strasbourg CEDEX, France

M. Prevost

IRCHA - 91710 Vert-le-Petit, France

Long-chain multidentate acyclic ligands (podands) (1) are of particular interest due to their great flexibility which can assume a fast complexation/decomplexation process. They also have great versatility in that it is easy to regulate the hypophily/hydrophily balance. Polypodand polymers with podands grafted on crosslinked polystyrene have been mainly studied in phase transfer catalyse (2). Such polypodand materials were developped in our laboratory to study their applications as ion-exchangers. Three exchangers with different lengths of podands have been synthesized and their complexation properties analyzed with heavy precious or semi-precious, and transition metals. A remarkable selectivity for mercury cation has been obtained together with a high capacity which increases with the length of the podand. This capacity is independent of the pH but strongly depends on the type of anions. In one exemple it decreases from 3 meq/g in chlorhydric medium to less than 0,1 meq/g in nitric medium. Some preliminary results of the structure of the formed complexes are also presented.

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MP-02

ACETATOTRIS/SULPHONATED TRIPHENYLPHOSPHINE/RHODIUM/I/ SUPPORTED ON ANION EXCHANGERS - A STABLE HYDROGENTATION CATALYST

Ferenc Joó
Institute of Physical Chemistry, Kossuth Lajos University,
P.O.Box 7, H-4010 Debrecen, Hungary

Fixation of ionic ligands suitable for formation of transition metal complexes on ion exchangers receives increasing attention because of its importance in catalysis /1/, chemical analysis /2/ and recovery of precious metals /3/. Of these ligands phosphines bearing either cationic /e.g. $-NR_3^+$/ or anionic /e.g. $-SO_3^-$/ substitutents play an outstanding role /1/.

It has been shown previously that Rh- and Ru-complexes of a sulphonated triphenylphosphine /m-sulphophenyl-diphenylphosphine, mSPØ_2/ can be easily and practically irreversibly anchored on Dowex- or Molselect-type anionites. An often encountered problem with the sulphonated analogue of Wilkinson's catalyst, i.e. $\text{RhCl/mSPØ}_2\text{/}_3$, especially when supported on an ion exchanger, is in its high susceptibility towards hydrolysis resulting in the formation of catalytically inactive, unidentified dark brown species.

We now report that applying $\text{Rh/OAc/mSPØ}_2\text{/}_3$ instead of the chloro-analogue makes the preparation of stable and active supported catalysts possible. In hydrogenation of crotonic acid the catalyst retained most of its specific activity as compared to that shown in homogeneous aqueous solutions.

The poster will discuss the preparation and properties of the catalysts and a probable mechanism of crotonic acid hydrogenation catalyzed by a suspension of ion-exchanger attached $Rh/OAc/\ /mSP\emptyset_2/_3$.

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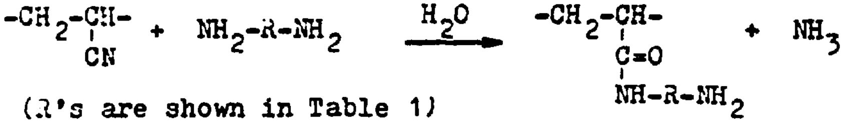
ACRYLIC ANION-EXCHANGERS AND THEIR SORPTION ACTIVITY TOWARDS COPPER

A.Trochimczuk, B.N.Kolarz, and M.Wojaczyńska

Institute of Organic and Polymer Technology, Technical University, 50-370 Wrocław, Poland

Introduction

The polyacrylonitrile sorbents, as well as weakly-basic ion-exchangers obtained by an aminolysis of their nitrile groups, have excellent sorption capacities towards organic compounds dissolved in water (1-3).



$$-CH_2-\underset{CN}{\underset{|}{CH}}- + NH_2-R-NH_2 \xrightarrow{H_2O} -CH_2-\underset{NH-R-NH_2}{\underset{|}{\underset{C=O}{\underset{|}{CH}}}}- + NH_3$$

(R's are shown in Table 1)

The fraction of converted nitrile groups in the modified sorbents is relatively small (ca.0.2) and depends on the structure of resins, primarily on their crosslinking degree (3).

In this work, the sorbents containing various amino groups were tested for the ability to form complexes with Cu(II). It is well known that this ability is related to the structure of ion-exchangers (4).

Experimental

The procedures used for preparing acrylonitrile sorbents, including those containing 20 wt.-% of divinylbenzene, were described elsewhere (3). The aminolysis was carried out with hydrazine (A), ethylenediamine (B), diethylenetriamine (C), and triethylenetetramine (D) as described in (5). The porous structure of the products was characterized as usual (2,3) and the ion-exchange capacity was determined using the Hecker method (6).

Copper was sorbed from $CuCl_2$ solution (400 mg/dm^3) at pH=5 in batch experiments. 0.2 g of air-dried anion-exchange resin (30-45 mesh) was immersed in 0.3 dm^3 of the solution. The concentration changes were followed spectrophotometrically.

Table 1. Characteristics of acrylic anion-exchangers

Sample	R	Ion-exchange capacity mmol HCl/g	Sorption capacity mmol Cu/g
A	-	1.2	0.4
B	CH_2CH_2	1.2	0.6
C	$CH_2CH_2NHCH_2CH_2$	2.4	1.14
D	$CH_2CH_2NHCH_2CH_2NHCH_2CH_2$	2.75	1.19

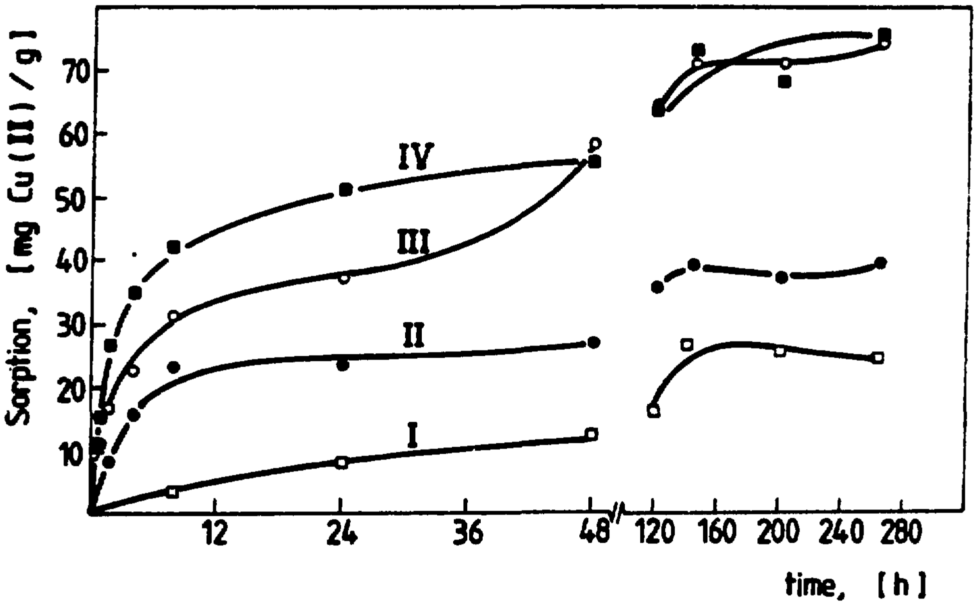


Fig.1. Uptake of Cu(II) vs time for acrylic anion-exchangers

Results and Discussion

If the formation of a complex Cu(amine)$_2$ is assumed, it appears that all amino groups in resin B are involved in the complex with Cu(II), while resin A uses only 67% of its groups.
In the remaining resins, some other types of complexes seem to be formed, as indicated by the amounts of Cu(II) per amino group (Table 1).

As follows from the uptake vs. time plots (Fig.1), the sorption equilibrium is reached at different rates for different resins. This is related to their structures.

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POLY/ST-CO-DVB/CHLOROSULFONYL RESIN - A VERSATITLE STARTING MATERIAL FOR SPECIAL ION-EXCHANGERS

R. Bogoczek
Technological Institute of Chemical and Food Industry,
Academy of Economics, 53-345 Wrocław, Poland

Introduction

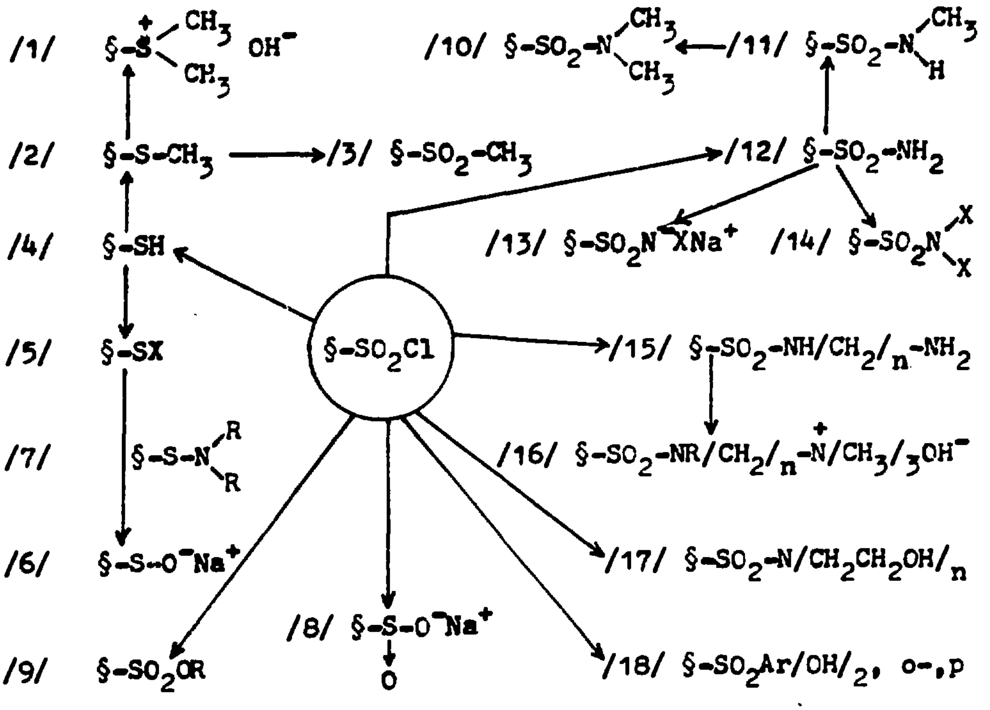
Chlorosulfonyl functionalized styrene-divinylbenzene copolymers can be obtained either by chlorosulfonation of St-co-DVB resins or by chlorination of the sulfonate derivatives of St-DVB copolymers. Previously the products obtained were not homogeneous i.e. they contained ca. 50-80% of $-SO_2Cl$ groups and the remaining amount of $-SO_3H$ groups. Using these unhomogeneous products some authors tried to obtain macromolecular derivatives of the sulfonyl group 1. . Recently it has become possible to obtain products containing exclusively $-SO_2Cl$ functional groups in ca. 4,0 mmol/g of a macroporous resin 2. . Therefor it seems necessary now to review some of the latest works on this subject and to carry out a number of new synthesis routes where the macroporous homogeneous poly/St-co-DVB/SO_2Cl resin undergoes nucleophylic substitution.

Experimental

The chlorosulfonyl resin has been treated with such nucleophylic reagents as ammonia, alkyl amines, alkylene diamines, sulphides etc. and than in some cases additionally with some electrophylic reagents such as alkyl halides or hypohalogenites. In other cases a number of reductive agents have been used. These reactions have been carried out in the presence of a number of organic liquids of various polarity, in the temperature range of 0°C up to 120°C.

Results and discussion

In the result of the various reactions a series of products have been obtained, which are shown in Fig.1. These products have a number of specific properties. And so 1,7,15,16 and 17 are anion-exchange resins with different basicity and selectivity. Again 4,11,12 and 18 are very weak acidic cation-exchangers showing some specific affinities towards cations, whereas 6,8 and 13 are weak or medium weak acidic cation-exchangers showing interesting behaviour towards cations. 18 has additionally electron-exchanging properties. 13 and 14 are oxidating and halogenating agents as well as dissinfecting materials for liquids. 2,3,5 and 9 are sorbents for organic nonionic substances. 3 and 10 can serve as quasi-solid reaction media, e.g. for interphase catalysis.



X = Cl or Br or I, R = H or CH_3 or C_4H_9

§ = St-co-DVB matrix

Fig. 1

Most of the obtained products have homogeneous functional groups. Others have the $-SO_3H$ group in the amount of 5 to 25% due to a side reaction running simultaneously with the main nucleophilic substitution. It is evident however that using homogeneous sulfonyl resins it is possible to obtain more satisfactory results than using unhomogeneous.

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DERIVATOGRAPHIC EXAMINATIONS OF POLY(St-co-DVB) TYPE CATION EXCHANGERS WITH PHOSPHORUS-CONTAINING FUNCTIONAL GROUPS

J.Morawiec

Technological Institute of Chemical and Food Industry,A.E.,
Komandorska 118-120, 53-345 Wrocław,Poland.

Introduction

A thermal stability of ion exchange resins,particulary cation exchangers is satisfactory for many applications.In ion exchange processes the temperature above 100°C is seldom applied.However,in certain regions of ion exchangers application (organic catalysis,nuclear energetics)the thermal stability of commercial cation exchange resins(sulfonic or carboxylic)turned out to be insufficient.There are many literature reports dealing with thermal behaviour of ion exchangers(1-9)but only a few contain comprehensive thermal studies.Derivatographic examination of some ion exchange resins was reported by Nagy and co-workers(5,6).Several Hungarian resins,anion and cation exchangers as well as some Lewatit products were tested,and relationships between the thermal characteristics,the ionic form of the resin,divinylbenzene content and dosage of radioactive were established.Thermal properties of phosphorylated polymers have also been reported(7-9).The thermal oxidative degradation of phosphorus-containing cation exchangers was investigated by Davankov and co-workers(8).A dependence between the phosphorus content in phosphorylated polymers and the loss of weight was observed by Pielichowski and Morawiec(7).

The ion exchange resins containing phosphorus in their ionogenic groups are considered to be more thermostable than the other ones.That is why we have taken the thermal studies on the organophosphorus resins which had been obtained in our laboratory.

Experimental

The thermal stability of organophosphorus cation exchangers obtained from St-DVB copolymers Wofatit type was studied by means of TG-DTG-DTA techniques.For the study a Paulik-Paulik-Erdey derivatograph(OD-102 MOM type,Hungary)was used and TG, DTG,DTA curves were recorded simultaneously.Examinations were performed in the atmosphere of air or argon.Measurements were carried out under non-isothermal conditions in the temperature range from 20 to 1000°C at the heating rate of 5 deg/min. All the measurements were performed for the resins in the H^+ form.The samples were dried at 105°C for 24 hours before any measurements.Subsequently they were powdered and the fraction 0,07-0,08 mm in diameter was taken in each case.

Cation exchange resins with gel and macroporous structure containing phosphinic or/and phosphonic acid functional groups were examined.The activation energies of thermal degradation of the tested cation exchangers were calculated by Horowitz-Metzger's method.Relationships between the thermal characteristics,the kind of functional group and structure of matrix were established.

Results and Discussion

It was confirmed on the basis of our investigations that derivatographic analysis was useful to examine a thermal behaviour of cation exchange resins. Comparative results for the products with various functional groups, e.g. $-PO_2H_2$, $-PO_3H_2$, $-SO_3H$, COOH, can particularly be evaluated. Thermostability of the obtained organophosphorus resins in comparison with sulfonic and carboxylic Wofatit type cation exchangers as well as with non-functionalized St-DVB copolymers was investigated and the general results can be summarized as below.

1. Thermostability of cation exchangers (with the same matrix) is influenced by the kind of their functional groups. They decompose at first, with liberation of gaseous products, e.g. SO_2, CO_2.
2. Resins containing phosphorus in their functional groups show the highest thermostability from the all cation exchangers tested. Among them, phosphinic resins (PO_2H_2) are more thermostable than the phosphonic (PO_3H_2) as well as macroporous products than the gel ones.
3. Among the commercial cation exchangers Wofatit type, carboxylic resins (obtained on the basis of acrylic acid-DVB copolymers) are more thermostable than the sulfonic, macroporous than the gel ones.
4. St-DVB copolymers show thermostability up to 200-310 °C and products with higher crosslinking (macroporous structure) are more stable to heat than the gel ones.
5. Chloromethylated St-DVB copolymers (applied as intermediate for the synthesis of the phosphorus-containing resins) decompose at the temperature range of 200-240 °C, what is probably caused by hydrogen chloride evolution.
6. Some of the resin tested show an endothermic effect([illegible] °C) connected with splitting off of the water from badly dried samples.
7. Thermal degradation of the matrix takes place above the temperature of 500 °C. In oxygen medium it is an exothermic process with weight loss of 60-100% up to 1000 °C, while it is an endothermic transformation in the atmosphere of argon which is accompanied by the weight loss of 46-50%.

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Structure and Ion Exchange Properties of Crystalline Antimonic Acid

S.Milesz[1], I.Mádi[2]

[1] Kossuth Lajos University, Isotope Laboratory, Debrecen

[2] Kossuth lajos University, Colloid Chemical Department, Debrecen

Introduction

Among the hydrous oxides of quiniquevalent metals the crystalline antimonic acid has been one of the most intensitively studied, owing to its high exchange capacity and high selectivities for certain elements. The structure of crystalline antimonic acid is built up essentially of two polymeric structures based on $Sb(OH)_6^-$ octahedra (1).

Experimental

On the basis of X-ray spectrum analyses crystalline antimonic acid of great purity is produced and used as a basic material in the experiments. The precipitate of antimonic acid was obtained by hidrolysis of $SbCl_5$ in water (2).

Results and Discussion

After determining an optimal sorbent quantity measurements are made as a constant ratio of the sorbent and solution. By means of scanning electronmicrographs of different enlargements the particle size distribution curve of the sorbent is made. It shows that the radius of the major part of the particles taking part in the sorption is about $10^{-6}-10^{-5}$m. Thus, knowing the diffusion coefficient, the expected fast sorption carrying out in 10-100 s is characteristic of the system..

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Under stirring the particles of antimonic acid aggregate and disaggregate and a dinamic equilibrium state is reached, which can be characterized by the known particle distribution. The separation possibilities of alkali metal ions as a function of pH are studied by a static labelling method. The acidity of the solution can considerably affect on the sorbed quantity. In strongly acidic solutions an equivalent exchange is found for Cs^+, K^+ and Rb^+ ions, while Na^+ ions sorb selectively. At smaller acid concentration none of the alkali metal ions show equivalent exchange, which proves assumed adsorption process (Fig. 1. shows the behaviour of Cs^+)

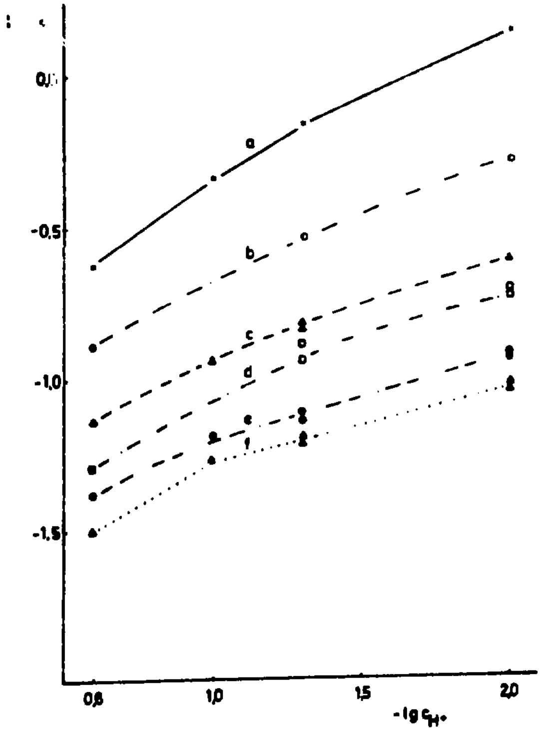

Fig1. The dependence upon the pH for the distribution coefficients (K_d) of Cs^+ on crystalline antimonic acid. Initial concentration of Cs^+: a-1,25·10^{-3}M, b-2,5·10^{-3}M, c-3,75·10^{-3}M, d-5,0·10^{-3}M, e-6,25·10^{-3}M, f-7,50·10^{-3}M.

MP-07

Ion Exchange Processes in Systems of Zn^{2+} and Ca-bentonite, Ca-soil or Ca-humate by Radioisotopic Labelling

I. Kónya[1], K. Szabó[2], M. N. Nagy[3]

[1,3]Kossuth Lajos University, Isotope Laboratory, Debrecen
[2] Present address: Tisza Chemical Works, Leninváros

Introduction

The study of exchange processes between Zn^{2+} ions and soil is important from several points of view: zinc is very important element in soils because it is the specific metal component of carbonic acid anhydrase enzyme as well as plays a role in the synthesis of proteins and auxine. Industrial wastes also contain zinc polluting the environment. These roles of zinc prove the significance of this study.

Experimental

10 ± 0,1 mg of the air-dry substances is measured into a beaker. Then 20 cm^3 $HClO_4$ solution of pH=5,3 is added and pre-stirred by a stirrer of constant rpm for 30 minutes. This time is sufficient to reach the solution equilibrium between the phases. Then the Zn^{2+} solution labelled by a radioactive isotope /^{65}Zn/ is added to the system. For the dilution of Zn^{2+} solution the equilibrium solution obtained during the pre-stirring is applied. The concentration of Zn^{2+} solution is 1×10^{-6} mol dm^{-3} or higher. After a determined experimental time the phases are separated by a Sartorius membrane filter and on the basis of γ radiation the radioactivity of the solid and liquid is measured under the same geometric and radiation absorption conditions.

Results and Discussions

One of the curves obtained for Ca^{2+}-S/Zn^{2+} exchange is shown in Fig. 1. On the ordinate the ratio of Zn^{2+} ions in the solid and the total amount of Zn^{2+} ions is plotted. On the abscissa the experimental times are shown.

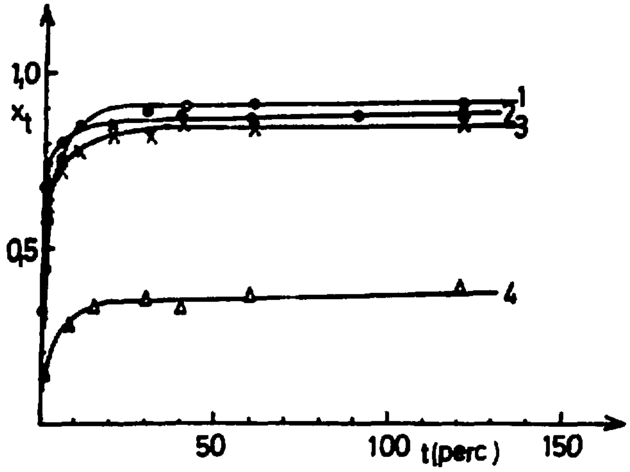

Fig. 1.

The rate curves were analysed on the basis of Christiansen's rate equation for consecutive reactions. Three different processes were found. On the basis of the rate constants, activation entalpy and entropy of the processes were calculated. The activation entropies show no systematic change. On the basis of activation entalpy, bentonite, humus and clay, or sand have to be considered separately. In the first three cases, the dominant process is the exchange of Ca^{2+}/Zn^{2+}*, while at sand adsorption. The kinetics of the exchange process is determined by the diffusion from the solution and the superponed exchange process. In the case of the third process, the surface diffusion likely plays a role, too.*

NEW COMPOSITE ION EXCHANGER - HYDRATED ANTIMONY PENTOXIDE IN PHENOLSULPHONIC MATRIX - AND ITS APPLICATION IN NEUTRON ACTIVATION ANALYSIS

A.Bilewicz[1], B.Bartoś[1], H.Polkowska-Motrenko[2] and J.Narbutt[1]

[1]Department of Radiochemistry,
[2]Department of Analytical Chemistry,
Institute of Nuclear Chemistry and Technology, Warsaw, Poland

Introduction

In the course of neutron activation analysis, chiefly that of biological samples, serious difficulties arise due to the high activity of ^{24}Na which obscures the gamma spectrum of the sample. Hydrated antimony pentoxide (HAP) has been commonly used to remove selectively the sodium ions from hydrochloric solutions of the analyzed samples (1). The application of crystalline HAP for this purpose is not free, however, from substantial drawbacks, especially important in column operation. These are: slow kinetics of the sorption process, irregular shape of the grains and low resistance of the material against hydrochloric acid at higher concentrations. In order to improve some of these properties, attempts were made to prepare a new sorbent, fine grains of HAP being built in a porous support.

Experimental

Powdered HAP was implanted into a matrix of a phenolsulphonic resin in the course of polycondensation (2). The sorption properties of the sorbent obtained were studied using the radiotracers. The sorbent was applied in the analysis of biological materials.

Results and Discussion

New composite ion exchanger comprised up to 60 % HAP in the matrix. Spherical grains of the sorbent were characterized by good mechanical properties and high stability in hydrochloric solutions up to 10 M HCl. The distribution coefficient of Na^+ for the composite sorbent in 7.5 M HCl (K_d = 200 cm^3/g) is close to that for pure crystalline HAP grains (K_d = 310), whilst the rate of the ion exchange is much greater for the former.

The composite sorbent obtained secured efficient (>95 %) removal of ^{24}Na from activated biological samples dissolved in 8 M HCl. The solution was passed through the column filled with 1 cm^3 of the sorbent (0.5-1 mm grains), at the flow rate 25 cm^3/h.

Due to its advantageous mechanical and physicochemical properties, the new composite HAP/phenolsulphonic resin seems to be a very promising sorbent for routine neutron activation analysis of biological materials.

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MP-09

PARTICLE SIZE MEASUREMENT OF ION EXCHANGE RESINS AND POLYMERS BY HIAC

by L S GOLDEN - Research & Development Manager,
Purolite International Limited
Pontyclun, S Wales, UK

ABSTRACT

With the increasing variety of applications for ion exchange resins comes a requirement for a means of measuring particle size which is more precise than wet or dry screening. For various reasons, outlined in the paper, the equipment becoming most popular in the industry is the Hiac Particle Size Analyser. Whilst this range of equipment is undoubtedly the most suitable for the purpose, it is evident that some users are unaware of the snags and precautions in operating this equipment.

The author has been using a Hiac Analyser for this purpose since 1976. Some interesting anomolies were found when using a CM-600 sensor and the paper discusses these along with describing the precautions with which the equipment must be set up, without which results can be practically meaningless. It also shows how using the wrong sensor, or even instrument model, for the job can give inaccurate results. Despite appropriate care in setting up the equipment, there are still certain limitations to the technique and the paper goes on to show how the author has attempted to overcome these.

MIXED INSOLUBLE ACID SALTS OF TETRAVALENT METALS - II[1] EFFECT OF COMPOSITION ON ION EXCHANGE PROPERTIES OF AMORPHOUS ZIRCONIUM - TITANIUM PHOSPHATES

S.K. Shakshooki, N. Naqvi, J. Kowalczyk, S. Khalil,
M. Rais and F. Tarish
Department of Chemistry, Al-Fateh University, Tripoli,
Libya, SPLAJ

Introduction

As ion-exchangers amorphous mixed zirconium-titanium phosphates are not similar to single salts of either Zr or Ti. Compositional effects are found to be well marked for the exchange of some trivalent and tetravalent metals such as lanthanides and some actinides. Maxima and minima are observed in the uptake of these metals ions at around fixed composition of the mixed exchanger. Most of the bivalent ions are sorbed weakly except for Hg^{2+} and Pb^{2+}.

Experimental

Gels are obtained by mixing appropriate amounts of $ZrOCl_2.8H_2O$ and $TiCl_4$ in 4M HCl solution with 40% excess of H_3PO_4 solution. Samples with reproducible properties were prepared by aging the gels in the mother liquor for 5 days. After filtration and washing, the filter cake was redispersed in water and filtered the next day. The same operation was repeated for 3 more subsequent days and the material was finally washed to pH=3. The materials so prepared were ZrP, ZrTiP and TiP in which ZrTiP represents a series of compounds containing 10%, 33.3%, 50%, 66.6% and 90% of Ti. Half of the material of each batch was pretreated with ethanol. Characterisation was made by chemical analysis, thermal analysis, X-ray and by pH-titration (2). Kd values were obtained for solutions of 0.05N of metal ion in 0.1N HNO_3.

Results and Discussion

Chemical and thermal analysis showed that the general formula of these compounds is $Zr_xTi(1-x)(HPO_4)_2.4H_2O(\pm 1H_2O)$. Most of the compounds show inflection for two protons (3). Kd values show a broad minimum near 50 mole percent of Ti in ZrTiP. Kd composition curves of Y^{3+}, La^{3+}, Eu^{3+}, Sm^{3+}, Gd^{3+}, Dy^{3+} and UO_2^{2+} are shown in Figure 1. The minimum

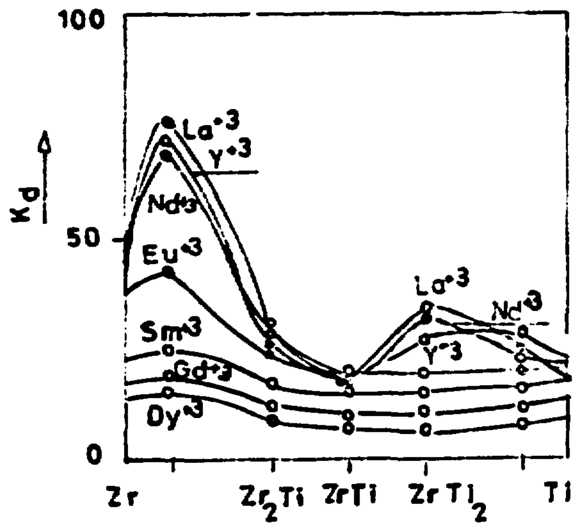

Fig.1 Kd values for water treated materials

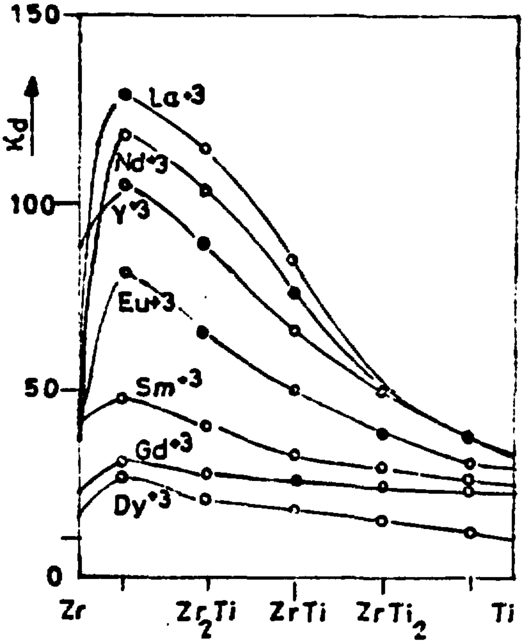

Fig.2 Kd values for alcohol treated materials

though still at ~ 50% now has two maxima at 10% and 66.6% in water treated materials. In alcohol treated materials the maximum at 66.6% is absent and the maximum at 10% intensifies Figure 2. At these maxima, the order of decreasing sorption approximately follows the order of lanthanide contraction. Th^{4+}, however, is exceptional by showing a maximum at 50% composition. Separating lanthanides from monovalent and bivalent metals by use of ZrTip (10% Ti) at pH 1-2 seems feasible..

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MP-11

INVESTIGATIONS ON THE SORPTION MECHANISM OF AMORPHOUS TITANIUM PHOSPHATE INORGANIC SORBENT

A.Ludmány and L.G.Nagy
Department of Applied Chemistry TU Budapest
Budapest, Hungary

Introduction

Determining of the sorption processes taking place on inorganic sorbents has not occured in spite of the fact that their application was getting to spread on several fields of radiochemistry. The results of our different investigations indicated that under given experimental circumstances the sorption processes on the amorphous titanium phosphate prepared in our laboratory were not or not only ion exchange processes. This may be the explanation of the specific sorption properties /only K^+, Rb^+ and Cs^+ ions are able to be bound/.

Experimental

The amorphous titanium phosphate was prepared by precipitation method using $TiCl_4$ and $/NH_4/_2HPO_4$ solutions as reagents Details of the method have been described previously (1) . The structure and the properties of a part of the products were modified by refluxing the precipitation either in mother liquor or in 10 molar phosphoric acid. As reference material titanium phosphate prepared under the circumstances described in(1) but applying as phosphate containing reagent phosphoric acid was used. Some charge of this type of the preparations was also refluxed in 10 molar phosphoric acid.

The structure and the properties of the sorbent were investigated by titration, X-ray powder diffraction, determining the solubility, measuring the specific surface area, determining the pore distribution, determining the sorption isotherms, and determining the selectivity. Because of the complexity of the system the experiments were extended to the liquid phase i.e. the structure, the hydration conditions and the possibility of ionpair formation were studied.

Results and Discussion

Evaluating the results of the X-ray measurements it was found that

- to ensure the specific sorption properties a certain degree of order /semi-crystalline structure spreaded on the whole bulk phase/ is needed
- the quality and the structure of the reagents used to introduce the phosphate group and the PO_4/Ti rate of the reaction mixture play an important role in the formation of α-TP

- the formation of α-TP from the amorphous state taking also the results of the solubility tests into consideration proceeds via the formation of anhydrous crystalline TP according to the hypothesis described in (2)
- in the amorphous sample the two phosphate groups being just next to a titanium atom are distorted comparing to those of the crystalline structure.

The selectivity studies showed that with increasing ion concentration above the loading of 1.0 mg ion/g sorbent a selectivity turn can be observed. Instead of the selectivity sequance $K^+ > Rb^+ > Cs^+ \gg Na^+, Sr^{2+}, In^{3+}$ determined for small column loadings the selectivity sequence $Rb^+ > Cs^+ > K^+ \gg Na^+, Sr^{2+}, In^{3+}$, was obtained. Both the selectivity sequence different from the literary data (3) and the fact that the amorphous titanium phosphate ion exchanger takes up Na^+ ions but no retention was observed at the own products indicate non-ionic exchange processes.

Between the sorption properties and the characteristics of the potentiometric titration curves no correlation was found. This suggests that the specific sorption processes take place at specific active sites.

The run of the sorption isotherms determined in acidic media of various concentrations makes probable complex sorption processes.

Summarizing the results of the investigations made in different directions it can be stated that the sorption processes on the amorphous titanium phosphate prepared in our laboratory are complex in strong acidic medium. The uptake of alkaline ions occurs not only by ion exchange but by irreversible sorption processes depending on the hydrogen ion concentration. The selectivity observed at the ions of hydrated ionic radius greater than 0.13 nm indicate the existance of active sites with specific geometrical structure on the sorbent. These are directly not connected to the pore size for the pore size of the amorphous product are greater with about one order of magnitude than the sizes of the ions, hydrated ions and ion-pairs existing in the liquid phase.

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ION-CHROMATOGRAPHY AND OTHER ANALYTICAL APPLICATIONS

HIGH-PERFORMANCE SEPARATIONS OF LANTHANIDES AND ACTINIDES ON DYNAMIC ION EXCHANGERS: THE ANALYSIS OF IRRADIATED FUELS.

R.M. Cassidy, S. Elchuk, C.H. Knight, L.W. Green and B.M. Recoskie

Atomic Energy of Canada Limited Research Company, Chalk River Nuclear Laboratories, Chalk River, Ontario, Canada, K0J 1J0

Introduction

Dynamic ion exchangers are formed by the reversible sorption of a hydrophobic ion onto a hydrophobic reversed phase to form a charged surface that can be used for ion exchange separations. Studies in our laboratories have shown that these exchangers offer rapid mass transfer for metal ions and exhibit column efficiencies that are comparable to that observed for modern separations of organic species. The combination of such systems with postcolumn-reaction detection offers a selective, sensitive (detection limits, 0.1 to 10 ng), and reproducible ($1\sigma < 1\%$) method for the determination of metal ions. Comparisons made with isotope-dilution mass spectrometry and other analytical techniques have also shown that these chromatographic techniques can be accurate to 1% or better (1,2). This paper will use the results of recent studies on high burnup UAl fuels to illustrate how these and other important features, such as versatility and savings in analysis costs, can be realized with dynamic exchangers. Some results of recent geochemical and waste management studies will also be included.

Experimental

The liquid chromatography system was assembled out of commercial components and interfaced with a glove-box facility for the analysis of active samples (1,2). The postcolumn reaction system (1-3) used Arsenazo III to react with the eluted metal ions and the complexes were monitored at 658 nm. The aqueous eluents contained α-hydroxyisobutyric acid (HIBA), (0.1 to 0.4 $\text{mol}\cdot\text{L}^{-1}$) and 1-octanesulfonate (0.001 to 0.05 $\text{mol}\cdot\text{L}^{-1}$), and the pH was normally in the range of 3 to 5. Fuel samples were dissolved in HNO_3, diluted in the mobile phase, and 100 μL were injected without any prior separation. The columns were 4 x 100 mm and were packed with 5 μm C_{18} bonded phases.

Results and Discussion

The selectivity of the dynamic ion exchange system was optimized by adjustment of the following parameters: effective exchange capacity of exchanger, pH of eluent, concentration and nature of complexing reagent used in eluent, and the chemistry conditions used for postcolumn reaction. The conditions used gave rapid separations for ng amounts of the fission monitor (La) and of the major fissioning element (U) in the presence of mg amounts of fission products and Al (see

Figures 1A and 1B). The estimated propagated error was 1.1% and the standard deviation for the ratio of mass spectrometric results was 0.9%; the agreement between HPLC and MS results was - 0.4%.

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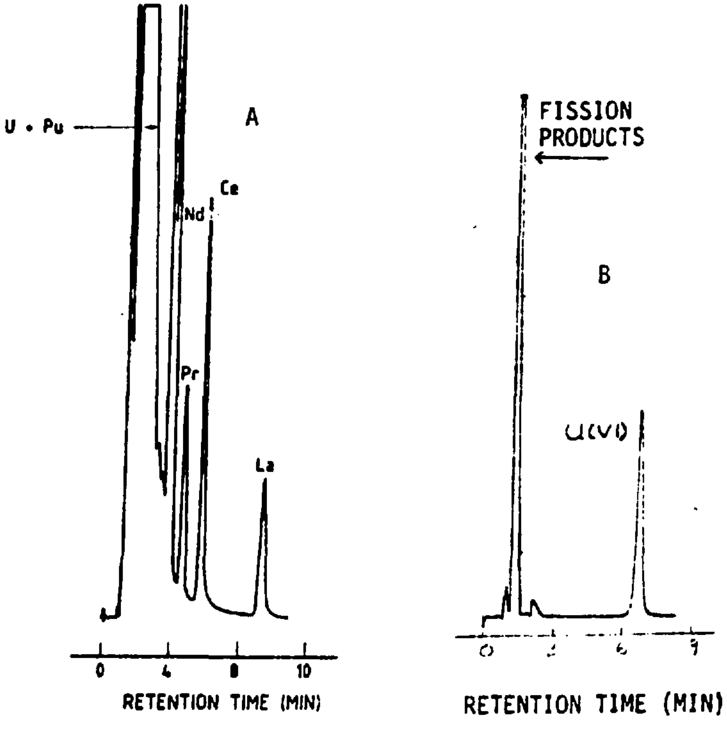


Figure 1. Determination of La and U in irradiated UAl fuel. Detection at 658 nm after a postcolumn reaction with Arsenazo III. Column, 4 x 100 mm 5 µm Supelcosil C_{18}. Curve A: eluent, 0.3 mol·L^{-1} HIBA, 0.01 mol·L^{-1} $C_8SO_3^-$, pH 3.8, 2.0 mL·min^{-1}; sample, 100 µL of diluted fuel solution containing - 70 ng La. Curve B: eluent, 0.25 mol·L^{-1} HIBA, pH 4.5, 2 mL·min^{-1}; Sample, 100 µL of diluted fuel containing - 2 µg U.

ION-PAIR EXTRACTION OF SALTS BY MIXED LIQUID ION EXCHANGERS

G. Harel and G. Schmuckler, Dept. of Chemistry
Technion - Israel Institute of Technology

ABSTRACT

An equimolar mixture of an anion and a cation exchanger, both liquid, in a diluent of low polarity, proved to be a selective as well as an efficient extractant for metal halides from concentrated aqueous solutions.

The relevant reaction can be formally represented by an equilibrium equation of the form -

$$CaCl_2 + 2R_3N + 2R'COOH \rightleftharpoons 2R_3NH^+Cl^- + \overline{(R'COO^-)_2Ca^{++}}$$

which is applicable to many halide salts of alkali and alkaline earth metals and of transition metals. The reaction can be reversed by bringing the organic phase into contact with pure water.

Fluorescence spectroscopy, with Rhodamine B hydrochloride as fluorophore, confirmed the formation of reversed micelles in the organic phase loaded with salts. Further proofs of micelle formation were furnished by NMR measurements, which showed that a fast proton exchange takes place between the carboxylic and the ammonium sites; and by measurements of molar conductance, which resulted in unexpectedly high values with increasing salt concentration in the organic phase.

LOW LEVEL ANION ANALYSIS BY MODIFIED ION CHROMATOGRAPHY

Klaus P. Müller
Kernforschungsanlage Jülich GmbH, Institute for Atmospheric
Chemistry, P.O. Box 1913, D-5170 Jülich, F.R.G.

Introduction

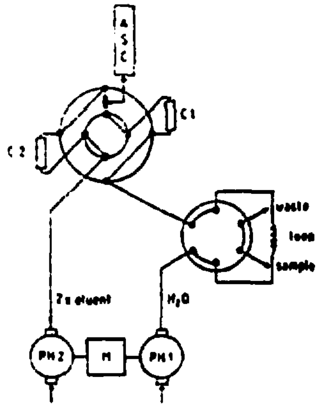
Commercial IC-systems with two columns and a conductance detector (1) can attain a detection limit of about 100 ppb. However, this is only true for the later eluting ions like nitrate and sulfate, the ions eluting early like fluoride and chloride are strongly influenced by the so called "waterdip", which is caused by the high water content and low conductivity in the early elution of aquous samples. This effect prevents the sensitive detection of the ions eluting early. On the other hand, there is a need to measure small volumes of aquous samples with low concentrations of ions: e.g. cloud water from background stations. In the following I describe a method which eliminates the waterdip and improves the sensitivity dramatically.

Experimental

A commercial two-headed HPLC-pump is used to transport a split stream of eluent through the analytical system. The first pump head (PH1, Fig. 1) carries pure water and the second (PH2), double concentrated buffer. The water stream passes the sample loop and the small preenrichment column C1. Then both streams are joined in a T-connection to form an eluent of the usual buffer strength. This procedure provides an eluent of constant buffer concentration at the head of the Analytical Separation Column (ASC).
After the preconcentration of the sample ions in the water stream on column C1, the valve is switched and the sample is backflushed by the buffer solution from C1 through a very small volume to the analytical column. Thus an excellent separation of the different ions in small volumes is obtained without the interfering waterdip.

Results and Discussion

The modification allows the analysis of samples with small volumes and low concentrations: The elimination of the waterdip improves the quantitative determination of the early eluting ions down to 0.1 ppb without any pretreatment, and because the modified system contains concentrator columns (C1, C2), the detection limit of all detectable ions can be lowered to the 0.01 ppb-range if samples of about 1 ml are insected. This permits the determination of the ion-content of environmental samples from very clean areas such as filter extracts of aerosols in the upper troposphere and of nitric acid in marine regions. As an example, the ion chromatogram of a bulk sample of airborne particles during the STRATOZ III flight experiment is shown in Fig. 2.



improved modified IC-system
with 2 concentrator columns

Figure 1

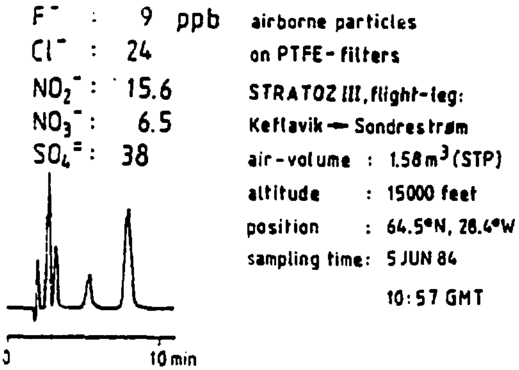


Figure 2

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A0-04

ALKALI AND ALKALINE EARTH CATIONS CHROMATOGRAPHIC SEPARATION ON SILICA GRAFTED WITH BENZO-18-C-6 CROWN ETHER

M. Lauth and Ph. Gramain

Institut Charles Sadron (CRM-EAHP) CNRS-ULP Strasbourg
6, rue Boussingault, 67083 Strasbourg Cedex, France

Introduction

The applications of crown ethers in analytical chemistry have been extensively developed and one of the most attractive applications is their use in liquid chromatography for cation separations. Previous works (1-3) show that the quality of the separations strongly depend on the preparation of the exchanger. In this paper we present the preparation of one exchanger with Benzo-18-crown-6 supported by modified silica-gel and its application in alkali, alkaline earth cation and anion chromatographic separations.

Experimental

The synthesis route is composed of four steps
- synthesis of 4'-(hydroxymethyl)benzo-18-C-6
- activation of silica gel (lichrosorb SI 100, 30 and 10µm Merck)
- grafting of a spacer (3-aminopropyltriethoxysilane and further reaction with 4-(chloromethyl) benzoyl chloride)
- grafting of the C.E. on the modified silica

Details can be found in ref. 4.
The silica was packed in a stainless column (l=13cm, id.=0.48cm)
Chromatographic experiments were performed with a classical system with detection by conductivity measurements. The eluent used was water with a flow rate of 0.24ml per minute.

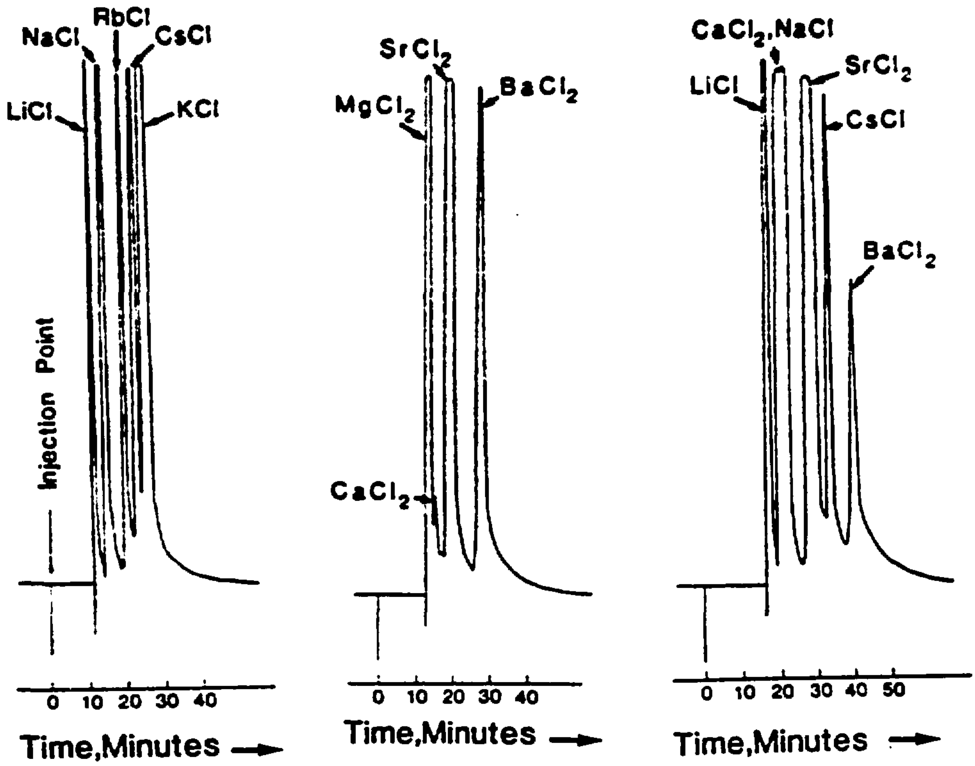
Results and discussion

The binding characteristics of the 30µm silica are shown in table 1. The hydrophobic nature of the exchanger is clearly put into evidence when considering that the maximum capacity is only obtained in methanol.
The chromatographic behavior is illustrated in figure 1, where separations of alkali, alkaline-earth cation and mixtures are represented. The injected quantities vary from 10 to 100µg.

With alkali metal chlorides, very good separations are obtained in less than 30 minutes. With alkaline earth metal chlorides only Ca^{2+}/Mg^{2+} are poorly separated. Moreover a very efficient separation of anions has been observed, partly as a result of the hydrophobic character of the exchanger.

Conclusion

The results obtained illustrate the exceptional binding properties of crown ethers. However such good performance can only be obtained by a very careful synthesis of the exchanger. It is believed that such exchangers offer new separation possibilities with the advantage of using pure water as the eluant.



capacity mmole/g calculated	capacity mmole/g experim.	salt	solvent	equilibrium time / mn
0.27	0.26	KSCN	CH_3OH	10
	0.24	KSCN	CH_3OH-H_2O 90/10	"
	0.23	$Ba(SCN)_2$	"	"
	0.13	KCl	H_2O	"
	0.09	$BaCl_2$	H_2O	"

Table 1 : Binding characteristics of the exchanger

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THE ROLE OF "ACIDIC" ALUMINA IN THE DETERMINATION OF PHOSPHATE IONS USING COLUMN CHROMATOGRAPHY

J E DAVIES, Lanterncroft, Leigh, Tonbridge, Kent, TN11 8QE;

R GRZESKOWIAK and J MENDHAM, School of Chemistry, Thames Polytechnic, Wellington Street, London SE18 6PT.

Introduction

An analytical method for the determination of low concentrations of phosphorus in steels and allied materials has been developed (1) in which α-alumina is used as an adsorption medium. In this method phosphate species present in strong acid solution are retained on a column and then eluted with sodium hydroxide. The effluent is subsequently used for the quantitative estimation of phosphorus.

The aim of the investigation was to determine the quantity of phosphorus capable of being retained on a column of α-alumina, the mode of adsorption of the phosphate species and the relationship, if any, between the phosphate species and the presence of other ions on the column.

Experimental

Solutions of different salts,

KCl, $KHSO_4$, K_2SO_4, KH_2PO_4, Na_2HPO_4, Na_3PO_4

were passed through a column of α-alumina and aliquots of effluent were titrated to pH7 either with dilute sodium hydroxide or sulphuric acid solutions. The investigation yielded the amounts of hydrogen and chloride ions eluted from the column and the quantity of the anions of the eluting solution adsorbed on the column. In the case of the eluents containing phosphates, the species present in the effluent were investigated by qualitative and quantitative analytical methods and infrared studies. X-ray photoelectron spectroscopy was used to study the phosphate species adsorbed on α-alumina.

Results and Discussion

The experimental evidence shows that:

(i) there is no quantitative relationship between the hydrogen ions present in "acidic" alumina and the amount of phosphorus adsorbed;

(ii) the quantity of ions retained is related to the particle size of α-alumina;

(iii) the process is a surface adsorption phenomenon;

(iv) the species retained on the column are hydrogen bonded:

(v) any phosphate species is retained as H_3PO_4;

(vi) the species are removed only if the eluent reacts with the adsorbed molecules, thus ammonia will elute sulphate (2) but sodium hydroxide is required for phosphates.

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CATION EXCHANGE CHROMATOGRAPHIC SEPARATION OF SCANDIUM IN MIXED SOLVENTS

A. G. Gaikwad[1] and S. M. Khopkar[2]

1. Department of Industrial Chemistry,
Saga University, Saga 840, Japan

2. Department of Chemistry
Indian Institute of Technology, Bombay 400 076, India

Introduction

The systematic investigations (1) were carried out on the cation exchange chromatographic behaviour of scandium on Dowex 50WX8 (1.2 × 20 cm) column. The earlier workers separated it only from lanthanum (2-3).

Experimental

About 10 mg of scandium was sorbed on column and was eluted with various mineral acids and salts as eluants. Based on this information mixture of 4 M hydrochloric acid along with the varying concentration of solvents such as methanol, ethanol, acetone, propanol, dioxane and tetrahydrofurane were used as the eluent. Scandium from effluent lot was determined complexometrically (4).

Results and Discussion

It was noted from the value of elution constant and distribution ratio, the selectivity scale for mineral acids was $H_2SO_4 > CH_3COONH_4 > NH_4Cl > NaCl > HNO_3 > HCl > NH_4NO_3$. While selectivity scale for mixed solvents in presence of 4 M hydrochloric acid was Methanol > Ethanol > Dioxane > Propanol > THF. Amongst salts chlorides of sodium and ammonium were effective at very high concentration while sodium nitrate was poor eluent.

Based upon these informations, several novel separations of scandium from multicomponent mixtures were developed.

The mixture of iron, manganese, aluminium, calcium and scandium was separated after sorption by eluting iron with 0.25 M hydrochloric acid in 80% dioxane, manganese with 0.75 M hydrochloric acid in 90% acetone, aluminium with 3 M hydrochloric acid in 60% ethanol, calcium with 1.5 M nitric acid and scandium with 1 M sulphuric acid.

A mixture of titanium, scandium, zirconium and thorium was separated by eluting titanium with 2 M hydrochloric acid in 40% propanol, scandium with 3 M hydrochloric acid, zirconium with 0.5 M sulphuric acid and thorium with 1 M sulphuric acid.

A mixture of bismuth, indium, scandium and lanthanum was separated after sorption by eluting bismuth with 0.25 M hydrochloric acid in 80% tetrahydrofurane, scandium with 1 M sulphuric acid and lanthanum with 4 M hydrochloric acid.

Finally separation of lead, gallium, scandium and cerium was achieved by eluting lead with 0.5 M hydrochloric acid in 60% acetone, gallium with 1 M hydrochloric acid in 90% tetrahydrofurane, scandium with 1 M sulphuric acid and cerium with 4 M hydrochloric acid.

In all separations 300 ml of volume of eluant was used. The eluents from effluant lot were determined spectrophotometrically with suitable chromogenic ligands.

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A3-07

PREPARATION OF ANION-EXCHANGE RESINS FOR ION CHROMATOGRAPHY ON A METHACRYLIC COPOLYMER MATRIX

U.Haldna, R.Palvadre and J.Pentchuk

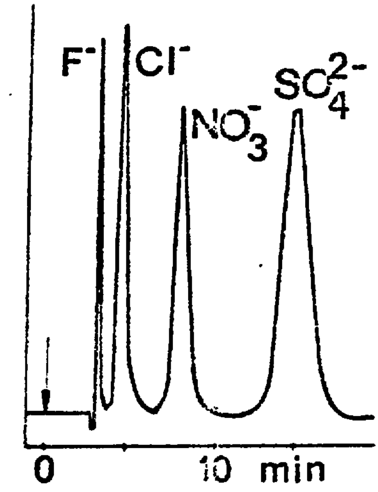
Institute of Chemistry, Academy of Sciences of the Estonian SSR, Tallinn, U.S.S.R.

Introduction

Ion chromatography makes use of a separation column containing a pellicular anion-exchanger of low capacity(0.005-0.05 meq/g).This special resin is usually based on a poly(styrene-divinylbenzene) matrix.Now, a procedure is proposed for the preparation of a low-capacity anion-exchange resin on a methacrylic copolymer matrix.

Experimental

Low-capacity (0.01-0.04)meq/g) pellicular anion exchangers can be prepared by treating a methacrylic copolymer matrix with an ethanolic solution containing a polystyrene-based anion exchanger and water-insoluble glue.After evaporation of ethanol the surface of the copolymer matrix will be coated with a water-insoluble pellicle of the anion exchanger and glue mixture.



Column 250×4mm,eluent 3 mM $NaHCO_3$ + 2.4 mM Na_2CO_3, 1 ml/min.

Results

The anion-exchange resin prepared exhibits satisfactory chromatographic performance - see the Figure.The columns filled with this resin can be used without changes in performance for several months.

SPECTROSCOPY OF ION EXCHANGER AND ITS APPLICATIONS

H. Waki

Department of Chemistry, Faculty of Science, Kyushu
University, Hakozaki, Higashiku, Fukuoka, Japan

What we are interested in is not the spectral nature of an ion-exchanger material itself, but the spectrum of chemical species sorbed in the ion-exchanger, because the latter occasionally gives a quite different pattern from that in an ordinary solution.

It is not difficult to obtain an absorption spectrum of the solid phase. The ion-exchanger particles are uniformly packed into a cell with a small volume of solution and the light attenuance is measured with an ordinary spectrophotometer, though in some cases an optically improved geometry may be devised to minimize the light loss by scattering.

The overall attenuance of this ion-exchanger layer is represented as

$$A_{meas} = A_{sc} + A_{mat} + A_{soln} + A_s \qquad (1)$$

where A_{sc} and A_{mat} denote the background attenuance due to scattering and absorption by the ion-exchanger matrix itself, respectively, A_{soln} the absorbance of the solution filled in the interstitial space between the solid particles, and A_s the net absorbance by the sorbed species. Generally speaking, the use of ordinary ion-exchange resins is limited to visible region because of their strong absorbability by aromatic group, while crosslinked dextran (Sephadex) ion-exchangers are usable in both visible and near-ultraviolet regions(1). The scattering background has, in any case, a great contribution to the total attenuance and therefore the minimization of this background may be essential in obtaining the correct absorption spectrum of the sorbed species of interest.

How can we utilize these absorption spectra of ion-exchanger phase? Applications are to 1) solution chemistry and coordination chemistry and to 2) highly sensitive chemical analysis, as described below.

1) Since the inside solution of ion-exchanger and the outer solution in equilibrium have considerably different properties from each other, the absorption spectra for these two phases are often different, indicating the presence of different (complex) species. But it is also true that the same species reveals always the same spectral pattern for the two phases, although some organic compounds sorbed show a considerable shift in wavelength by adsorptive interaction to the ion-exchanger matrix. These facts may lead to the possibility ~~of~~ finding of new chemical species and of spectral assignment for a certain complex, as well as understanding of the ion-exchange reaction mechanism involving complexation and/or

polymerization. We have so far found $Cu_2Cl_7^{3-}$ (2), $Ni(SCN)_6^{4-}$ (3), $(CrO_4^{2-})_n$ (4), UCl_5^-, etc. as new species present in anion-exchange resins and their characteristic absorption spectra.

Besides, the observation of ion-exchanger phase spectra may offer the information on what species should be assumed in the ion-exchanger in determining stability constants of complexes. Any spectral indication on the presence of complex species in a cation-exchanger may require us to apply Fronaeus' method instead of Schubert's method.

2) The most important application of ion-exchanger phase spectrum may be the sensitive determination of trace components in solutions (5,6). These components are rapidly concentrated on ion-exchanger of small quantity from the solution of large volume and the solid phase attenuance is directly measured. The net absorbance by the sample component, A_{RC}, can be expressed as

$$A_{RC} = \epsilon_{RC} \cdot l_R \cdot C_{RC} = \epsilon_{RC} \cdot l_R \cdot C_0 \cdot \frac{V}{mv} \cdot \frac{1}{1+V/Dm} \qquad (2)$$

after cancellation of the background attenuance. Here C_{RC} and C_0 are molar concentrations of the sample component in the ion-exchanger and in the initial solution to be analyzed, respectively, ϵ_{RC} its molar absorptivity in the solid phase, l_R the mean light path penetrating the solid phase, V the solution volume, m the ion-exchanger weight, v the swollen ion-exchanger volume per unit weight, and D the distribution ratio of the sample component(ml/g). Therefore an effective way of enhancing the sensitivity of analysis is to increase V/m or l_R. Especially the use of a longer cell is advantageous, because the absorbance by sample species is approximately proportional to cell length while the scattering background increases only gradually with cell length. Even a 20 mm cell can be employed in some cases and more than 100 times sensitivity over the corresponding solution spectrophotometry can often be obtained. For instance, barium whose concentration is less than 10^{-8} M could be determined using QAE-Sephadex with UV absorption of the chloro complex anion.

In the lecture the development of ion-exchanger phase absorptiometry will be reviewed with some new data of increased sensitivity with longer cells and another type of solid phase spectrophtometry, ion-exchanger fluorimetry, recently attempted by us will also be presented.

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AO-03

GOLD EXTRACTION WITH POLYMERIC COMPOSITES PREPARED BY γ-RADIATION POLYMERIZATION COUPLED WITH IMMOBILIZATION

S. Belfer and M. Streat[2]

1. The Institutes for Applied Research, Ben-Gurion University of the Negev, Beer-Sheva, Israel

2. Department of Chemical Engineering & Chemical Technology, Imperial College, London

Solvent-impregnated resins (SIR) based on the incorporation of selective liquid extractants into crosslinked polystyrene resins have been used for the selective extraction of several metallic ions from aqueous solution. Although these materials give high selectivity and exchange capacity, they provide very slow kinetics and suffer from gradual release of the extractant from within the polymer matrix. This latter drawback can be eliminated by immobilizing the extractant into the polymer network, which can be grafted onto the surface of silica gel.

The route of synthesis adopted during this work involved radiation-induced polymerization on silica gel, coupled with immobilization of the extractant.

The presentation will describe the results of a study of the chemical performance of the resins prepared by this method. (patent pending). A representative resin containing Alamine-336 extractant was used to study gold extraction from cyanide solution. Two samples were used, H1-2 and A1-5, which differ in the nature of their polymer.

The adsorbent (0.2 g) was treated overnight with a large excess of 5 N hydrochloric acid. The sorbent was then separated and washed with deionized water. A gold-bearing solution was prepared by dissolving gold metal in a mixture of concentrated hydrochloric and nitric acid. An appropriate amount of this solution was added to 0.15% sodium cyanide. The gold cyanide solution (10 cm^3) was adjusted to pH 6 with hydrochloric acid then mixed with 0.2 g of adsorbent in the protonated form. It is essential to provide adequate agitation, since the process itself is likely to be film-diffusion-controlled at low concentrations. Gold in solution was analyzed by atomic absorption spectrophotometry.

A typical equilibrium curve for samples A1-2 and A1-5 is shown in Fig. 1. The samples were left in contact with the solution for 10 minutes which was enough to reach equilibrium. The gold concentration in solution was varied from 30 to 250 ppm, and the sorption of gold reached a value of 10 mg/g sorbent (Fig. 1). The rate of gold sorption was studied at 20 and 55 ppm initial gold concentrations. At 20 ppm gold and pH 6, 100% of the gold was sorbed within the first minute of reaction for sample A1-2. Sample A1-5 reacted more slowly, i.e. 50% sorption after one minute, and complete reaction after 10 minutes (Fig. 2). At 55 ppm gold at pH 6, the behavior of both sorbents was similar and indicated that about 80% sorption occurs in one minute and that the reaction reaches equilibrium in about 10 min.

Elution experiments were performed with several eluates. Loaded resin (0.2 g) was treated with 10 cm^3 of 0.01 N NaOH, 0.1 N NaOH, or 4 N KSNC.

Batch experiments were performed with moderate agitation over 2.5 hours, and the gold concentration measured in the eluant indicated that gold was readily eluted from the adsorbent by each eluant solution.

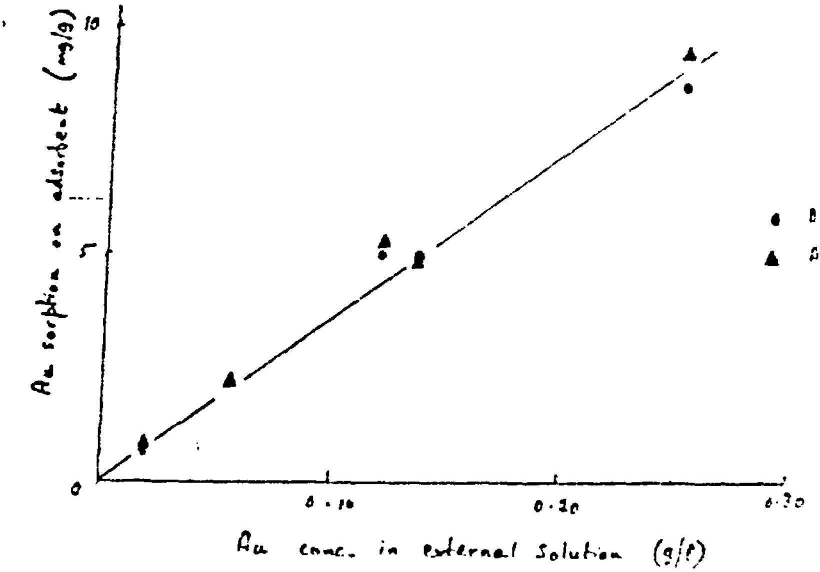

FIG. 1 EQUILIBRIUM CURVE FOR GOLD SORPTION

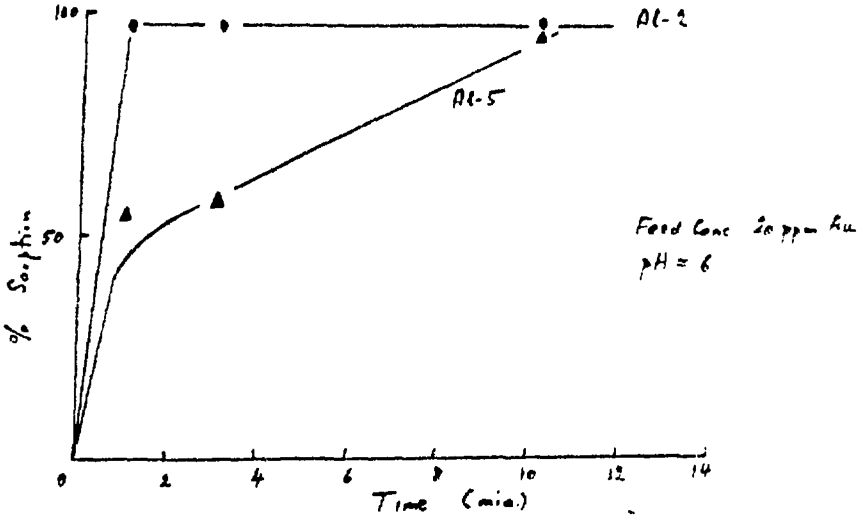

FIG. 2 SORPTION KINETICS

EVALUATION OF THE USEFULNESS OF AMINES IN SEPARATION OF GOLD FROM SOME PLATINUM METALS ON CELLULOSE ION EXCHANGER CELLEX P

Krystyna Brajter and Krystyna Słonawska
Department of Chemistry, University of Warsaw, Pasteura 1,
02-093 Warsaw, Poland.

Introduction

Ion exchange became extremelly usefull as the separation method when adopted for the trace metal separation from the great excess of other metal ions before their determination by atomic absorption spectrometry /AAS/ /1,2/. At gold determination by AAS in the presence of platinum metal ions some interferences were observed. For this reason preliminary separation of gold from some platinum metals was worked out.

Experimental

Cellulose ion-exchanger Cellex P with phosphonic groups was used. The retention of Au/III/, Pt/IV/, Pd/II/, Ir/IV/, Ir/III/ and Rh/III/ in the presence of following amines: ethylenediamine, 1,3-diaminopropane, triethylenetetraamine, tetraethylenepentaamine in function of pH by the batch method was investigated. For the metal determination AAS method with electrothermal atomization was used.

Results and discussion

Good differentiation of the retention of Au/III/ from platinum and iridium in the presence of ethylenediamine was observed. In the dynamic conditions the possibilities of the separation was confirmed. The method has been applied to the determination of gold in different samples of platinum chloride.

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PRECIPITATION ION EXCHANGE: SORPTION STUDIES OF METAL OXALATES ON STRONG AND WEAK ANION EXCHANGERS

S.C.Chaurasia, S.G.Iyer and Ch. Venkateswarlu
Analytical Chemistry Division, Bhabha Atomic Research Centre
Bombay 400 085, India

Introduction

Sorption of metal ions is reported as precipitates on strong anion exchangers when solubilities of their salts are less than 1.5 g/l$^{(1)}$. Contrary to this, Pb is sorbed as sulphate from 50% methanol but not Ba and Sr$^{(2)}$. The variations in the sorption of metal ions in the carbonate form are attributed to kinetic factors$^{(3)}$. Sorption of Ca as oxalate on weak and strong anion exchangers has been studied in our laboratory to understand the mechanism of precipitation ion exchange$^{(4)}$. This paper deals with the sorption of Ag, Ca, Cu and Th as oxalates as a function of cation concentration in the feed.

Experiments and Results

Dowex 2x8 (strong) and AG 3x4A polyamine type (weak) exchangers were converted to oxalate form by passing 1.0 M potassium oxalate. In the case of AG 3x4A, 2.4 meq was converted into the oxalate form and 0.6 meq to OH$^-$ form. Known volumes of stoichiometrically neutral solutions of salts (500 µg/ml to 0.01 µg/ml) were passed through columns (0.4 x 10 cm) and washed with water. The sorbed metal ion was eluted with 1N HNO$_3$ and determined. The data are presented in table 1.

Discussion

It has already been shown in our lab that calcium is sorbed as oxalate in 1:1 ratio on both strong and weak anion exchangers with a difference that precipitation occurs predominantly on the surface of the resin beads of the strong exchanger (visible) while it is inside the beads in the weak one (not visible)$^{(4)}$. Data in table 1 further reveal that calcium is not sorbed on both exchangers when its feed concentration is 1 µg/ml or less. In other cases, sorption is quantitative with as low a concentration as 10 ppb except in the case of Ag on strong exchanger.

In the case of copper (II) the presence of anionic oxalate complex is indicated from the spectra of the copper loaded resin. In the case of Ca and Th on weak exchangers interaction of metal with oxalate is found to be in stoichiometric proportion to form a precipitate from saturation experiments. The deviations observed by earlier workers$^{(2)}$ from the solubility of metal salts may be due to the sorption of anionic complexes rather than the formation of precipitate on the exchanger.

Table 1. Sorption of metal ions on the oxalate form of exchangers as a function of feed solution concentration

Column dimension: 0.1x10cm; flow rate: 1 ml/min; volume of feed soln.: 10 ml; 100 and 200 ml in case of 100 and 10 ppb solutions.

Element	Resin	% of metal ion sorbed with concentration of feed solution (ug/ml)					
		500	100	10	1	0.1	0.01
Calcium	AG 3x4A	>99+	95	35	0	-	-
	Dowex 2x8	98	88+	20	0	-	-
Silver	AG 3x4A	>99	>99	>99	>99	> 99	>99
	Dowex 2x8	*	*	98+	84	5	0
Copper	AG 3x4A	>99	>99	>99	>99	>99	>99
	Dowex 2x8	>99	>99	>99	>99	>99	>99
Thorium	AG 3x4A	>99	>99	>99	>99	>99	>99
	Dowex 2x8	>99+	>99+	>99	>99	>99	>99

* Precipitate is visible on the surface of resin beads
\+ Precipitate moves down through void volume.

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SULFUR SPECIES DETECTION IN LOADED MEDIA BY ION COLUMN.CHROMATOGRAY

P. MODOLO

UNIREC - Chemical Analysis Department - BP 34 - 42701 FIRMINY - FRANCE

Introduction

Several authors (1-3) have studied detection of sulfur species as SO_4^{2-} , SO_3^{2-} , S^{2-} in water or in diluted effluents. The detection of this species in loaded media or in media containing high quantities of dissolved species such as NaCl , Na_2SO_4 or H_3BO_3 ask us a lot of question. Chromatographic analysis is disturbed by phenomena such as mutual interferences between anions, or saturation of the conductimetric detector and of the separation column.

Experimental

A ion-suppressed chromatographic system with double detection (conductimetric and amperometric) allowed us to get detection limits as good as those obtained in diluted media.

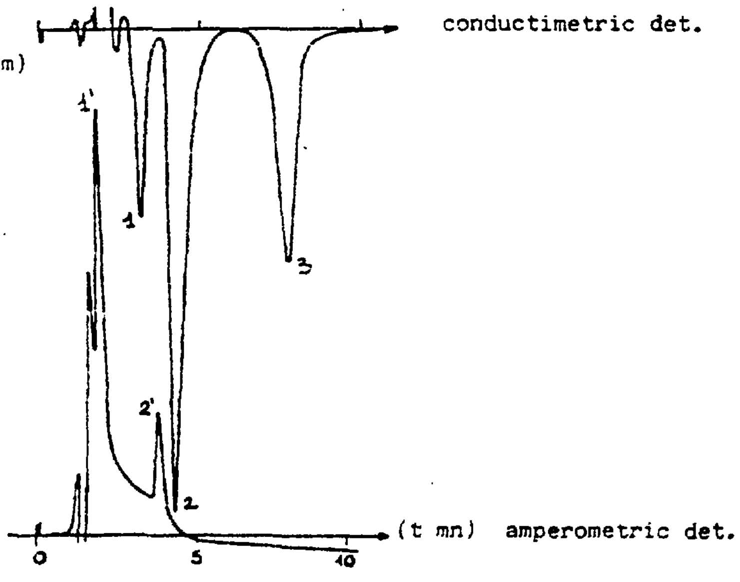
Figure

We can see on the following figure, the general espect of chromatograms obtained with such a system.

test chromatogram

medium : H_3BO_3 (7000ppm)

1 : Cl^-	
2 : SO_3^{2-}	0,4ppm
3 : SO_4^{2-}	0,4ppm
1': S^{2-}	0,4ppm
2': SO_3^{2-}	0,4ppm



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OPTIMIZING AND COMPARATIVE STUDY OF SUPPRESSED AND NON-SUPPRESSED ION-CHROMATOGRAPHY FOR SEPARATION OF ALKALINE EARTH IONS

Hajós, P., Kecskeméti, T. and Inczédy, J.
Institute of Analytical Chemistry
University of Vèszprém, H-8201, Veszprém, Hungary

Introduction

The ion-exchange behaviour of alkaline earth ions are very similar and their binding on the cation exchange resin in the separator column is very strong. Two methods are applicable for IC separation of these ions using Zn^{2+}/H^+ and EnH_2^{2+}/H^+ eluents in the case of suppressed and non-suppressed techniques, respectively [1] [2]. This work deals with the optimization of the eluent pH, eluent composition in both systems. The results obtained by the above methods are compared.

Experimental

A Dionex ion-chromatograph (Model 10 IC) was used throughout this study. Separations were carried out on the same cation separator column (Biotronik IV. KA, 3x100 mm) for both systems and on a 9x250 mm suppressor column for the suppressed system. All samples were prepared from reagent grade (Baker BV) salts.

Results and Discussion

1. The optimum eluent concentration for both eluent systems was found to be $5x10^{-4}...10^{-3}$ mole/ℓ (Fig. 1 and Fig. 2).

2. It was found that the optimum eluent pH ranges are 2,5...4,0 and 4,0...4,5 for the suppressed and the nonsuppressed system, respectively.

3. These parameters represent a compromise between good resolving power of the separation and the length of the retention time.

Fig. 1

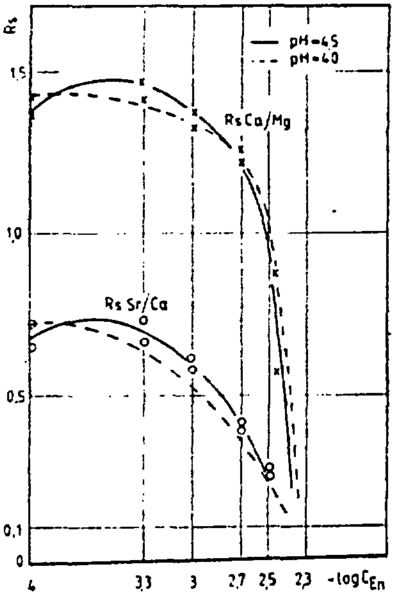
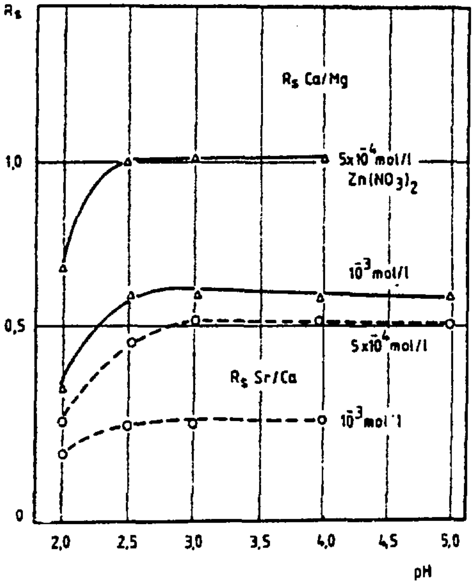


Fig. 2



4. The linear relationship between $\log D_M$ and $\log[\mathrm{eluent}]$ predicted by eqns. $\log D_M = \log K_1 + \log Q/2 - \log[EnH_2^{2+}]$ and $\log D_M = \log K_2 + \log Q/2 - \log[Zn^{2+}]$ were tested. The observed plots were linear and showed slopes of (-0,97...-1,16) and (-0,83...-1,07) in the optimum pH ranges. These results are in agreement with the theoretical slope of -1,00.

5. The retention time of ions in the non-suppressed system are smaller (10 min/3 ions vs. 20 min/3 ions).

6. The sensitivity of the suppressed method is higher for all alkaline earth ions. The analytical results of the two methods were evaluated statistically.

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AP-03

REDUCED WATER UPTAKE AND ION-CHROMATOGRAPHIC PERFORMANCE OF SURFACE SULPHONATED CATION EXCHANGERS

Hajós, P. and Inczédy, J.
Institute of Analytical Chemistry
University of Veszprém, H-8201, Veszprém, Hungary

Introduction

In our previous papers [1][2] we described the preparation of ion-chromatographic grade cation exchangers by surface sulphonation. Cation exchangers of varying capacities were produced by this method from St-DVB copolymers of varying DVB content. This work deals with the swelling of these resin, wich can be investigated by the measurement of the water uptake.

Experimental

Water content of the wet resins were determined by the centrifugation method. The difference between the wet weight and the dry weight gives the water uptake. A microcoulometric method was used for the determination of the capacity of ion--exchanger.

Results and Discussion

The reduced water uptake of the surface sulphonated resin is meant here as the water uptake of the functional groups restricted to the surface of the exchanger. It can be expressed by the following equation:

$$S_r = S - S_o(1-Q_s/Q_t)$$

where

S_r is the reduced water uptake (mgH_2O/g dry H-form resin)
S is the measured water uptake of the surface sulph. resin

S_0 is the measured water uptake of St-DVB copolymer
Q_s is the capacity of the surface sulph. resin (mmole/g resin)
Q_t is the theoretical capacity of completely sulph. resin.

The $S_0(1-Q_s/Q_t)$ term are characteristic for the water uptake of the unsulphonated core. The results of water uptake as a function of DVB content and capacities of the resins are presented in Table 1.

Table 1

DVB content (%)	capacity (mmole/g) Q_s	water uptake (mgH$_2$O/g resin) S	reduced water uptake (mgH$_2$O/g resin) S_r	molar water uptake (mgH$_2$O/mmole resin) S_r/Q_s
2	0,191	332	201	1052
	0,165	304	172	1042
	0,137	269	136	993
	0,027	165	30	1100
	0,019	157	22	1158
	0	136	-	-
12	0,081	89,7	40,5	500
	0,043	73,9	24,3	565
	0,027	65,7	16,0	593
	0,016	59,3	9,5	594
	0	50,0	-	-

At a fixed degree of crosslinking the reduced water uptake appears to be approximately a linear function of the capacity, and the results of molar water uptake are nearly constant. On the other hand, resins of low DVB content showed higher water uptake and are likely to possess higher rates of exchange. The performance of these resins differing in DVB content and capacities, i.e. swelling properties was compared directly by ion-chromatographic separations of cations.

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AP-04

Multicolumn Ion Chromatographic determination of nitrate and sulfate in waters containing humic substances.

Eva Hoffmann, György Marko-Varga*, Istvan Csiky and Jan-Åke Jönsson. Dep. Analytical Chemistry, Univ. of Lund, P.O.Box 124, S-221 00 Lund, Sweden.

The analysis of nitrate and sulfate in natural waters is of great biological and environmental significance. A large variety of traditional techniques has been used for their determination (1). All these techniques are influenced by the presence of humic substances in the samples and there is a continous need for selective methods.

In recent years, the technique of non-suppressed ion chromatography (IC) has become a sensitive and efficient method for anion analysis. Also ion chromatographic determinations are severly desturbed by interferences from humics since those substances adsorb irreversibly to the quarternary amine groups in the separation column and destroy the column performance.

Recently we investigated different kinds of chemically bonded liquid chromatography phases for the selective adsorption of humics prior to ion chromatographic determination of anions(2). The chemically bonded amine material was found to be superior. Furthermore, a clean-up method using commercially available solid phase extraction columns of similar type was developed(3,4).

In this poster a three-column ion chromatographic system for the removal of humic substances from natural waters, and subsequent concentration and determination of nitrate and sulfate using non-suppressed ion chromatography is presented.

Humic substances are removed using disposable adsorption columns packed with chemically bonded amine silica material. The sample is directly transferred to an ion exchange column where the anions are concentrated ca 10 times. After reversing the flow, the ions are transferred to a third column where they are separated and quantified. The detection limit is less than 1 mg L^{-1} of nitrate or sulfate in water containing 45 mg L^{-1} of humic acid.

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AP-05

CHROMATOGRAPHIC STUDIES ON MIXED DERIVATIZED ZIRCONIUM PHOSPHATE AND DEXTRANE GELS

J. Környei and L. Szirtes
Institute of Isotopes of the Hungarian Academy of
Sciences Budapest, Hungary

The gels were obtained from crystalline zirconium phosphate and its derivatives by defoliation and solvatation of the single layers of them. The mechanical stability of this type of gels isn't high enough for using them in column operation.

In order to study their chromatographic properties a mixture of them with dextrane gel was prepared. In this mixture a neutral dextran gel has been chosen so the zirconium phosphate part contained the functional groups, like = = P-OH, $=P-CH_2-CH_2-COOH$, etc.

The separation of Ga transferrin from Ga-complexes of citrate, edta, lactate, respectively, were carried out using a column with a length of 350 mm and diameter of 10 mm, filled with above mentioned mixed gels.

The results concerning the preparation of the mixed gel and the separation carried out using them are collected in this paper.

AP-06

ANS LOADED RESIN AS A SELECTIVE ION EXCHANGER FOR THE SEPARATION OF SILVER FROM OTHER METAL IONS

K.Brajter and E.Dąbek-Złotorzyńska
Department of Chemistry, University of Warsaw, 02-093 Warsaw
Pasteura 1, Poland

Introduction

The complexes forming resins prepared by the simple modification of the common anion exchange resin with sulphonated aromatic complexing agents display high selectivity for the prefered counter ions as we have demonstrated /1-4/. This paper describes the properties of the macroporous anion exchange resin Amberlyst A-26 loaded with 8-amino-naphtalene-2-sulphonic acid /ANS/. ANS immobilized on Amberlyst A-26 transforms it into a kind of the selective exchanger towards silver ions. We have shown that selective separation of Ag/I/ from other metal ions is possible.

Experimental

The exchange capacity of complexing agent by batch method was determined. The stability of the modified resin towards mineral acids was investigated. The retention of metal ions on modified with ANS was determined. The concentration of metal ions was determined by AAS.

Results and discussion

The retention of metal ions on ANS loaded resin was investigated as a function of pH. At low pH values good differentiation of the selectivity of Amberlyst A-26-ANS loaded resin was observed. As results the conditions for the selective separation of Ag/I/ from the following metal ions: Cu/II/, Pb/II/, Zn/II/, Ni/II/, Co/II/, Fe/III/, Cd/II/ were established. Experiments performed in dynamic conditions confirmed that in 0.05 M HNO_3 the selective separation of Ag/I/ from all above mentioned metal ions is possible. The method was adopted for determination of silver in copper ores.

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AP-07

ION EXCHANGE COLUMN CHROMATOGRAPHIC METHOD FOR THE DETERMINATION OF THE CYSTINE CONTENT OF FODDERS AND FOODSTUFFS IN CYSTEINE FORM

Csapó, J. - Csapó, J.

Agricultural College of Kaposvár, Hungary

Introduction

Merkaptoethanesulphonic acid (MES-OH) is widely used for the determination of tryptophan in peptides and proteins [1] . This method is relaiable only for pure peptides and proteins, although the results for carbohydrate containing samples are better than those obtained by any of the earlier methods. In a study of the effect of the MES-OH on the hydrolysis of proteins we realised that the cystine content of the proteins can not be determined with this method because of the reduction of cystine to cysteine, and presumably also, due to the formation of the tioether bond between the cystein and the sulfohydril group of the MES-OH. This work is concerned with the ion exchange column chromatographic determination of the cysteine and through the cysteine the cystine content of foodstuffs and fodders can also be obtained.

Experimental

The MES-OH hydrolysis of the proteins were performed in cleaned and dried medical ampoules. The cystine and the samples (50 mg) were hydrolysed with 5 cm^3 MES-OH (3 mol/dm^3) at 110 ± 2 °C. After hydrolysis the ampoules were cooled, opened and 10 cm^3 NaOH (1 mol/dm^3) was given to them. The content of each ampoule was washed into a 25 cm^3 volumetric flask and a 1 cm^3 aliquot portion was used for the amino acid analysis.

Results and discussion

Using the cystein, produced from cystine and MES-OH, as a standard the cystine content of different samples were determined and compared to the results obtained by the methods of Moore [2] who uses hydrochloric acid (3 mol/dm^3), Liu [3] who recommends p-toluenesulphonic acid (3 mol/dm^3) and Hirs [4] who proposes hydrochloric acid (6 mol/dm^3) after the performic acid oxidation step. The amino acid analysis gave the quantity of the admixed cystine with a higher efficiency than 90%. As a result of our research we pointed out that at the MES-OH hydrolysis the cysteine resulting from the cystine appears at the place of proline on the chromatogramme and in the case of proteins of high cystine content it may cause an error in the analysis of proline. Similarly to the effect of the MES-OH, the reducing agents may cause a decrease of the casteine and an increase of the proline concentration during the analysis. Since the proline and cysteine can not be separated by the conventional buffer systems, a new method was elaborated by changing the pH, the sodium ion concentration and the alcohol content of the buffers. Using this method, the amino acid analysis of different kind of feathermeal of high cystine content have successfully been made.

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AP-08

STUDIES ON THE EXTRACTION OF LANTHANIDE(III)-ETHYLENEDIAMINE-TETRAACETATE COMPLEXES WITH ALIQUAT-336

R. Király and E. Brücher

Department of Inorganic and Analytical Chemistry,
Kossuth University, Debrecen, H-4010 Hungary.

Lanthanide(III)-ethylenediamine-tetraacetate ($LnEDTA^-$) complexes are of high importance both in the cation- and anion-exchange chromatographic separation of lanthanides. The distribution coefficients of the complexes $LnEDTA^-$ on strongly basic anion-exchange resin of H_2EDTA^{2-} form exhibit a maximum in the middle of the lanthanide series, which was explained by a change in the denticity of the coordinated ligand [1]. On the basis of the similar trend of the distribution coefficients and the stability constants of the $Ln(EDTA)(HEDTA)^{4-}$ as well as $Ln(EDTA)_2^{5-}$ complexes, it was assumed that the lanthanides are bound in the resin phase as 1:2 metal to ligand complexes [2].

Recently we have studied the extraction of complexes $LnEDTA^-$ with the liquid anion-exchanger of quaterner ammonium type Aliquat 336. M[LnEDTA] complexes ($M^+=Na^+$ or K^+) were prepared in solid form and their aqueous solutions were equilibrated with Aliquat 336 dissolved in different organic solvents.

The distribution coefficients of the complexes $LnEDTA^-$ increase with increasing concentration of the liquid anion-exchanger and decrease with the rise of the electrolyte concentration in the aqueous phase.

The distribution coefficients obtained with equal volumes of 1.0 M Aliquat 336-chloride (dissolved in cyclohexane) and 0.02 M K[LnEDTA] solutions (pH ≈ 7) at 25°C are the following

La	Ce	Pr	Nd	Sm	Eu	Gd	
1.71	1.33	1.23	1.07	0.87	0.75	0.87	
Tb	**Dy**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**	**Y**
0.74	0.82	0.72	0.68	0.74	0.65	0.75	0.70

The average reproducibility of the distribution coefficients is about ±0.05.

The distribution coefficients drop from La to Eu and their trend between Gd and Lu is also decreasing. The change in the distribution coefficients indicate a decrease in the size of complexes from La to Lu. In this direction the structure of complexes becomes more and more rigid due to the lanthanide contraction and the number of water molecules coordinated in the inner sphere probably also decreases by one in the middle of the series.

The complexes $LnEDTA^-$ extracted into the organic phase have been investigated by electron- and ^1H-NMR spectroscopie methods. The structure of complexes in the two phases was found to be very similar. The partition of water between the aqueous and organic phases was also investigated. From the data some information was obtained for the mechanisms of the extraction of complexes $LnEDTA^-$.

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STUDIES ON THE EXTRACTION OF GALLIUM AND ALUMINIUM WITH DIALKYL-DITHIOPHOSPHORIC ACIDS

I. Tóth, Z. Szabó and E. Brücher

Department of Inorganic and Analytical Chemistry
Kossuth University, H-4010 Debrecen, Hungary

The separation of gallium from aluminium is of practical importance, since gallium is most frequently produced from the Na-aluminate liquor of the Bayer process. On the basis of the difference in the electronic structure of Ga^{3+} and Al^{3+} ions we assumed that Ga^{3+} has higher affinity to ligands containing sulphur donor atom(s).

The extraction of Ga^{3+} and Al^{3+} has been studied with the liquid cation-exchangers di-n-butyl-dithiophosphoric acid (DBTPA) and di-(2-etilhexyl)-dithiophosphoric acid (DETPA) which were prepared from P_2S_5 and the appropriate alcohol.

The partition of Ga^{3+} and Al^{3+} has been studied between equal volumes of aqueous and organic phases. As diluent kerosene was used. The extraction coefficients rise with increasing pH and the values obtained with DETPA are about one orders of magnitude higher than those obtained with DBTPA. The trend of the extraction coefficients with increasing pH can be interpreted assuming the extraction of species $M(DBTPA)_3$ and $M(DETPA)_3$. The extraction coefficients are about two orders of magnitude higher for Ga^{3+} than for Al^{3+}, making possible their separation in a quite broad interval of pH. The extent of extraction of both Ga^{3+} and Al^{3+} decreases at higher pH and at $pH > 10$ there is practically no extraction.

The extraction of Ga^{3+} and Al^{3+} with DETPA has also been studied in the presence of n-octanol or tri-n-butyl-phosphoric acid. With the use of thesecompounds the values of extraction coefficients practically did not change, but the separation of the phases was much faster.

The IR spectrum of the solid $Ga(DBTA)_3$ is very similar to that of Na(DBTA), indicating a predominantly ionic bonding in the Ga-complex.

EXTRACTION OF METALS BY POLY(4-VINYLPYRIDINE) RESIN

D.A.MOHAMMED

Iraqi Atomic Energy Commission ,Baghdad, Iraq.

INTRODUCTION : Attempts to use poly(vinylpyridine) resins,in which the pyridine moiety takespart in complex formation, for the separation of metal ions have been made by several investigators [1,2] .

This paper describes the sorption and desorption behaviours of metal ions on poly(4-vinylpyridine) resin .

EXPEREMINTAL : The polymer was prepared by the method described by sugii [1] .Using the method described by Mohammed [3] ,the characterization and application of the resin for separation of Fe(III) ,V(V), Mo(VI) and Nb(V) was carried out .

RESULTS AND DISCUSSION : The sorption and desorption characteristics of Fe(III), V(V), Mo(VI) and Nb(V) on poly(4-vinylpyridine) resin have been investigated from hydrofluoric acid medium .Vanadium, molybdenum, niobium are quantitatively sorbed from a wide range of the acid concentraion and the results are included in FIG.I.Also sorption and desorption kinetics were examined for all the ions investigated (using selected eluentswhich are IM HF,2M HCl, 3M HF-3M HCl and 4M NH_4Cl-1M NH_4F for the recovery of Fe(III),V(V),Mo(VI) and Nb(V) respectively) . The test shows that the sorption and desorption rates for all the ions have a resonable value

Based on the obtained results, a chromatographic separation schem for Fe(III), V(V), Mo(VI) and Nb(V) was achieved using a solution containing various amounts of the ions in 1M HF .The ions were then eluted successively using the selected eluents and the results are shown in Table I.

Three steel samples were analysed for vandium, molybdenum, and niobium using the established procedure and the results are included in table II.

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Table I. SEPARATION OF Fe,V,MO AND Nb IN A SYNTHETIC SOLUTION

Metal	Added mg	Found mg	Eluent	Recovery
Fe	150	150.5	M HF	100.4 ± 4
V	2.5	2.45	2M HCl	98.0 ± 2
Mo	1.3	1.5	3M HCl-2M HF	101.5 ± 3
Nb	2.3	2.45	4MNH$_4$Cl-1M NH$_4$F	98 ± 5

Table II. ANALYSIS OF STEEL SAMPLES

B.C.S. standard No.	Metal Ion	certified value %	found value %
407/1	V	0.18	0.175 ± 3
	Mo	0.78	0.76 ± 3
	Nb	1.0013	1.00 ± 2
467	Nb	1.06	1.1 ± 4
401/1	V	0.52	0.53 ± 2

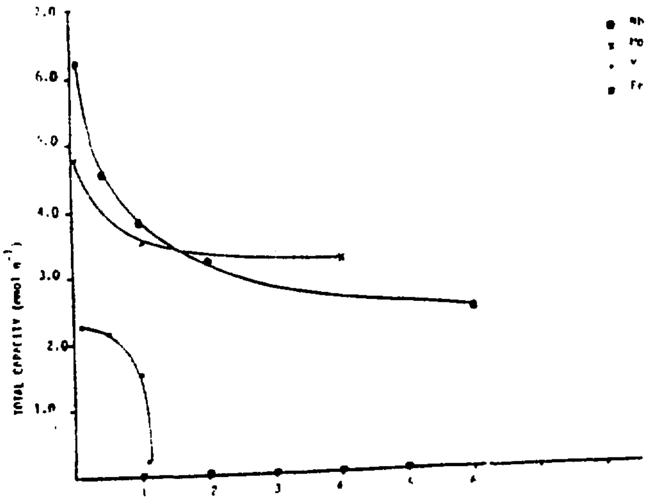

FIG.1 TOTAL CAPACITY OF PAMP RESIN FOR Fe(III),V(V),Mo(VI) AND Nb(V) AS A FUNCTION OF HF CONCENTRATION.

Preconcentration of Trace Elements Using Cellulose Exchanger

J. Borszéki[1], G. Knapp[2], K. Müller[2], W. Wegscheider[2]

[1]Dept. of Anal. Chem. Univ. of Veszprém, HUNGARY

[2]Dept. of Anal. Chem., Technical Univ. Graz, AUSTRIA

Cellulose filters have been prepared with covalently bounded 8-hydroxyquinoline.
Features of this oxin-exchanger were investigated by using a column technique.
Separation of matrix elements (Ca, Mg) was practically perfected, and the precontration of Mn, Fe, Co, Ni, Cu, Zn, Cd at a given pH-value has been performed effectively. The elution with diluted nitric acid resulted in a matrix-free preconcentrated solution suitable for the determination of trace elements by ICP-OES or GF-AAS technique. Capacity of the oxin-cellulose ion-exchanger has been determined using ^{65}Zn isotope element which gave a value of 170 µmol/g.

Effect of linkage and elution on the cellulose exchanger (in dependence on pH) has been investigated, and a suitable value of pH = 5.6 was stated for all elements except Co. The effectivity of linkage was above 90% or in several cases over 95%, and the recovery was in all cases total. The exchanger can be used for the enrichment of trace elements in the concentration range of pg-ng/l during a series of 60-70 elutions without a loss of capacity.

The results were checked by a standard solution of EPA and by NBS-SRMS ashed by means of a High Pressure Asher

(HPA-System: Prof. Knapp).

The analysis was carried out by a Perkin-Elmer Spectrometer ICP-6000, and a P-E Model AAS-5000.

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THE USE OF LIGAND EXCHANGE FOR THE SEPARATION OF AMINOACIDS AND ACIDS ON CATION EXCHANGERS

J.Lasłowska, K.Gąsińska, M.Piątek

Institute of General Food Chemistry, Technical University of Łódź, Poland

Introduction

Ligand exchange is an advanced technique for the separation of anionic mixtures or neutral compounds which are able to form complexes with metal ions. The separation mechanism is the same as in ionexchange chromatography with the same only difference that ligands are exchanged instead of counterions. In comparison with other chromatographic methods the advantage of the ligand-exchange process is that the formation of a complexes represents, as a rule, a more specific interaction than ordinary physical sorption or ion exchange. In the present study, the separation of the mixture of aminoacids or the mixture of aromatic acids was attempted using a synthetic cation exchangers containing metal ion such as Cu^{2+}, Zn^{2+}, Mn^{2+} or Fe^{3+}, Ce^{3+} and Al^{3+}.

Experimental

The chromatograms were developed by the elution technique introducing the sample to the top of the column. Dowex 50 WX 10 200/400 mesh resin was used as the cation exchanger. The conversion of the cation exchanger from H^+ form to the Me^{n+} form was performed in the columns, by passing a solution of the metal salt to the breakdown point.

Results and Discussion

Based on the experimental results, values of stability constants $(\log \beta_n)$ and the separation parameters were calculated (Table 1 and 2).

Table 1. The values of $\log \beta_n$ of the complexes of metal ion with aminoacids, found by the ion exchange method.

Complexes	$\log \beta_n$		
	Zn^{2+}	Mn^{2+}	Cu^{2+}
$[M(Ala)]^+$	4,50	3,01	6,50
$[M(Ala)_2]^0$	5,00	3,20	7,20
$[M(pro)]^+$	4,80	3,23	6,83
$[M(pro)_2]^0$	5,00	3,51	7,0
$[M(Arg)]^+$	3,50	2,75	5,40

Based on the values $\log \beta_n$ and the theory of Jacymirski we obtain:

$$p = a + n \cdot b \cdot p\beta^0$$

where b-polarization of aminoacid and $p\beta^0$-stability constant of complexes with alanine.

Table 2. Separation of acids on the cationite bed in the Fe^{3+} form. Eluent: H_2SO_4, 0,01 mol/dm^3

Sample	t_R min	k'	R_s	α	N
Benzoic acid	5,80	3,82	1,50	1,56	788
Cinnamic acid	8,20	7,08	1,20	1,10	1150
4-Hydroxy-benzoic acid	10,31	9,27	1,58	1,18	495

On the basis of the obtained results, one can state that by the selection of a proper counterion able to form complexes considerably higher selectivities can be achieved.

COMPARISON OF ANION-EXCHANGE PROCEDURES IN Al(III) TRACES RECOVERY

C.Sarzanini,E.Mentasti,M.C.Gennaro and V.Porta
Dipartimento di Chimica Analitica, Università di Torino
Via P. Giuria 5 , 10125 Torino. Italia

Introduction

Aromatic complexing agents containing sulphonic acid groups are particularly useful in separation of metal ions on anion-exchange resins as shown earlier (1,2,3).
The ability of Pyrocatechol Violet (PV) in alluminium-matrix separation and preconcentration is here investigated by two methods based on complex formation coupled with anion-exchange resin or column chelation procedure.Synthetic samples are investigated in the presence of interfering agents.

Experimental

Thermostated borosilicate glass columns were employed in which a slurry of 1.0 g of macroporous anion-exchanger, Bio-Rad MP 1 (100-200 mesh), was supported. Costant flow of samples through the column was ensured by rotary vacuum pump. Metal concentration measurements were performed by dc argon plasma emission spectrometry. PV and all other reagents were of analytical grade and high purity water (HPW) was employed.

a.Precomplexation-Anion-Exchange (PAE)

1.0 g of AG MP 1 is rinsed and preconditioned with HPW to the proper pH. 100 and 1,000 ml solutions containing 10.0 μg of Al(III) added to 2.0 ml and 7.0 ml of 0.05 M PV respectively are brought to the desired pH. The samples are fluxed through the column washed with HPW after the elution.

b.Chelating-Agent-Loaded-Resin (CALR)

The chelating-agent-loaded-resin was prepared by flowing 4.0 ml of 0.05 M PV solution through the column paked with 1.0 g of resin, chloride form. The loaded resin bed was washed with HPW at the same pH of the next experiments.Release of chelating agent is not shown in all cases. Al(III) solutions as in previous procedure were fluxed through.
The metal is recovered in both procedures by acid elution (1.0 ml of 1.0 N HCl + 9.0 ml of 0.1 N HCl).
The metal recovery as a function of pH was evaluated taking into account the computed species distribution.
Interferences of most common surfactants: cetyltrimethylammonim bromide (CTAB), sodium dodecylhydrogen sulphate (SDS) and poly(ethylene glycol) (POLY) were tested. Potentially interfering salts including K_2HPO_4 ,NaCl as well as the effect of competing ligand nitrilotriacetic acid (NTA) were evaluated.
The methods were also tested at part per bilion levels of Al(III). Synthetic samples (1,000 ml) containing Al(III) spike (10.0 μg) were enriched with the described procedures at the optimum pH for the metal

recovery. The spikes found were 100.0 ± 1.7 and 92.5 ± 0.9 % for three indipendent measurements respectively with PAE or CARL procedure.

Results and Discussion

The most significative results are shown in Table 1. The PAE procedure resulted more suitable to collect and preconcentrate Al(III) traces. The reduced recovery showed by CALR method was demonstrated to depend on pH decrase during complex formation into the column so that 1/1 (metal to ligand) complex is favored and released from the column. The good results obtained in the presence of interfering agents and of high ionic strenght suggest the suitability of PAE procedure as an analytical method to preconcentrate Al(III) traces in natural systems.

Interferent type	conc. µg/ml	Al(III) recovery % PAE	CALR
CTAB	5.0	98.8 ± 1.0	94.4 ± 0.7
	20.0	*	90.5 ± 0.7
	50.0	*	87.2 ± 0.9
POLY	5.0	99.6 ± 0.5	94.5 ± 0.9
	20.0	100.8 ± 1.8	94.9 ± 0.4
	50.0	101.2 ± 0.6	93.4 ± 0.1
SDS	5.0	99.1 ± 1.1	94.8 ± 0.9
	20.0	98.8 ± 0.4	96.2 ± 1.0
	50.0	98.4 ± 0.1	96.9 ± 1.0
NTA	275.0	99.8 ± 0.6	95.7 ± 0.4
	2750.0	99.3 ± 2.9	95.8 ± 0.4
K_2HPO_4	100.0	99.8 ± 0.4	96.3 ± 0.7
	200.0	100.2 ± 0.7	94.0 ± 1.3
	500.0	100.4 ± 1.0	94.3 ± 0.6
NaCl	0.1 M	94.2 ± 0.1	99.9 ± 0.7
	0.5 M	91.2 ± 0.5	104.4 ± 1.2

* In these conditions, separation of insoluble products occurs.

Table 1. Effect of Interfering Agents on % Al(III) Recovery (PAE:pH 7.0, CARL:pH 9.0; 0.1 µg/ml Al(III) solution).

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CONDUCTOMETRIC CONTROL OF ION EXCHANGE PROCESSES I. NON-CONVENTIONAL CONDUCTOMETRIC SENSORS USED IN PRODUCTION OF ULTRAPURE WATER

Cs. Muzsnay[1], Edit Forizs[2] and R. Gabruş[2]

1. Department of Inorganic and Analytical Chemistry of Babeş-Bolyai University, Cluj-Napoca, Romania
2. Institute of Chemistry, Cluj-Napoca, Romania

Introduction

Advances in microelectronics, trace chemical analysis, medicine, purification technologies - chemical, pharmaceutical, cosmetics, electroplating, printing, etc. - photography, mechanical precision, air conditioning, etc. are placing extraordinary demands on the quantities of ultrapure water. Due to reserches (1,2), developments and quality controls, there is now a better understanding of the structure of liquid water and its impurities, and of the purification methods. In recent years, the number of sensitive laboratory tests has greatly increased. The easiest and fastest method of measuring water purity is the conductometric one. Because of numerous control points, the number of sensors used are increased in deionisers. For instance, the Kemotron Company produces water purification devices and plants with about 25 control points (3). The electrodes requirements of ion-chromatography is also considerable. The non-conventional conductometric sensors have advantages over the high priced Pt (or Au) sensors (4).

Experimental

It was studied the following two types of the non-conventional - from point of view of electrode material used - sensors in both stationary and continuous flow condition: 1) Ring shaped electrodes made from Inconel inox wires in amphibious use. 2) The lance-type inox sensors for using both in c.a. and c.c. techniques. The most important characteristic of these cells consist in the fact that is composed from a plastic tube, which represents the wall of sensors being pinked with two or more sharp inox needles - for a.c. technique are preferred 3 electrodes. The c.c. technique presumes cells with four needle-formed electrodes. Two sorts of needle has been used: a) sharpened Inconel lances, b) Cr-Ni coated sharp lances. When the polyethylene tube is wound up in disk-form, the obtained four electrodes type sensors have greater mechanical stability than the linear one. The cell temperature is maintained constant easier with gases than with liquids.

In order to obtain the ultrapure water a recirculation system was operated with the following principal components: 1. Dofin pump, 2. Reservoir, 3. Pressure regulation vessel, 4. Ring shaped inox sensor, 5. Tap, 6. Tap and conductometric sensor, 7. Mixed bed cartridges, 8. Filter and adsorbent cartridges.

Numerous ion exchange attempts was made with Roumanian ion exchangers. The following resins was used: Vionit AT-1, AT-1E, AT-1R, and AT-14 (anionexchangers), Vionit CS-3 and CS-3R (cationexchangers). From these resins was prepared the regenerable mixed beds or was used the neregenerable mixed bed Vionit CA ion exchanger. For the production of ultrapure water a didistilled or deionised water with a maximum conductivity of 5 µS/cm is necessary es primary product.

Results and Discussion

The cell constants (C) of the studied sensors in a.c., at concentrations greater than 1 mM, increase with the concntration growth. In ultrapure water the C value is constant. The c.c. conductivity measurements carried out with the Cr-Ni couted sensors are more exact than those performed with the other sort of needles.

The deionizing effect of the mixed bed is extraordinary. With the obtained and controlled ultrapure water various conductometric, magnetic, flow injection, etc. measurements was carried out. It was studied the comportments of sensors with varying yields and pressions of deionized water in recirculation system.

The increases of cell constant with electrolyte concentration is in connection with the polarization of sensors in a. c. (2). In very dilute solutions the results are not affected by polarization effects. The errors of conductivity determination obtained in c.c. with the lance type sensors can be reduced by the corresponding choose of the measuring electrodes distances. In the case of great stream velocities, precious conductivity measurements can be performed only by vigurous maintenance of the constant temperature. The ion exchange processes, in mixed beds take place step by step in six stages up to the exhaust of the resins.

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AP-15

THE PREPARATION OF 8-HYDROXYQUINOLINE SUBSTITUTED SILICA GEL FOR DETERMINATION OF STRONTIUM-90 FROM NATURAL WATER

Gy. Szabó, J. Guczi, D. Stúr

"FRÉDERIC JOLIOT-CURIE" NATIONAL RESEARCH INSTITUTE FOR RADIOBIOLOGY AND RADIOHYGIENE, BUDAPEST, HUNGARY

INTRODUCTION

Strontium-90 is one of the most hazardous fission product for long-term exposure. Strontium-90 is normally measured by separating and counting its daughter product yttrium-90 from solutions at or near radioactive equlibrium (1).

8-hydroxyquinoline is a well-characterized and well-known reagent (2), over 60 metal ions react with oxine to form complexes.

Silica immobilized 8-hydroxyquinoline is stable over a wide pH range of 0-9 (3,4). The chelation characteristics of the gel functionate well in saline media and high ionic strength samples (5).

EXPERIMENTAL

The preparation of 8-hydroxiquinoline substituted silica gel was based on Hill's (3) and Weetall's (4) procedures.

3-/2-aminoethylamino/propyl silica gel made by treating the silica gel of 0,063-0,1 mm with 3-/2-aminoethylamino/propyl-trimethoxysilane, was reacted with p-nitrobenzoyl chloride and the $-NO_2$ group was reduced to $-NH_2$ with Na-dithionite. After diazotization silica gel derivative was produced by a reaction with 8-hydroxyquinoline.

The determination of metal binding capacity of preparated silica gel was carried out by copper-uptake measurement (6).

The strontium-90 and yttrium-90 was separated from each other by metal chelation with 8-hydroxyquinoline substituted silica gel. The surface water samples were taken from Danube.

The copper was quantified by atomic absorption and all radionuclides were counted as oxalate precipitates by low-background beta-counter.

RESULT AND DISCUSSION

The capacity of 8-hydroxyquinoline substituted silica gel, has been found 217 μmol g^{-1}.
A new method has been developed for separating low-level activities of β-emitting yttrium-90 from natural water; as follows. The pH of the surface water samples is adjusted to 5,5-6,7 with 1 mol/l sodium acetate. The gel and the appropriate carrier are added, and mixed. After two hours, the gel is filtered and [illegible] with 1 mol/l hydrocloric acid. A few milliliters of saturated ammonium oxalate solution is added to the acid solution and the pH adjusted to 3,0. The precipitate of yttrium oxalate was filtered, washed and transferred to aluminium counting planchets, [illegible] before counting. The recovery of yttrium-90 is [illegible].

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THE SEPARATION OF RARE-EARTH METALS BY ION-EXCHANGE ELUTION DISPLACEMENT FORMATION CHROMATOGRAPHY METHOD

E.A. Chuveleva, O.V. Kharitonov, L.A. Firsova, P.P. Nasarov
Institute of Physical Chemistry, Academy of Sciences of the USSR, Moscow

Abstract not received

THE EFFECT OF ABSORBED DOSES OF IONIZING RADIATIONS ON THE SEPARATION OF RARE-EARTH METALS BY ION-EXCHANGE DISPLACEMENT COMPLEX FORMATION CHROMATOGRAPHY METHOD

L.A. Firsova, E.A. Chuveleva, O.V. Kharitonov, P.P. Nasarov,
Institute of Physical Chemistry,Academy of Sciences
of the USSR, Moscow

Abstract not received

AP-18

Preparative Separation of Radioactive Aminoacids

I. Kleinmann, V. Svoboda

Institute for Research, Production and Application of Radioisotopes

102 27 Praha 10, Czechoslovakia

The aminoacids universally labelled with ^{14}C are prepared from acid or enzyme hydrolyzate of proteins, separated from algae grown in atmosphere of radioactive carbon dioxide. When scaling - up the methods based on polystyrene matrix strong cation exchangers and citrate eluents, mutual peak deformation of some aminoacid pairs were observed. This could be explained if different isotherm shapes are postulated. Results of computer simulations are presented.

Therefore, maximal throughput may be influenced not only by sample amount applied an the column, but also by changing the injected sample concentration. Other parameters /pH, alcohol and citrate concentration, Li-Na ion ratios/ were also examined.

In the second step, desalting of aminoacid fractions was performed, using polyethylenglykol - methylmetacrylate based ion exchangers. The decrese of unspecific hydrofobic intraction enabled the use of simple, volatile organic acids as eluents for separation from citrate and natrium/lithium ions. The procedure for separation from enzyme hydrolyzate enables prepare twenty common aminoacids.

DYNAMICALLY COATED COLUMN FOR THE SEPARATION OF INORGANIC ANIONS BY ION CHROMATOGRAPHY

E. Papp
Department of Analytical Chemistry, University of Veszprém
H-8201, Veszprém, Hungary

For the separation of inorganic anions, recently chemically bonded hydrocarbon stationary phase has been recommended. Coating the surface by an amine with hydrophobic moiety a chromatographic column with easily changeble ion exchange capacity can be obtained [1]. Detection of the inorganic ions can be achieved by adding weak aromatic acids in the eluent and with an indirect UV-spectrophotometric method [2].

The surface of the LiChrosorb RP-18 stationary phase was coated with cetil-trimetil-ammonium-bromide (Cetrimid) using 24 (v/v) methanol containing aqueous eluent. For the purpose of the indirect UV detection KH-phthalate was used. The separation and retention of the Cl^-, NO_2^-, Br^-, NO_3^-, SO_4^{2-} and I^- ions were studied as a function of the Cetrimid content of the column, KH-phthalate concentration of the eluent as well as the quality and quantity of the buffer components mixed in the eluent phase.

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ION EXCHANGE TECHNOLOGY

A UNIVERSAL THEORY ON THE BEHAVIOR OF ORGANIC MATTER DURING THE DEIONIZATION OF WATER WITH ION EXCHANGE RESINS

Dr. R. Kunin, Consultant

Rohm and Haas Company, Philadelphia, Pennsylvania

The role of organic matter during the deionization of water by ion exchange resins is essentially the last of the basic problems that remains unsolved. The removal of the inorganic components present in water supplies by means of ion exchange resins is well understood and poses no basic technical problems. Although usually present as a minor component in most water supplies, the organic matter component of the waters around the world, particularly surface water supplies, poses may problems during the deionization of water with ion exchange resins.

Practically all of the organic matter present in our water supplies can be removed by some "virgin" ion exchange resins. Unfortunately, some of the organic matter is irreversibly adsorbed and removal of organic matter in subsequent operational cycles is drastically impaired resulting in increasing organic matter leakage. Further, a thin film of irreversibly adsorbed organic at the outer layer of an ion exchange resin will result in poor kinetic performance, particularly with respect to silica and other slow diffusing ions. Organic matter not removed by the ion exchange resins of a deionization system will pass into the steam generator of a thermal electric plant forming volatile organic and inorganic acids that cause serious corrosion. The same unadsorbed organic matter will result in failures in the components of the electronic industry. In general, the desired quality of the high purity process water for most industrial operations requires the complete removal of the organic matter present in water supplies.

The basic problem we have faced with respect to the removal of the organic matter component of water supplies by means of ion exchange resins is our lack of understanding of the nature of the organic matter. Unfortunately, the organic matter present in water supplies is, in essence, of an undescript nature and its behavior with respect to ion exchange will vary with the climatic season and geographic lication. In essence, a proper understanding of the nature and behavior of organic matter as related to the performance of ion exchange resins during the deionization process also requires an understanding of soil chemistry and the related hydrological chemical processes.

Although the organic matter is quite complex, recent studies now permit one to formulate a "universal" theory concerning the nature of the organic matter and its behavior with respect to ion exchange phenomena. This paper will describe this theory and how it may be applied in designing and operating an ion exchange deionization system effectively and efficiently. Further, the paper will describe how the theory can be used in selecting the proper ion exchange resins, formulating a proper regeneration procedure and developing an adequate pretreatment process. Finally, the theory will explain why some systems are quite successful in some geographic locations but behave poorly in others and why the acrylic-based anion exchange resins are preferred over the styrenic-based anion exchange resins in many situations.

TO-02

A COMPREHENSIVE APPROACH TO CYCLIC REGIMES IN MULTICOMPONENT FIXED-BED ION-EXCHANGE OPERATIONS.

M. Bailly[1], L. Aranyi[2] and D. Tondeur[1]

1. Laboratoire des Sciences du Génie Chimique - CNRS-ENSIC
   1, rue Grandville 54042 Nancy, France

2. Veszprem University of Chemical Engineering, Schönherz
   z.u. 10, Veszprem, Hungary

The optimal design of fixed-bed ion-exchange or adsorption operations requires the knowledge of the cyclic steady-state corresponding to given operating conditions, and possibly the knowledge of the sensitivity of such steady-states to changes in the operating conditions. Unfortunately, the features of the cyclic steady-state are not easily predictable, except in some special cases, from first principles, or from non-cyclic information, or without a knowledge of the transients that lead to it. We propose here a comprehensive approach, with the purpose of obtaining qualitative and semi-quantitative trends. This approach is based mainly on the equilibrium theory and relies on a model of the cyclic behaviour.

First, the rules governing the concentration profiles for a single step input are recalled ; these rules give the number of fronts generated, the order of breakthrough of the various species, the relative concentration changes, the sharp or dispersive character of the fronts. The effects of feed composition and of equilibrium coefficients on the breakthrough behaviour are discussed, for saturation and regeneration.

From these properties, we may conviently investigate a simple "model" of cyclic operation, in which the adsorbent is mixed after each step, and the concentration profiles thus made uniform. Such a cycle is shown to give results intermediate between the co-current and the countercurrent operations, and sometimes yields a good approximation for the operating capacity of both. The effect of feed composition and equilibrium coefficients may then be estimated semi-quantitatively from the model cycle. It is emphasized that the determining factors of the cyclic regime may be very different from that of the separate saturation and regeneration steps.

These considerations are applied to such operations as water softening and water denitration. In the first case, the order of selectivities of the cations is the same in saturation and regeneration. In denitration, on the other hand, selectivity reversals may occur between sulfate and other ions. The consequence of this phenomenon on the design strategy of the cyclic operation are discussed.

LIGAND EXCHANGE SORPTION OF ARSENATE AND ARSENITE ON CHELATING RESINS IN FERRIC ION FORM : I. WEAK BASE CHELATING RESIN DOW XFS-4185

M. Chanda, K. F. O'Driscoll and G. L. Rempel

Department of Chemical Engineering
University of Waterloo, Waterloo, Ontario, Canada

Introduction

Ligand exchange sorption on chelating resin-bound ferric ion can be used for removal of ligand type pollutants from waste water and their recovery in iron-free concentrated form (1). The process is applicable to those ligands in aqueous effluents which form alkali-decomposable complexes with ferric ion. The weak-base chelating resin Dow XFS-4195 in ferric ion form has been found to be effective for the removal and recovery of both arsenate and arsenite from dilute aqueous solutions by this process.

Experimental

The chelating ion exchange resin XFS-4195 (wet mesh size 24-48 Tyler) obtained from Dow Chemical was activated by treating with 2M HCl and then complexed with iron by agitating with a large volume of 1% solution of $FeCl_3.6H_2O$ (pH 2.0) for 4 hours. Measured amounts of the resin were vigorously shaken on a mechanical shaker with definite volumes of arsenate/ arsenite in tightly stoppered flasks for 20 hours at 25°C and the concentration of the residual sorbate was measured by atomic absorption spectrometry. The effects of pH and background salt concentration on the sorption were measured. The sorption of arsenate/arsenite was also measured as a function of time under conditions of vigorous agitation at 25°C.

Results and Discussion

The useful pH ranges for sorption on XFS-4195(Fe^{3+}) resin are 3-6 for arsenate and 7-10 for arsenite. The equilibrium data for sorption of arsenate (pH 5.0) and arsenite (pH 10.0) on the resin are plotted in Figure 1.

Fig. 1 Sorption isotherms for (a) $AsO_4{}^{3-}$ (pH 5.0) and (b) $AsO_3{}^{3-}$ (pH 10.0) on XFS-4195(Fe^{3+}) resin. Temperature 25°C; resin loading 4.0 g ℓ^{-1}

The Langmuir isotherm equation provides an excellent fit to the sorption data, giving correlation coefficients higher than 0.998. The saturation sorption capacities for arsenate and arsenite are determined to be 46 mg As/g wet resin and 51 mg As/g wet resin, respectively. The sorped species are readily stripped with dilute sodium hydroxide into an iron free concentrated form, respresenting more than 100 fold enrichment compared to the influent concentration. The stripped resin is readily re-activated to its original capacity by treatment with a 10% $FeCl_3$ solution acidified to pH 0.8.

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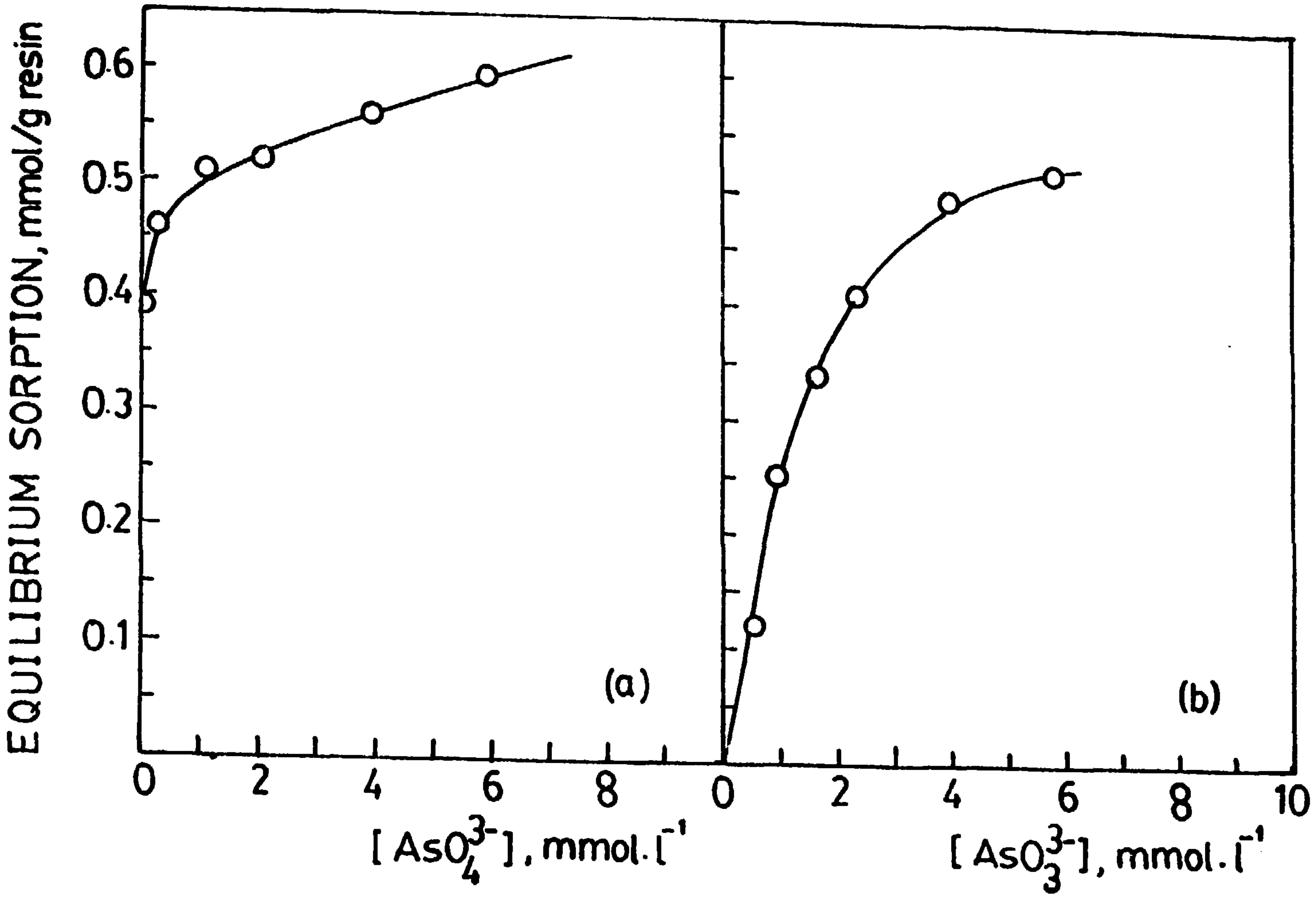EQUILIBRIUM SORPTION, mmol/g resin
0.6
0.5
0.4
0.3
0.2
0.1
(a)
0
2
4
6
8
[AsO_4^{3-}], mmol.l^{-1}
(b)
0
2
4
6
8
10
[AsO_3^{3-}], mmol.l^{-1}

Fig.1

Sugar Juice Softening Using Sodium Hydroxyde In Thin Juice For Regeneration

H. DESMORIEUX[1], L. ARÁNYI[2], S. MARQUES[1], G. GREVILLOT[1]
1. Laboratoire des Sciences du Genie Chimique
   C.N.R.S.-E.N.S.I.C., 1 rue Grandville, NANCY, France
2. Veszprém University of Chemical Engineering
   Schönherz Z. u. 10., VESZPRÉM, Hungary

Introduction

Sugar juice softening by ion exchange is widely used in sugar factories in order to prevent scaling of evaporators. After exhaustion, the regeneration of the bed is usually carried out with a sodium chloride solution. This method has two main disadvantages: dilution due to the requirement of washings with water and pollution by the calcium chloride in the waste effluent. In order to eliminate these problems, a new process has been proposed and is actually working in some factories. This process uses a sodium hydroxyde solution in thin juice as the regenerant and during regeneration, calcium is removed from the resin as a calcium saccharate complex. The spent regenerant is returned to carbonation and thus the chloride waste problem is completely solved. In addition, no water is introduced in the process. The purpose of the present work is twofold: first, to elucidate the mechanisms involved in this process by means of column experiments; second, to develop a model accounting for these simultaneous mechanisms (namely ion-exchange, adsorption, complex formation, precipitation).

Experimental

The experimental set-up comprises a feed pump, a column(60cm H; 1.5cm ID) maintained at 60°C by water circulation in a surrounding jacket, a pressure drop (capillary) to prevent degassing in the bed, and a fraction collector. At the initial state of experiments, the entire ion exchange bed is in calcium form. Regeneration experiments have been conducted at different sugar concentrations in the regenerant, the sodium hydroxyde being fixed at 1N and the temperature of the bed at 60°C.

Results and discussion

The results are compared with classical regeneration (NaCl) and with model simulations. Fig.1. shows a typical experimental history together with the model result. First we can observe that the sodium front is rather abrupt compared with a classical one which would be dispersive due to the lower affinity of sodium relatively to calcium. Here, the formation of a calcium-sugar complex in solution reverses the affinity of the two cations. Second, we can observe a large peak of calcium; the left-hand side of it is delayed, relatively to NaCl regeneration; this is interpreted by some adsorption of the complex on the resin. This is confirmed by a simultaneous decrease in sugar concentration. Following the peak, a tail at low calcium concentration is interpreted as dissolution of a precipitate. This tail disappears at higher sugar concentrations. A mathematical model including ion exchange, complexation, adsorption and precipitation has been built. Simulations represent the main characteristics of the experimental results.

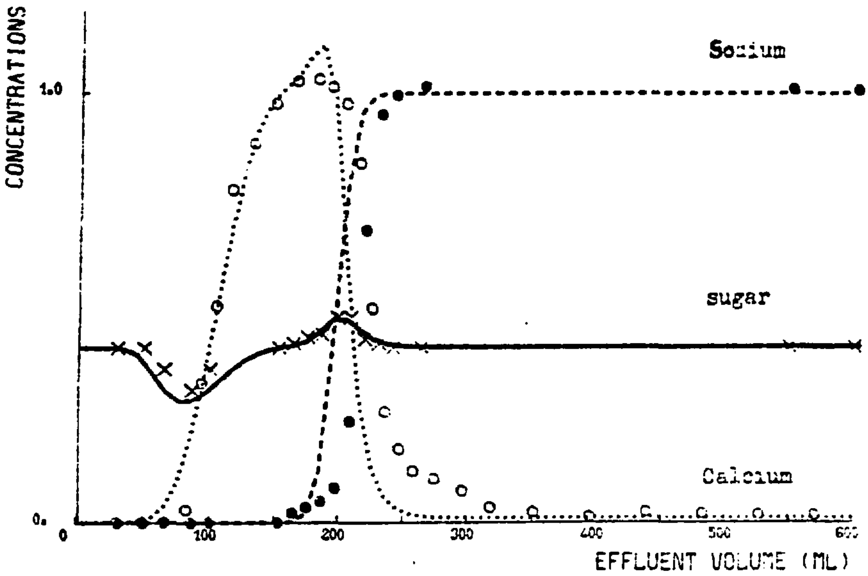

Figure 1. : Typical experimental and model history. Concentrations are in eq/liter for sodium and calcium, and in mole/liter for sugar.

Acknowledgements

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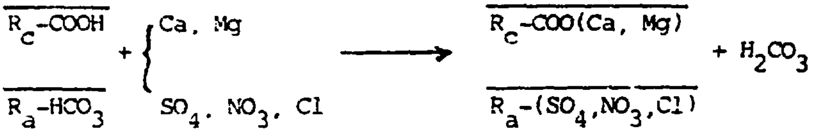
COMBINED HARDNESS AND NITRATE/SULFATE REMOVAL FROM WATER BY THE CARIX ION EXCHANGE PROCESS

W. H. Höll

Karlsruhe Nuclear Research Center, Institute for Radiochemistry,
Karlsruhe, F.R.G.

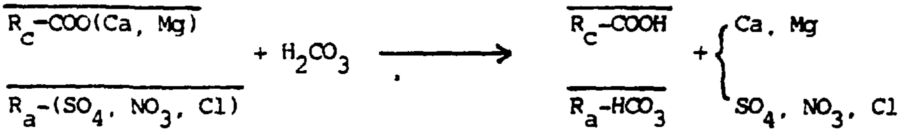
Basic Principle

A simultaneous removal of earth alkali ions and of anions of strong acids can be achieved by the combined application of a weakly acid ion exchange resin in the free acid form and a strongly basic resin in the bicarbonate form. Neutral salts are thus replaced by carbonic acid, from which CO_2 can be degassed:



$$\begin{matrix}\overline{R_c\text{-COOH}}\\[2ex] \overline{R_a\text{-HCO}_3}\end{matrix} + \left\{\begin{matrix}\text{Ca, Mg}\\[2ex] \text{SO}_4\text{, NO}_3\text{, Cl}\end{matrix}\right. \longrightarrow \begin{matrix}\overline{R_c\text{-COO(Ca, Mg)}}\\[2ex] \overline{R_a\text{-(SO}_4\text{,NO}_3\text{,Cl)}}\end{matrix} + H_2CO_3$$

Since weakly acid ion exchangers can be regenerated by carbonic acid and since the anion exchanger has to be loaded by bicarbonate ions, both resins can be regenerated by carbonic acid ($CO_2 + H_2O$). Regeneration efficiency can be strongly improved, if both resins are stored in a mixed bed, in which each of the exchangers favours regeneration of the other one:



$$\begin{matrix}\overline{R_c\text{-COO(Ca, Mg)}}\\[2ex] \overline{R_a\text{-(SO}_4\text{, NO}_3\text{, Cl)}}\end{matrix} + H_2CO_3 \longrightarrow \begin{matrix}\overline{R_c\text{-COOH}}\\[2ex] \overline{R_a\text{-HCO}_3}\end{matrix} + \left\{\begin{matrix}\text{Ca, Mg}\\[2ex] \text{SO}_4\text{, NO}_3\text{, Cl}\end{matrix}\right.$$

Advantages

This so-called CARIX-process (CARIX = CArbon dioxide Regenerated Ion eXchangers) has some particular advantages:

- Carbon dioxide is a non polluting chemical for regeneration,
- Due to the simultaneous regeneration of both resins with the same regenerant the effluent contains only the amount of salt which was

eliminated in the service cycle. As a consequence the process is non polluting.

- The process can be adapted to different objectives of water treatment only by suitable choice of the ratio of resin volumes.

Development of the process

In a first step of development, laboratory scale experiments demonstrated that CARIX can be applied to drinking water treatment, since it allows a sufficient reduction of hardness, sulfate, and nitrate concentrations. From 1983 the process was tested in technical scale in a pilot plant for 5 m³/h throughput, built by the WABAG company. Experiments in five different water works in the F.R.G. with different objectives of partial demineralization of drinking water showed, that CARIX allows also an economic treatment of drinking water /1/. Based upon the results of the pilot scale experiments a first big plant for 170 m³/h throughput was constructed for hardness removal as the main objective. This plant went into service in October 1985. Results will be given at the conference.

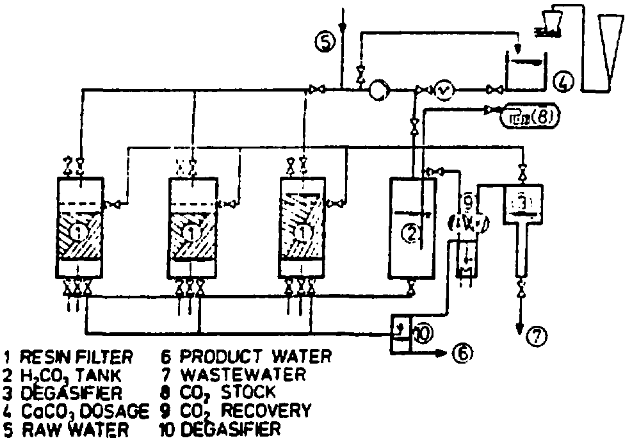


Fig. 1: Simplified scheme of the CARIX plant in Bad Rappenau

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THE SORPTION OF PHENOLS ON MACROPOROUS METHACRYLATE COPOLYMERS CONTAINING ETHYLENE AMINE GROUPS

J.Hradil[1], M.Wojaczyńska[2], F.Švec[1] and B.N.Kolarz[2]

1. Institute of Macromolecular Chemistry of the Czechoslovak Academy of Sciences, 162 06 Prague 6, Czechoslovakia
2. Institute of Organic and Polymer Technology, Technical University, Wyb.Wyspiańskiego 27, 50-270 Wroclaw, Poland

Introduction

Up to now, only styrene-divinylbenzene ion exchangers - both strongly and weakly basic anion exchangers, and even cation exchangers - have been recommended for the sorption of phenols (1,2). We were trying to find out, therefore, how macroporous methacrylate copolymers bearing ethylene amine groups which proved useful already in the sorption of sulfur dioxide would behave in this case (3,4).

Experimental

The macroporous copolymer of glycidyl methacrylate and ethylene dimethacrylate (40 wt.%) (5) was modified by a reaction with ethylenediamine, diethylenetriamine and triethylenetetramine. The uptake of phenols (p-aminophenol, p-hydroquinone, phenol, p-cresol, p-chlorophenol and p-nitrophenol) from aqueous solutions having the concentration 0.005 mol/l and passing at the flow rate 21.6 ml/h through a column 0.8 cm in diameter containing 0.1 g of the sorbent was detected by means of a differential flow refractometer.

Results and Discussion

All materials investigated in this study are capable of a considerable sorption of phenols which is affected by the type of both the sorbent and the sorbed phenol. The amounts sorbed from 0.005 mol/l solutions range from 0.07 to 1.03 mmol phenol/g. It may be said that the more polar methacrylate matrix compared with the styrene-divinylbenzene one is more advantageous for the sorption of phenols. The sorption of phenols decreases with increasing pK of the ion exchangers. In the sorption from strongly diluted solutions (0.064 mmol/l) it was possible, by using a single sorbent volume, to purify 50 volumes of the aqueous solution, but the total sorption capacity was somewhat lower than in the case where more concentrated solutions were used.

The sorption capacities in the ln Q form were successfully correlated by linear relations of free energy of the Hammett type. In the case of macroporous copolymers not bearing functional groups the best correlation was obtained with the π constants derived from the dissociation constants of phenoxyacetic acids. Hence, physical adsorption predominates in this case, because the sorption process is in the first place affected by the induction effect of the substituent. A similar state was observed for sorbents having ethyleneamine groups in

the Cl-form.
The best correlation for sorbents bearing ethyleneamine groups in the OH-form was obtained using the σ_p constants derived from the dissociation constants of benzoic acids. Hence, the binding of phenols proceeds via an ionic bond, and this is why mesomeric effects are operative along with the induction ones.

Table 1. Sorption properties of methacrylate copolymers

Sorbate	Amount sorbed, Q, mmol/g			
	G60EDA		G60DETA	G60TETA
		[a]		
p-aminophenol	0.089	0.094	0.073	0.071
p-Dihydroxybenzene	0.135	0.101	0.130	0.124
p-Cresol	0.178	0.088	0.148	0.124
Phenol	0.433	0.164	0.478	0.214
p-Chlorophenol	0.408	0.128	0.264	0.246
p-Nitrophenol	1.033	0.111	0.930	0.797

[a] Sorbents in Cl-form

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THE THEORETICAL ANALYSIS OF THE INFLUENCE OF THE SELECTIVITY OF ION-EXCHANGER ON THE ION EXCHANGE KINETICS

Yu.S. ILNITSKY
Institute of Inorganic chemistry of Siberian Branch of Academy of Science of USSR, Novosibirsk, USSR

The major limiting factor for diffusional kinetics of ion exchange is a steric factor. But very often ion-exchangers have a high selectivity to different ions with equally good steric factors. The cause of the selectivity lies in different strenghs of chemical interactions of migrating ions with active centers of an ion-exchanger.

We have developed a theory of the influence of fast, compared with diffusion, reversible chemical reactions on the interdiffusion of ions in a condensed media. It has been shown that the chemical interactions of migrating ions with active centres significantly modifies the nonequilibrium diffusion which, under these conditions, represents a kind of dissipative process in a nonlinear medium and is described by a system of time-dependent Ginzburg-Landau equations.

Algorithms have been worked out and a program of calculations of the physical kinetics of reacting diffusing systems has been produced, which represent the process of ions interdiffusion in a solid or liquid phase accompanied by a fast reversible chemical reaction with active centres and/or oppositively diffusing ions.

A series of computational experiments for studying the influence of fast reversible reactions on the interdiffusion of charged particles was carried out. In the frames of the developed theory a detailed picture of time- and space behaviour of the concentrations, fluxes and effective coefficients of diffusion of ions depending on the chemical and transport parameters of the investigated system was obtained. The results significantly supplement and more exactly define previous views on the diffusion of ions in a condensed media.

TO-08

PERFORMANCE OF ION EXCHANGE RESINS IN THE ACTIVE CIRCUITS OF PRESSURISED WATER REACTORS

By R. Couderc and P. Ambrus
Duolite International, S.A. - Vitry-sur-Seine - France

Introduction

Ion exchange resins used for the purification of various circuits in nuclear power stations have to remove radioactive impurities. They have to maintain activity below a threshold value both in the primary coolant and in the secondary loop, as well as in effluent streams.

Results and discussion

New ion exchange materials with a high selectivity and purity have been developed in order to remove specific radioactive isotopes.

Three types of ion exchange resins are available at present for this purpose:

1. Gel type conventional polystyrene resins.
2. Phenol-formaldehyde resins with special chemical structure and therefore particular properties.
3. High selectivity macroporous polystyrene resins (Cs selective).

All these types have conventional functional groups. Chelating resins are also being used for the removal of certain isotopes (silver, antimony, etc.).

Industrial performances achieved in European Nuclear Power Utilities are being discussed.

Due to their high purity, all these resins can be used to achieve maximum purity without any risk of releasing contaminants.

URANIUM RECOVERY BY CONTINUOUS ION EXCHANGE IN A PILOT PLANT

F. Delmas and C.J. Coelho

Laboratório Nacional de Engenharia e Tecnologia Industrial (LNETI), Lisboa,Portugal

A continuous ion-exchange pilot plant enabling the recovery of uranium from low grade solutions with a capacity up to0,5m^3 h^{-1} is described in this paper.

The pilot plant was built in LNETI facilities with the financial support of International Atomic Energy Agency under its regular programme for 1983-1984 and consists basicly on an absorption column, a washing column and an elution column.

The absorption column is PVC-glass made with 8 stages of 0.8 meters each and a surface area of 77.6 square centimeters. It operates by a countercurrent fluidized bed technique, similar to that used in the Cloete and Streat contactor. Special distributor plates,designed in LNETI,were used and compared with the traditional perforated plates, giving promising results.

A versatile and accurate system for resin transfer between stages and the withdrawal of resin from the first stage to the transfer vessel has been developed and sucessfully tested, in order to achieve the entire or partial hold-up of resin per cycle.

The SS AISI 316L elution column is insulated and heated by a water jacket and operates by an incipient fluidization technique. It was designed with some improvements in order to remove steam and air bubbles formed inside the resin bed during the operation.

The results obtained during preliminary tests in the absorption column are reported in this paper.

Feeding synthetic uranium solutions at pH=1.8, containing120mg

U_3O_8, 22g SO_4^{2-} and 2.5g Fe^{3+} per liter at linear velocities ranging from 0.65 to 0.72 cm/s, were used in these tests. Barren solutions less than 1 ppm U_3O_8 were achieved.

The simplified pilot plant flowsheet is shown in Figure 1. Table I summarizes data on absorption from synthetic liquors.

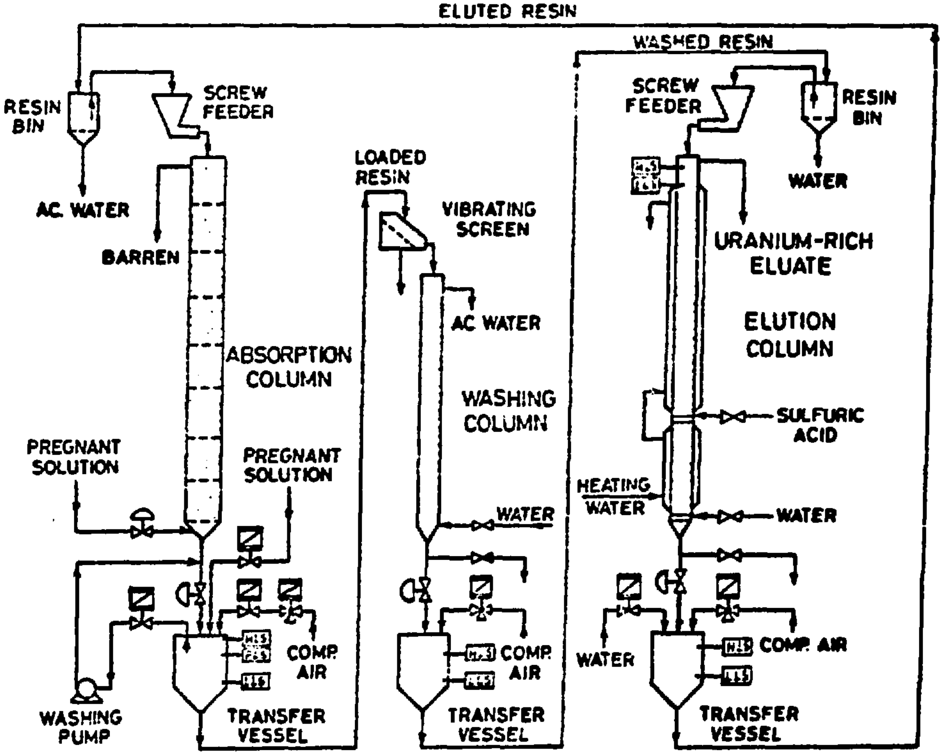

Fig.1-Pilot plant flowsheet

Table I. Uranium absorption from synthetic solutions.

	Column diameter (cm)	Feed U_3O_8 (g/l)	Flow-rate (l/h.cm^2)	Barren U_3O_8 (g/l)	Resin loading (g/l)
Test I	10	0.121	2.32	<0.001	13.9
Test II	10	0.120	2.58	<0.0015	14.7

SELECTIVE RESINS AND SPECIAL PROCESSES FOR THE SOFTENING OF WATER, SEA WATER AND BRINE.

H. Hoffmann, F. Martinola
Bayer AG, Leverkusen

Introduction

Highly selective ion-exchange resins and suitable technology are necessary for the proper softening of water with high concentraction of sodium salts and of solutions concentrated as saturated brine. For many applications the request for nearly zero hardness is a precondition as for the use of the softened water in

sea water distillation
produced water for reinjection in oil fields
electrolysis of brine in membrane cells.

Experimental

1. Evaluation of selectivity, kinetics and operating capacity of acrylic resins
   iminodiacetic resins
   aminophosphonic resins

2. Evaluation of residual hardness with various technologies

2.1 Regeneration with brine
WS System
Liftbed System
Intersive fraction Process

2.2 Regeneration with brine and acid/caustic
Liftbed system including selective resins
Multistep system

2.3 Selective resins in sodium form.

Results and discussion

1. **Selective resins**
   Acrylic resins have highest capacity but lowest selectivity. Aminophosphonic resins show fastest kinetics but also iminodiacetic resins are a good choice.

2. **Special technologies**
   Depending on the raw water composition the residual hardness achieved can be lower than

2.1 5 ppm $CaCO_3$ - brine regeneration,
2.2 1 ppm $CaCO_3$ - brine-acid/caustic,
2.3 20 ppm Ca - selective resins

Copper Extraction From Silver Refining Electrolytic Baths Using Ion-Exchange Parametric Pumping

L. ARÁNYI[2] S. MARQUES[1], G. GREVILLOT[1]
1. Laboratoire des Sciences du Genie Chimique
C.N.R.S.-E.N.S.I.C., 1 rue Grandville, NANCY, France
2. Veszprém University of Chemical Engineering
Schönherz Z. u. 10., VESZPRÉM , Hungary

Introduction

Copper extraction from concentrated silver refining electrolytic baths is presently performed using periodic batch cementation.In order to increase the economy of the overall process,we propose here thermal parametric pumping to remove continuously copper from the bath.
Parametric pumping processes use the properties of an adsorbent or an ion-exchange resin to have a shift in equilibrium distribution with temperature.For example, on the sulfonic cation exchanger DUOLITE C265 used here, with a silver-nitrate/copper-nitrate mixture, silver is more strongly fixed by the resin at 15°C than at 60°C. Thus , when percolating the mixture through the fixed bed alternately in one direction and then in the other, changing the temperature of the bed synchroneously, silver accumulates in the effluent of one end of the column and copper accumulates in the other effluent.The main interest of the process is to avoid the use of any chemicals and therefore the need for subsequent retreatment,as opposed to cementation or other classical processes.
In previous papers(1,2), we demonstrated the possibility of performing this separation. In the present paper we propose to develop three points:- 1, describe a semi-continuous parametric pump using one column with feed at the top and both top and bottom withdrawals- 2, present a model taking into account electrolyte sorption and mass transfer in addition to pure ion-exchange -3, discuss both experimental results and simulations.

Experimental

The experimental set-up is shown on Fig.1. The column (100cm height; 2.5cm ID). The column is cooled (15°C) or heated (60°C) by means of jacket. Each end of the column is connected to a reservoir which receives the solution from the column during a half-cycle and keeps it for subsequent reflux during the next half-cycle. Up-flow coincides with the hot half-cycle. Products are withdrawn from the reservoirs by means of suction tubes. Feed is introduced each cycle at the top of the bed just before down-flow reflux. Repeated automatic cycles are performed by means of a microprocessor.

Mathematical model and results

Because of the relatively high total concentration (about 1mol/liter) the electrolyte sorption cannot be neglected. We propose a mathematical model in which both ion-exchange and electrolyte sorption are taken into consideration simultaneously.. The system of partial differential equations is solved numerically by an explicite finite difference technique. Fig.2. shows the experimental and calculated results of a semi-continuous experiment. Good agreement is observed. Other experiments have been conducted in order to examine the influence on separation and productivity of some parameters such as flowrate, feed and withdrawal volumes and reflux ratio. From a practical point of view we can see that it is possible to obtain a bottom product containing copper almost free of silver while the productivity is satisfying.

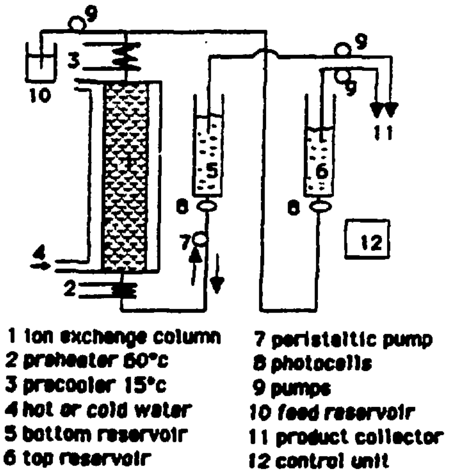

Figure 1.:Experimental set-up

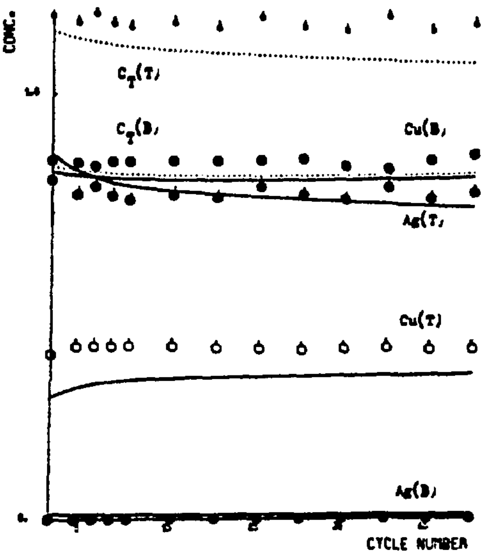

Figure 2.:Top(T) and bottom(B) productconcentration (eq/l)
for a typical run
CT= Total concentration
Feed= 0.5N Ag^+; 0.5N Cu^{++}

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THERMAL ION EXCHANGE PARAMETRIC PUMPING IN CASE OF SIGMOID ISOTHERM

T. Szánya, L. Hanák and P. Szolcsányi

Department of Chemical Process Engineering, Veszprém
University of Chemical Engineering, Veszprém, Hungary

Introduction

The thermic separation of potassium and calcium ions can extremely well be realized in a liquid - solid ion exchanger system characterized by a strongly temperature dependent ion exchange equilibrium. The equilibrium curve is of sigmoid shaped. Experiments were carried out with aqueous potassium and calcium chloride solution of maximum 1 equ/dm^3 concentration, between 15 and 60 ^{o}C temperature and the strongly acidic VARION-KSM was applied as cation exchanger.
Fig. 1 presents the Ca^{++}/K^{+} exchange on VARION-KSM.

Experimental

The system discussed above was investigated in a thermal ion exchange parametric pumping separator, operated batchwise. The parameters of the experiments were as follows:

- the volume of solution pumped during one half of a cycle: 50, 100, 200 and 300 (cm^3);
- the volumetric flow rate of the solution was: 0.05, 0.09, 0.20 and 0.35 (dm^3/h);
- the total cation concentration of the solution was: 0.1, 0.5 and 1.0 (equ/dm^3);
- the initial ionic ratio (X_{K^+}) was: 0.2, 0.5 and 0.8 (dimensionless)
- the length of ion exchange column was: 50, 100 and 150 (cm)

In a given experiment all other parameters were held constant. These parameters are: the operating temperature (15 and 60 °C), the ID of the ion exchanger column (1 cm), the quality and particle diameter of the VARION-KSM ion exchanger resin (0.7 mm) the position of the solution storage bottles, the duration of the cooling and heating periods (20-20 minutes), the volume of dead spaces, etc.

At the termination of each half cycle, samples were taken from the cold and hot storage tanks by a microsyringe and the suitably diluted samples were analyzed. The potassium and calcium concentrations of the sample were determined by a ZEISS-AAS/1 type atomic absorption spectrometer.

The determined data and their relationships are shown in Fig. 2.

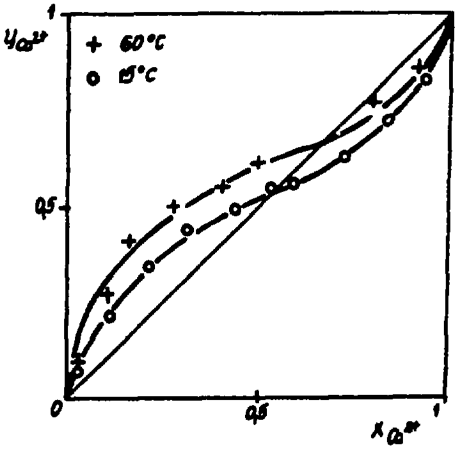

Fig. 1 The isotherm of Ca^{++}/K^{+} exchange on VARION-KSM resin

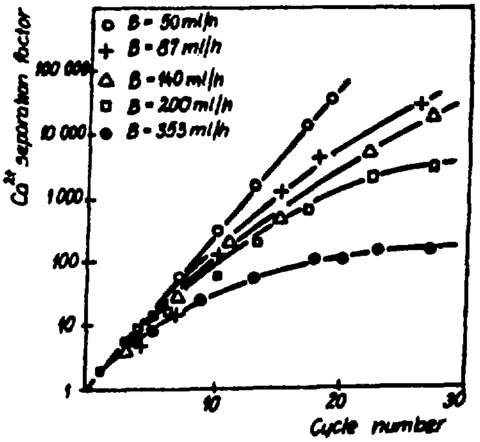

Fig. 2 Ca^{++} separation factor vs. volumetric liquid flow rate

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TP-03

ION-EXCHANGE SYSTEM FOR CONTROL OF BORIC ACID CONCENTRATION IN REACTOR WATER OPERATED AT 20 °C AND 80 °C

Iv. Dobrevsky, G. Konova

University of Chemical Technology, Bourgas, Bulgaria

It has been found that the strongly-basic anion exchangers have different sorption capacities toward H_3BO_3 at different temperatures /1/.

Recently, the most often used ion-exchange methods of boric acid concentration control in the reactor coolant in PWR are realized at temperatures 10 °C (for sorption process) and 60°C (for desorption process)/1/.

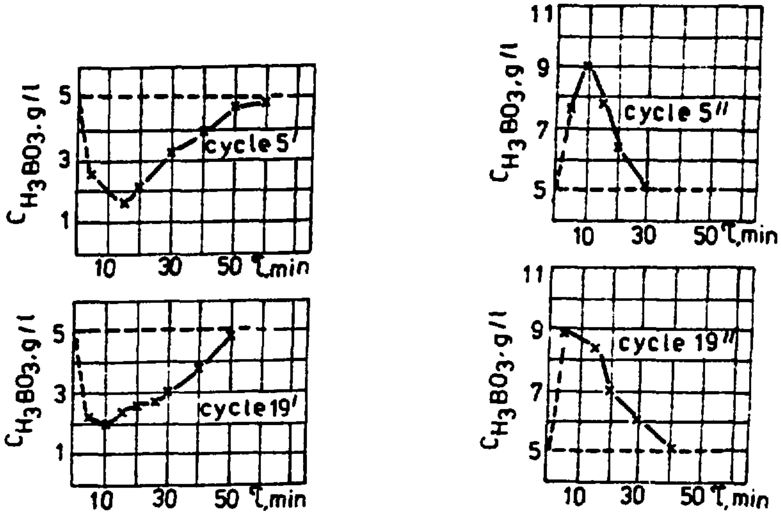
We carried out investigations to establish whether ion-exchange control of H_3BO_3 concentration in reactor water can proceed in a technologically more favorable temperature range, viz. sorption at 20 °C and desorption at 80 °C. To this end the boric acid ion-exchange capacity of the strongly-basic anion-exchanger Wofatit RO (nuclear grade) was investigated at temperatures 20 °C and 80 °C and at boric acid concentration in the contact water solution varying between 1 and 10 g/l. It was establiched that by changing the temperature of the contact water solution, without using any reagents, the anion exchanger at 80 °C has sorption capacity with 20 g H_3BO_3/l resin smaller than at 20 °C./2/.

In order to check the operation of the proposed modification of the regime of the ion-exchange system for changing H_3BO_3 concentration, pilot-scale experiments were conducted. For that purpose a special pilot plant, maintaining 20 °C during sorption and 80 °C during desorption of reactor water was built. The filtration flow rate varied between 15 and 18 l/h.

The pilot-scale experiments using reactor water bypassed from one of the VVER-440 reactors at Kozlodui Nuclear Power Station, confirmed that 1 liter of Wofatit RO is capable of sorbing and desorbing 20 g/l boric acid when changing the temperature from 20 °C to 80 °C of the water solution containing H_3BO_3.

The 20 cycles of sorption (at 20 °C) and desorption (at 80 °C) with reactor water confirmed that the sorption-desorption effect of the ion-exchanger remains practically constant. Using reactor water containing 5 g/l H_3BO_3 and the respective concentrations of alkylating asmixtures: KOH and NH_4OH and 0,1 mg/l chloride ions.

As evident from Fig. 1, the pattern of concentration change of boric acid in the filtrate after the filter temains practically the same when varying alternately the temperature of the flowing reavtor water from 20 °C to 80 °C and vice versa.



(a) (b)

Fig. 1. The Concentration change of H_3BO_3 in the filtrate after the ion-exchange filter by the filtration of reactor water at 20 °C (a) and 80 °C (b).

The obtained results gave ground to begin the desingn of a commercial plant for ion-exchange control of H_3BO_3 concentration in the reactor water by changing water flow temperature from 20 °C to 80 °C and vice versa.

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CONCENTRATION OF BORIC ACID SOLUTION BY THERMAL REGENERATION USING ANION EXCHANGE RESIN

M. KIVÉS, P. HALMOS, J. INCZÉDY

Department of Analytical Chemistry, University of Veszprém,
H-8201 Veszprém, Hungary

INTRODUCTION

The amount of boric acid absorbed by strongly basic anion exchanger at a fixed pH depends on the temperature and the concentration of boric acid [1].

The purpose of this work was to prepare boric acid solution of higher concentration (above 10 g/dm^3) from diluted boric acid (2 g/dm^3) by thermal regeneration, without using any chemicals.

Result and Discussion

Strongly basic anion exchange resin (Varion ATN, borate form) was saturated at 20 °C with solution containing boric acid in different concentrations.

Elutions at the higher temperature (80 °C) were made with solutions containing boric acid of the same concentration used for the saturation and lower concentration boric acid solutions as well.

Based on the results of these experiments loading and elution curves were obtained. Volumes of the boric acid solution required for the saturation and elution were determined.

Knowing the required volumes of the boric acid solution a multicolumn system was designed. Each column was contacted with the solutions, coming from the previous column. In this way the same amount of concentration enhancement was reached at each column.

Using the procedure developed, a feed solution of 2 g/dm^3 can be processed to obtain a solution with higher ($>$ 10 g/dm^3), and with a lower ($<$2 g/dm^3) boric acid concentration.

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TP-05

SELECTION AND EVALUATION OF ION-EXCHANGE PROCESSES FOR THE RECOVERY OF RADIONUCLIDES FROM COOLANT WATER

Gy. Várterész

"FJC" National Research Institute for Radiobiology and Radiohygiene, Budapest, Hungary

Introduction

Activity and compositions of coolant used to surveillanced by gamma spectrometry. The gamma spectrum of coolant water appeared complex enough to warrant chemical separation of the radionuclides (1). Separation of a complicated mixture of radionuclides has been performed with cation and anion ion-exchange resins (2).

Experimental

Materials

Dowex 2x8(Cl form) Serva Feinbiochemica GmBH Co. 50-100 mesh. I.Number of column in Fig.1.

Bio-Rex 40 (Na^+ form) Bio-Radlaboratories, Richmond, California 200-400 mesh II.Number of column in Fig.1.

Chelex 100(Ca^{2+})Bio-Rad Lab.50-100 mesh.III.Number of column in Fig.1. Resin columns used to 18 cm in length are 1 cm in diameter. The flow rate was 1 cm^3/min.

Experimental Procedure

The "classical" ion-exchange technique of Kraus and Moore (3) 1953 was used to separate ^{59}Fe, ^{60}Co and ^{65}Zn in certain effluents. Chelating resins make it possible to concentrate radionuclides from coolant water and select them from the major components on different groups. Possibilities of separating the elements in three suitable for gamma-spectrometric analysis observed scheme in figure 1. After selection of ion-exchange processes had been performed three groups of radionuclides; ^{131}I on column No.I., ^{137}Cs-^{22}Na-^{42}K on column No.II; ^{60}Co-, ^{54}Mn-^{95}Zr-Nb on column No.III.

Measurement of relative activity

Ion-exchange chromatography combined with Ge(Li) detector to determine each radionuclide in the coolant water. 15 ml aliquot of coolant mixture filled in a polyethylene tube and its activity (A_1^0) was gamma-spectrometric analysis.
After selection of ion-exchange processes the effluent from each columns was collected. 15 ml portion of certain effluent was taken in a polyethylene tube and its activity (A2) was measured. Quantitative and selective separation, verified by gamma spectrometry.
The recovery coefficient (R) was then calculated from expression:

$$R = \frac{\text{bonded radioactivity on columns } A_2 \text{ (I;II;III)}}{\text{radioactivity of the coolant mixture } A_1^0}$$

equipment:a Ge(li) detector and 4 K multichannel analyser of ICA:

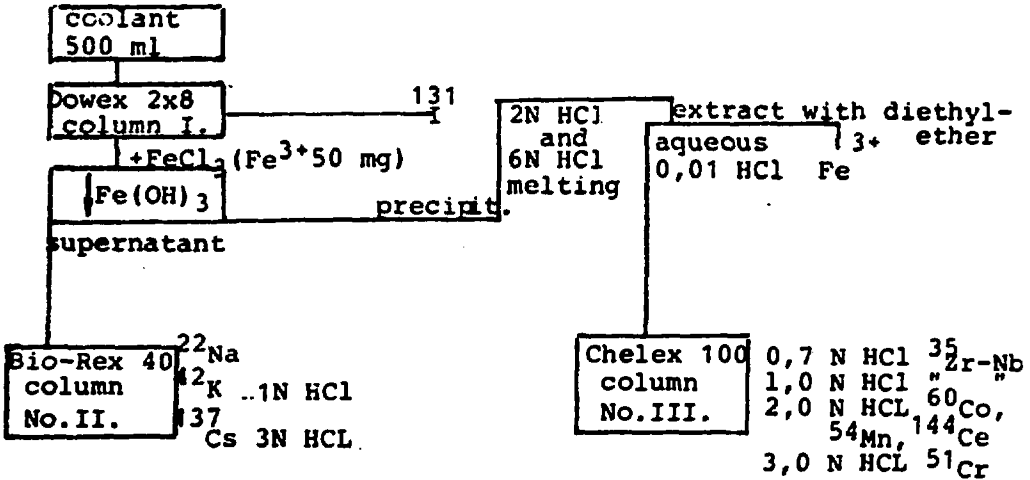

Fig.1. Scheme of ion-exchange processes

Results and Discussion

The recovery coefficient (R) results of synthetic mixture investigation is shown in Table 1.

Table 1

Ion-exchange resins	^{131}I	^{137}Cs	^{42}K	^{22}Na	^{144}Ce	^{95}Zr-Nb	^{60}Co	^{54}Mn	^{51}Cr
Dowex 2x8	0,98	-	-	-	-	-	-	-	-
Bio-Rex 40	-	0,99	0-81	0,82	-	-	-	-	-
Chelex 100	-	-	-	-	0,85	0,90	0,95	0,86	0,93

Under the above experimental conditions the separation of 9 important radionuclides into 3 groups had been achieved (T.I.). Recovery coefficient was calculated relative to the peak areas of gamma spectra. The specific separation of radioiodine from the mixture of the important fission product with good separation 98 percentages on Dowex 2x8. Average bond of alkali metal on Bio-Rex 40 resin was performed with 98 percentages. Concentration and selection of corrosion products had been realized with 89.8 percentages. Error of recovery coefficient was calculated ± 0,08 on the basis of parallel determination.

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MUNICIPAL WASTEWATER PURIFICATION BY ION EXCHANGE AND ADSORPTION METHODS

J. Hlavay, K. Földi-Polyák and J. Inczédy

Institute for Analytical Chemistry, University of
Chemical Engineering, Veszprém, Hungary

Introduction

Ammonia removal from wastewaters can selectively be carried out by clinoptilolite. Optimal operation conditions including the pH and the loading flow rate of influent water and the particle size range of the ion exchanger have been established (1). Phosphate removal can be achieved either by ion exchange (2) or by adsorption (3). Usually, activated alumina is used for the adsorption but the removal efficiency can be increased by chemically treated activated alumina.

Experimental

Laboratory experiments were carried out with 3,2 cm x x 15 cm columns filled with 80 cm^3 ion exchanger. In all cases, the 0,5-1 mm particle size range of commercially available raw materials was used and the flow rate of the synthetic wastewater was 5 BV/h. Treatment of the materials was as follows: Na-form clinoptilolite was produced by pumping 10 BV of 10 g $NaCl/dm^3$ solution through the bed. The activated alumina was treated by 10 BV of 0,7 g Ca and 0,5 g Mg/dm^3 solution. Synthetic wastewater was prepared by tap water containing NH_4Cl and KH_2PO_4 salts. Ammonia and phosphate concentration of the solution was measured by standard methods. Two columns were connected in series: the raw wastewater was loaded to the top of the column filled with Na-form clinoptilolite and the effluent went to the second column filled either with activated alumina or Ca, Mg-form alumina.

Regeneration of the spent clinoptilolite and alumina bed was carried out by 15 BV 10 g NaCl/dm^3 (pH > 11) and 25 BV 1 M NaOH solutions, respectively.

Results and Discussion

Part of the results of the experiments is shown in Table 1.

Table 1. Removal of ammonia and phosphate from municipal wastewater.

run 1: column 1 and 2: Na-form CL and activated Al_2O_3
run 2: column 3 and 4: Na-form CL and Ca, Mg-form Al_2O_3

run	treated water	loaded		ion exchanged and adsorbed		regeneration	
		NH_4^+ (mg)	P (mg)	NH_4^+ (mg)	P (mg)	NH_4^+ (mg)	P (mg)
1.	784	2131	1153	966	964	889	871
2.	782	2176	1078	1002	974	877	751

The complete saturation curves were obtained for both pollutants. 4 mg NH_4^+/dm^3 and 2 mg P/dm^3 were chosen as breakthrough concentrations. Up to these levels, 80 BV and 400 BV, respectively, can safely be treated. Therefore, the spent clinoptilolite has to be regenerated five times during the phosphate exhaustion. From the regenerants, the ammonia can be air-stripped and the phosphate can be precipitated.

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Silver ion-exchange properties of natural Hungarian mordenite and clinoptilolite

E.Czárán, E.Domokos, Á.Mészáros-Kis, J.Papp

Central Research Institute for Chemistry, Hungarian Academy of Sciences, H-1525 Budapest P.O.Box 17, Hungary

Introduction

Silver zeolites may be used as desinfectants due to the bactericide effect of silver ions in water treatment or in emergency cases in transforming e.g. sea water into drinking water.

Experimental

Silver ion-exchange of natural rocks containing mordenite and clinoptilolite was carried out starting by the transformatio of the heterocationic samples (containing mainly K, Ca and Na) into the sodium form by boiling 10 g of the samples with 100 cm^3 2M NaCl solution three times each for 3 h.

Subsequent analysis of the samples showed that ion-exchange was almost complete.

Silver ion-exchange isotherms were taken at 298 K using a total molarity of 0.1M.

After attaining equilibrium, the solution phase and solid phase were analysed, and the results plotted in equivalent fractions.

Results

Preliminary experiments with the heterocationic forms of both mordenite and clinoptilolite showed that the calcium content of the natural samples is difficult to remove with dilute solutions. Therefore an exhausting ion-exchange for the sodium form was performed and the sodium zeolite was used as starting sample.

A comparison of the ion-exchange properties of the two natural zeolites is made on the basis of the results obtained.

Ammonium ion exchange properties of Hungarian clinoptilolite and application for wastewater treatment

A. Mészáros-Kis, J. Papp, E. Czárán

Central Research Institute for Chemistry of the Hungarian
Academy of Sciences, H-1525 Budapest, P.O.Box 17, Hungary

Volcanic rocks containing natural clinoptilolite have high ion exchange selectivity for ammonium ions. Experimental conditions including laboratory and pilot plant scale ammonia removal investigations have been discussed in great detail by many authors.

Our aim was to investigate the ion-exchange process from preliminary static experiments through laboratory scale dynamic procedures up to pilot plant dimensions applying the same raw material.

At the laboratory scale the removal of ammonium-ions from a model solution was studied under dynamic conditions in an ion-exchanger column (BV = 40 cm^3) filled with clinoptilolite fractions of different particle sizes. The degree of ion-exchange was studied at different solution concentrations, different grain sizes and different flow rates.
Experiments for the regeneration of the exhausted filling were carried out at 5-100 g dm^{-3} KCl solution at pH $\approx$ 7 and 12.
A KCl concentration of 20 g dm^{-3} and pH $\approx$ 12 the maximum limiting value of the NH_4^+ concentration of the regenerating solution was about 1000 mg dm^{-3}. The regenerating solution was freed of ammonium ions by precipitation in the form of $MgNH_4PO_4 \cdot 6H_2O$ at a pH of 9-9,5.

Pilot plant experiments, including a 50 m^3/day capacity ion-exchange system were carried out for the removal of ammonium from communal sewage. The volume of the ion exchanger bed was 1 m^3, the particle size: 0.5 - 2.0 mm and at 4 mg dm^{-3} breakthrough limit the ion-exchange capacity was about 3,9 mg NH_3-N/g clinoptilolite.

STUDIES ON THE KINETICS OF ION-EXCHANGE LEACHING OF THE HUNGARIAN RHODOCROSITE ORE OF URKUT ORIGIN

G. Dobos

Flat Glass Factory of Salgótarján, Salgótarján, Hungary

In the last 30 years great efforts were made to develop an economical process for the production of manganese from the rhodocrosite ore deposit of Urkut. Pyrometallurgical experiments were unsuccessful, because of the relatively low manganese and high iron, silicon as well as phosphorous content of the ore. Hydrometallurgical enrichment seems to be very simple as acidic solutions dissolve the $MnCO_3$ content quite selectively, but due to the bad filterability and large amount of undissolved host minerals, it is difficult to acheive a satisfactory yield for manganese.

Recently we have suggested the use of strongly acidic cation-exchange resins in H^+-form as leaching reagent. Adding the resin to the aqueous pulp of the ore, the metal carbonates dissolve and the metal ions bind in the resin phase.

For the experiments Varion KSM resin was used. The ore was milled and the grain size of the sample used for the kinetic measurements was less than 200 μm. The kinetics of dissolution of the ore samples and the ion-exchange have been studied gasvolumetrically as well as by determining the concentration of manganese by complexometry or polarography (the reactions were stopped at given times).

The ion exchange leaching reaction was found to be a first order one, but the Arrhenius plot of the rate constants obtained between 20 and 45 °C was not linear. The energy of activation obtained from the data near to 20 °C is about 60 kJ/mol, while that obtained at higher temperatures is about 28 kJ/mol. The activation energy of the acidic leaching of the ore was found to be 20 kJ/mol, while that of the ion exchange reaction between the H^+ and Mn^{2+} ions, was about 71 kJ/mol. These data indicate that in the leaching of the ore by ion-exchange resin of H^+ form both the ion-exchange and the dissolution of the ore can play a rate controlling role. At higher temperatures the ion-exchange seems to be the slower reaction, which predominantly controls the rate of the whole process. The rate of leaching can be accelerated by adding a small amount of electrolyte - e.g. Mn^{2+} or H^+ ions - into the pulp. The resin can be regenerated with a solution of HCl, when $MnCl_2$ solution is obtained.

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A STUDY ON THE MECHANISM OF SILICA FOULING OF ANION EXCHANGE RESIN

Zhang Guowei Zhang Yong Xu Genfu Zhao Guirong Liu Xiuzhen
Guo Shouhai

Beijing Research Institute of Uranium Ore Processing,
Beijing, China

Introduction

The relationship between silica fouling of the strong base anion exchange resin and polymerization of silicic acid or size of polysilicic acid molecule was studied.

Experimental

The exchanger: The strong base anion exchange resin
The test solution: The synthetic solution containing silicic acid.
The cryoscopic method of sodium sulphate decahydrate was used for the determination of degree of polymerization of silicic acid.

Results and Discussion

Experimental results show that the plotted curves are N-shaped which represents the relation between the logarithm of the half life (τ) and the initial pH value of the solution. The concentration of silicic acid influence the adsorption of silica and the polymerization of silicic acid within the resin. The half life (τ) can be used for calculating the order of polymerization reaction, which is about four, and hence silicic acids within the resin polymerize rapidly when their concentration increase. The amount of silica adsorbed by resin increases with the increase of molecular complexity of silicic acid and reaches maximum when molecular complexity is 3.3 (Shows in table 1).

Table 1. The relationship between the molecular complexity of silicic acid and the maximum amount of silica adsorbed within resin

molecular complexity of silicic acid	1.0	2.0	3.3	4.3
maximum of amount of silica adsorbed within the resin SiO2 %	0.88	1.13	1.30	0.98

The table 1 shown the size of silicic acid molecule has a significant effect on the silica fouling of the resin. The high content of low molecular polysilicic acid in the solution results in high amount of adsorbed silica within resin, besides the polymers of silicic acid present in the resin accelerates the rate of polymerization of silicic acid within resin. The added salts, especially fluoride, have an effect on silica fouling of resin.

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ION-EXCHANGE KINETICS OF STRONG BASE ANION EXCHANGERS ON CONDENSATE TREATMENT

Z.Matějka,V.Vlčková and M.Jilečková
Institute of Chemical Technology,
Dept. of Power Eng.,16628 Prague,Czechoslovakia.

The strong base anion exchangers in condensate treatment plants are nowadays operated at very high flow rates. Under these limiting conditions the exchange kinetics can greatly affect the effectiveness and performance of the resin bed. The rate of anion exchange for two specific cases has been experimentally studied in this work, using the shallow-bed technique with infinite solution volume.

A) The comparison of anion exchange kinetics in the mixed bed and single bed.

Several reports have been published recently (1-4) showing that residual concentration of anions in the effluent from the single bed column is lower than that from the mixed-bed column. As a possible reason is suggested (1), among other factors, the more favourable exchange kinetics in the single bed.

Results and Discussion

The results received in our study point out quite clear the kinetic superiority of a mixed-bed over single-bed: in an alkaline solution (pH 9.5) proceeds the exchange $OH^{-}-Cl^{-}$ in the mixed-bed by 29% faster than in the single bed and in the neutral solution (pH 6.1) by 16% faster.
Conclusion: Ion-exchange kinetics is not responsible for the mentioned higher leakage of anions from the mixed-bed column than from the single-bed column during condensate treatment. As a probable explanation of this phenomenon should be considered the incomplete separation of the mixed-bed components, lower breakthrough capacity of the resins in the mixed-bed and also the mixed-bed hydraulics.

B) Kinetics of ternary exchange $OH^{-}-Cl^{-}-SO_4^{2-}$ and the effect of organic fouling.

It has been observed (5-9) that under limiting kinetic conditions (i.e. at very high solution flow-rate) the SO_4^{2-} ions pass through the resin bed into the effluent sooner than Cl^{-} ions do.The kinetics of divalent anions (SO_4^{2-}) sorption is further deteriorated by organic fouling or by the long-term exposure to the elevated temperature. The mechanism and reason of this selective effect is not sufficiently revealed as yet.

Results and Discussion

Sulfate ions are taken up at a slower rate than chlorides in the early phase of exchange in a ternary system $OH^{-}-Cl^{-}-SO_4^{2-}$ (Fig.1). This is the reason for preferential breakthrough of sulfate ions at very high solution flow-rate. Chromatographic bands in the resin bed exchange zone are formed, under this condition, according to the kinetic but not selectivity behaviour of ions, as is common at the low flow-rates. In this study was monitored the kinetics of ternary exchange $OH-Cl-SO_4$ for styrene and acrylic strong base resins. The effect of the low molecular weight (surface active compounds, aromatic acids) and high molecular weight (anionic polyelectrolytes) organic matters was investigated. Also the changes in kinetic behaviour of resins caused by their exposure to the elevated temperature were followed.

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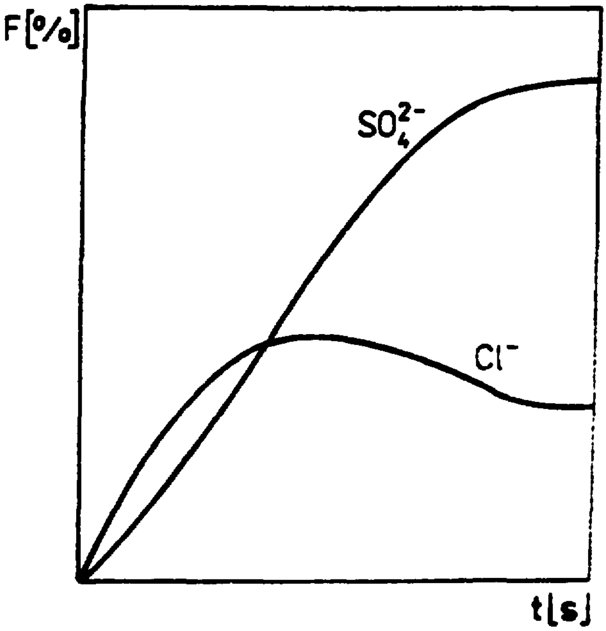

Fig. 1: The rate of ternary exchange $OH^{-}-Cl^{-}-SO_4^{2-}$ on strongly basic resins.

EFFECTS OF USING WASTES ON THE ION-EXCHANGE TECHNOLOGY

[illegible], M.Erdélyi, M.Csővári, L.Ferenc

Mecsek Ore Mining Enterprise

Introduction

An industrial method for the reduction of production costs is the replacement of expensive materials by cheaper ones. At the hydrometallurgical processing of uranium such a possibility is the replacement of technical quality sulfuric acid by the acid wastes of other branches of industry. The introduction of acid wastes into the technological process is only with careful pretesting and continuous checking allowed,otherwise the economical result is questionable e.g. because of an unexpected breakdown. One of the most sensitive operation of the technological process for contaminating materials is the ion-exchange.

Experimental

We have got an offer for using sulfuric acid wastes originating from the production of polymers.

The neutralized waste acid contains numerous components which are deleterious from environmental point of view.

With the aim of comparision synthetic solutions were prepared from waste and technical sulfuric acid for the following investigations:

1) The value of equilibrium capacity of the ion-exchange resin and the uranium distribution coefficients in low and high concentration range were determined.

2) Ageing investigations were carried-out in 100 cycles in order to determine the degree of change of the useful capacity and mechanical stability of the ion-exhange resin.

Before application for technological purposes the equilibrium capacity, mechanical stability and grain-size distribution of the resin stored in the ion-exchange system and the work-line of running system were determined.

After introduction of waste acid into technological system the condition of ion-exchange is continuously tested as follows:

1) Time by time the capacity, mechanical stability and grain-size distribution of the resin is controlled in accordance with the prescriptions of the standard;

2) Using technological solutions the capacity and uranium distribution coefficient of the ion-exchange resin is regularly determined.

3) Modelizing the plant circumstances resin sample is prepared in ion-exchange column for comparison purposes.

Results

By the help of the above mentioned method the degree of effects exerted by contaminating materials for the ion-exchange was determined. The yearly damage of ion-exchange resin is of 1-2 %, so its application seems to be economical.

PRODUCING OF HYDROCHLORIC ACID USING ANION EXCHANGE RESIN

M. Csővári, B. Czeglédi, M. Erdélyi, L. Stocker, R. Egry
and S. Tündök

Mecsek Ore Mining Enterprise

In processing of uranium ores for the recovery of uranium from solutions anion exchange resins are often used. The saturated anion exchanger can be eluted by different eluents. If chloride containing solutions are used for these purposes and the elution is carried out in countercurrent operation the anion exchanger leaves the system in cloride form.

In this paper data are presented concerning producing hydrochloric acid from the above mentioned chloride form resin. The anion exchanger of chloride form can be obtained in a special process as well. Research work was carried out to determine the possibility of producing hydrochloric acid solution from the anion exchanger of chloride form with the aim of reusing this solution for elution process.

Investigations were carried out using anion exchange resin Varion AP chloride capacity of which was 1,45 mol/dm^3. An experimental system consisting of two columns /height: 1,5 m, diameter: 3 cm/ was made. Onto the top of the first column anion exchanger of chloride form was continuously added at a flow rate of 300 cm^3/h and onto the top of the second column anion exchanger from the bottom of the first column /which was mainly of hydrosulfate form/ was fed. To the bottom of the second column water at a flow rate of 750 cm^3/h was given, from the top of this column sulfuric acid containing solution was obtained. Concentration of sulfuric acid in this solution was increased by adding conentrated sulfuric acid after which the solution obtained was fed to the bottom of the first column. On the top of the first column hydrochloric acid containing solution was obtained.

Concentration of hydrochloric acid in mol/dm^3 was approximately the same as the concentration of sulfuric acid in mol/l of fed solution.

As a result of the investigation it was determined that more than 95% of the chloride sorbed on anion exchanger could be removed in the form of hydrochloric acid. On the basis of these data technology of producing hydrochloric acid containing solutions from different chloride containing wastes was elaborated. Nowadays the process is used in industrial scale in hydrometallurgy of uranium ores.

FACTORS INFLUENCING MIXED BED WATER QUALITY

P. Hübner and V. Kadlec

ČKD DUKLA, Research Institute of Water Treatment,
Prague, Czechoslovakia

Introduction

There are two kinds of leakage which determine the effluent mixed bed water quality. First, it is so-called "elution leakage", caused by an imperfect way of the regeneration process. The second so-called "kinetic leakage" is due to the inability of the mixed bed to sufficiently reduce the influent concentration to the target level at higher specific loading. Whereas the elution leakage is important at the beginning of the working cycle and then gradually decreases, the kinetic leakage slowly increases as the exhaustion continues. By improper regeneration procedure the over-all ionic contamination of the effluent during the working cycle is predominantly caused by the elution leakage.

Experimental

The experiments were carried out on laboratory scale wi all styrene-DVB mixed bed combinations of new resins fr three different resin manufacturers. At the same time the samples of used Wofatit resins were tested. The volume of mixed bed was 200 ml in a ratio 1:1, the influent was the demineralised water with conductivity 3-5 μS/cm. The mixed resins were rinsed till the almost constant value at the specific loading 120 bed volumes per hour.

Results and Discussion

There is a general opinion that the most important factor influencing water quality is incomplete separation of the resins before the regeneration. We have confirmed that with the increasing cross-contamination the effluent quality proportionally decreases. However, not all types and even not all

Table 1. Conductivity of the mixed bed effluent

Type of cat. resin	$\varkappa_{25°C}$ µS/cm
gel 8-10% DVB	
Wofatit KPS	0,072
Lewatit S 100	0,210
Amberlite IR 120	0,068
macrop. 20% DVB	-
Wofatit KS 10	0,230
Lewatit SP 120	0,060
Amberlite 200	0,082
macrop. 12% DVB	
Lewatit SP 112	0,074
Amberlite IR 252	0,060

20% of cat. resin contaminated with NaOH

Type of an. resin	$\varkappa_{25°C}$ µS/cm HCl	H_2SO_4
gel		
Wof. SBW new	0,068	0,058
used	0,340	0,190
Lew. M 500	0,100	0,124
Amb. IRA 400	0,058	0,058
macroporous	-	-
Wof. SZ 30 new	0,060	0,066
used	0,112	0,060
Lew. MP 500	0,068	0,056
Amb. IRA 900	0,070	0,064

20% of anion resin contaminated with HCl /H_2SO_4/

resins of the same type behave in the same manner /see Table 1./. All the resins either new or used, when properly separated, gave perfect results with the effluent conductivity of around 0,06 µS/cm. The effect of regenerant level, rinsing and mixing is less important.

All the strong base resins having been in contact with the regenerant acid exhibited prolonged rinse before the mixing. However, after the mixing with the cationic resin the new resins gave good quality of water. In the case of used resins, the gel Wofatit SBW compared with the macroporous Wofatit SZ 30 exhibits worse water quality, undoubtedly due to the lower resistance of gel matrix against organic fouling.

The new as well as the old cation exchangers give the same results, but there is a difference between the same types from different manufacturers, probably given by the different homogenity of the matrix.

The presented results allow to diminish the influence of improper separation techniques /cross-contamination/ by the proper choise of the resin combination at given separation procedure.

RECOVERY OF TRACE AMOUNTS OF PLATINUM FROM SOLUTIONS OF AROMATIC AMINES ON ION EXCHANGE RESINS

W. Ratajczak, A. Koprowski and K. Zięborak

Research Institute of Industrial Chemistry, 01-793 Warsaw,
Poland

Introduction

In the process of reduction of dinitrobenzene to toluilenediamine /TDA - poliurethane intermediate product/ 60÷70% of Pt catalyst have been lost. It has flown away from the reactor in the very diluted solution /Pt concentration less than 1 ppm/ in the reaction mixture. The paper reveals a practical method of recovery of Pt from such very diluted water-organic mixtures.

Experimental

Ion exchanger column filled with a tested ion exchanger bed was fed with synthesis aqueous TDA at volume feeding rate 4 to 16h^{-1}. The bed temperature was 80÷90°C. After 700÷1500 volumes of TDA solution had been supplied, the ion-exchanger bed was removed from the column and analysed for Pt content. The following ion exchangers were tested: Wofatit KPS, Wofatit MC-50, Wofatit AD-41, Amberlite IRA-94S, Amberlite IRA-45, Amberlite IRA-900, and Amberlite IRC-718.

Results and Discussion

It has been found that Pt can suitably be extracted from TDA solution on an anion exchanger bed. This finding seems to prove that Pt is present in TDA solution in an anionic complex form. Pt sorption was preferrably carried out on Wofatit AD-41 bed. 1 cm^3 of Wofatit AD-41 retained up to 1 mg of Pt. Concentrated Pt was separated by burning the anion exchanger away. The ashes contained up to 40% of Pt. An industrial scale plant according to the above process was started-up. It enables retaining 80÷90% of Pt dissolved in the synthesis aqueous TDA.

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ION EXCHANGE RESINS IN TREATMENT OF EFFLUENTS FROM CUMENE SYNTHESIS

W. Ratajczak, K. Zieborak

Research Institute of Industrial Chemistry, 01-793 Warsaw,
Poland

Introduction

The process of synthesis of cumene in the presence of $AlCl_3$ catalyst gives 3÷4 m^3 of waste-water per 1 ton of produced cumene. The amount of waste-water containing aluminium salts and hydrocarbons can be reduced by sorption method/1/. An application of macroporous cation exchangers for reduction of waste-water volume in the process is the object of the work.

Experimental

The reaction mixture containing cumene, alkylbenzenes and 0,1 ÷ 0,25% of $AlCl_3$ was passed at 40÷50°C through 1,5 dm^3 bed /55 cm height/ of Wofatit KS-10 cation exchanger at vol. feeding rate $6÷12h^{-1}$. The eluate was analysed for Cl^- and Al^{3+}. Reactivation of the bed was performed by countercurrent pass of distilled water at vol. feeding rate 2÷3 h^{-1}, follwed by fluidizing of the bed with upward stream of nitrogen. Drying the bed with hot /70÷90°C/ nitrogen for 2÷3 hours completed its preparation for the following cycle of $AlCl_3$ sorption from cumene synthesis mixture.

Results and Discussion

It has been found that macroporous sulphonic cation exchanger is capable of complete removal of $AlCl_3$ from cumene synthesis mixture. 1 dm^3 of cation exchanger retaines up to 100 g of $AlCl_3$ at 50°C. Reactivating water consumption is less than 3 vol/bed vol. The presented method enables the waste-water volume to be reduced to 10% of that produced by the previous-state-of-the-art method of cumene synthesis.

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APPLICATION OF ION EXCHANGE RESIN FOR PREPARATION OF β-CYCLODEXTRIN OLIGOMERS

I. Haklits, B. Keszler, G. Kovács

Research Institute for thePlastics Industry
Budapest, Hungary H-1950

Introduction

Water soluble β-cyclodextrin / β-CD/ oligomers are prepared by known processes /1-3/. The oligomers are obtained in aqueous solutions with high salt contents. In certain applications practically salt-free CD-oligomers are needed. In order to obtain oligomers with such qualities, the product should undergo additional, tedious separation processes. Instead of this method a more economical one-step process is recomended, where the polymerization is carried out in the presence of anion exchange resin.

Experimental

The water soluble β-CD oligomer was prepared by polycondensation of β-CD or carboxy-β-CD with epichlorohydrin in aqueous alkali solution in the presence of Varion AD, AT or ATM anion exchange resins at 333 K. The reaction period was 2,5 hours. Molecular mass and distributions were determined by GPC. CD carboxyl group, chlorine content and the capacity of the anion exchange resin were measured by conventional analytical methods.

Results and Discussion

It was found that polymerizing β-CD's with epichlorohydrin, in the presence of anion exchange resins instead of using large quantities of NaOH, the product contained considerable less salt /i.e. 1-1,8 % compared to 15 %/. The optimum conditions can be achieved with Varion AT 660 resin: strong base anion exchanger with high degree of crosslinking 1,26 w/% However, in this case the water required for removal of the larger quantity of adsorbed polymer on the surface of the resin dilutes considerable the final product.

We have not observed any irreversible binding of β-CD or β-CD oligomers onto the surface of the resin. The capacity of the resin remained 97 % of the original one after 15 cycles.

Contrary to the bimodal molecular mass distribution of the oligomer prepared by conventional methods, the oligomers obtained in this process showed unimodal distribution.

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EXPERIMENTS ON REACTIVE EXTRACTION OF PENICILLIN G FROM FERMENTATION BROTH

F. Vinczi and J. Bálint

BIOGAL Pharmaceutical Works, Debrecen, Hungary

Introduction

Reactive extraction allows recovery of penicillins on higher pH under favourable stability conditions. This process has been applied only for aqueous solutions of penicillin G /1,2/, so we aimed at the investigation of the reactive extraction of this compound from fermentation broth.

Experimental

Penicillin G was extracted from filtered fermentation broth with the iso-butyl acetate solution of liquid ion exchanger Amberlite LA-2 at pH 4.5, then the crude potassium salt of penicillin G was prepared. Control extraction was made at pH 2.5 without liquid ion exchanger.

Degree of extraction, as well as purity and yield of the product was determined.

Results and Discussion

It was demonstrated that pH of recovery could be increased from 2.5 to 4.5 with application of liquid ion exchanger while product quality remained constant. So decrease of the decomposition loss of extraction resulted in the increase of yield for production.

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APPLICATION OF ION EXCHANGE RESINS IN WATER TREATMENT

K. Salacz - Morelli

National Institute of Hygiene, Budapest, Hungary

Ion exchange resins are used in some water purification technologies, e.g. for removal of nitrate ions from drinking water or of ions from waters applied in therapy.

The results of the qualitative examinations showed that depending on the ion form of the resins (H^+ or Na^+ and OH^- or Cl^-), the content of organic compounds of the treated waters was differently changed.

Determination of the organic content of the waters can be carried out by COD measurement but the results are not reliable for the characterization of the organic compounds dissolved from the resins. Therefore, the total organic carbon (TOC) content of the water treated on ion exchanger has to be determined. For qualification of the resins this measurement is essential.

The methods available today are not able to give informations about the change of the water quality taken place during the ion exchange treatment. The qualitative and quantitative determination of the organic compounds dissolved from the resins can only be carried out by mass spectrometry.

NEW ASPECTS of APPLICATION of ION-EXCHANGERS in WATER PURIFICATION

V.D. GREBENJUK

A.V.Dumanski Institute of Colloid and Water
Chemistry, Ukr. Ac. Sci., Kiev, USSR

The new aspects of application of ion-exchangers have been considered: electrofiltration of water from microparticles and separation of uni- and bi-charged ions using ion-exchange charge-selectiv membranes.

Electrofiltration is a new scientific trend, the practical achivements of which can be used for water purification from microparticles and microadmixture concentrations in liquid medium as colloid. Water purification and colloid particle concentration are possible due to the electric field in the filter. Colloidal particles get induction dipole moments and are localized in certain places of electric filter. After filtration of a certain volume of liquid, the sorbed particles are either washed- out by water, or dissolved by a proper reagent. Their chemical substances are analysed then by liquid chromatography. IEF-500 industrial electric filter has been developed with 500 litre/hr capacity of ultra pure water, electricity consumption is 30 W hr/m^3 and water specific resistanse is 20 mOh cm. There are no microparticles in purified water.

Separation of uni- and bi-charged ions is necessary for preparatory purposes in laboratories and for complex purification of saline water to produce fresh water and valuable mineral substances. In the later case unicharged-selective membranes enable us to reduce standards of water liffed for electrodialysis as to multi-charge ion content. It also enables to get highly concentrated brine as well as dialysate of increased hardness.

The ratio of fluxes through membrane from salt mixture solution is determined by ion mobility and their concentration in the membrane. Owing to this a number of ways to change specific permeability of membranes:

1. The change of ion mobility ratio in membrane by it's material modification.
2. Relative change of surfase concentratio of counter-ions by fixing ion-exchange and neutral films on membrane surfase.
3. Concentration ratio change of counterions by the change of electrodialysis conditions (current density, solution flow velocity along the accepting side of membrane, general salinity of the solution without it's compositional change).

Absolutely new technology of hard water demineralization and concentrated brine production without treatment of desalinated water or brine has been elaborated using uni-charged selective membranes.

CADMIUM REMOVAL FROM WASTE-WATER BY ION-EXCHANGE

I.Haklits[1], A. Nagy[2], L.Kiss[1], P.Simon[1], O.Nagy[3]

1. Research Institute of Plastics Industry
2. North-Hungarian Chemical Works
3. Technical University of Budapest

Introduction

In order to diminish the severe environmental problems of the accumulator mass producing plants, an ion-exchange system was elaborated for treating the cadmium-containing waste-water.

Two characteristically different streams were treated. The first one /WI/ has 0,5-2,0 g/dm^3 cadmium content and about 6-8 times higher amount of Al and Mg. In the other stream /WII/ the cadmium concentration is 0,01-0,15 g/dm^3 and it cointans nearly equivalent amount of the other two ions. Because of the associate ions and the volume difference of two order of magnitude /WII WI/, separate treatments were necessary, first of all with the view to economy.

Experimental

As the cadmium forms an anionic chlorocomplex in hydrochloric acid medium, the disturbing effect of Al and Mg ions can be eliminated by treating stream WI on Cl-form strongly basic anion-exchange resin. In this case the Al and Mg ions go through the column, while the cadmium complex is adsorbed. Solution WII, which has a relatively low cadmium content, is preconcentrated by binding the total amount of cation on a H-form strongly acidic cation-exchange resin and recovering by elution with hydrochloric acid.

The acidic concentratum is carryed back into stream WI.

Results and Discussion

The optimum hydrochloric acid concentration for the anionic treatment is 3,5 % m/m. In this case, the operating capacity is 0,6 mval/cm^3, when Varion AD is used. The bound cadmium complex can be easily decomposed by water and solution of 5000 mg Cd/dm^3 can be gained. The resin remains in Cl-form, therefore the column requires only conditioning with 3,5% m/m hydrochloric acid.

The operating capacity of the cation-exchange resin is 1,2 mval/cm^3 in case of Varion KS. Regeneration of the cationic resin with an 8 % m/m hydrochloric acid yields a solution of 4000 mg Cd/dm^3.

The elute from the anion-exchange column is precipitated with sodmium hydroxide and the sludge can be fed back into the technology. The cation-free solution from WII can be treated on a strongly basic anion exchange column and the produced demineralized water can be recycled.

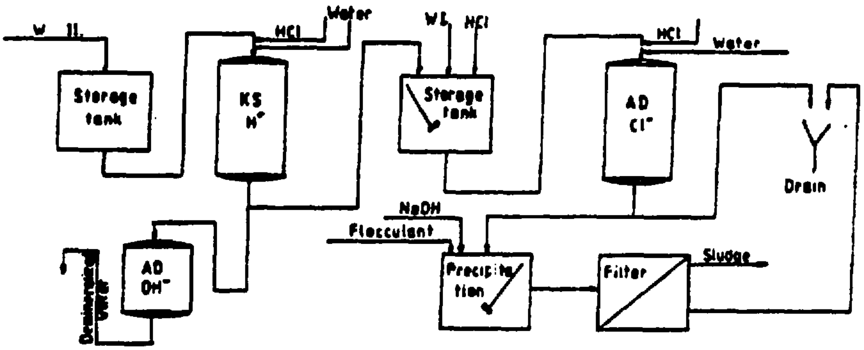

Fig 1. Flow sheet of the process

AMMONIA REMOVAL BY SLOVAK NATURAL CLINOPTILOLITE

Horvátová, É.
Water Research Institute, Bratislava,L.Svobodu, 5., CSSR

Static and dynamic experiments were carried out for removal of ammonia from water by natural Slovakian zeolite. Untreated and Na-form clinoptilolite were used in the experiments. In the static experiments the initial ammonia concentration ranged between 10 and 2740 mg/dm^3. Equilibrium data and selectivity coefficients were calculated. It was concluded that the Na-form clinoptilolite is selective for ammonia over the entire range of zeolite composition.

In the dynamic experiments three different model solution (56, 106 and 134 mg NH_4^+-N/dm^3) were used and the breakthrough capacity was measured. Finally, ammonia was removed from industrial waste water and the Na-form clinoptilolite proved far superior compared to the untreated material.

AUTHOR INDEX

LATE CONTRIBUTIONS

ABSTRACT

ION EXCHANGE KINETICS. TRANSIENT PHENOMENA IN REACTION MECHANISMS

Petruzzelli D.[1],Liberti L.[1],Boghetich G.[2],Helfferich F.G.[3],Passino R[1]

(1) Istituto di Ricerca Sulle Acque, C.N.R., 5, Via De Blasio,
70123 Bari, Italy.
(2) Istituto Chimica Applicata, Facolta' Ingegneria,
Universita, di Bari, 200, Via Redavid, 70125 Bari, Italy.
(3) Department of Chemical Engineering, The Pennsylvania
State University, University Park, Pa,16802, U.S.A.

Introduction

Modelistic interpretation of experimental data in ion exchange kinetics has been demonstrated a lacking approach in several cases, due to mathematical indeterminations.

Mathematical approach should be supported by direct visualization of transient phenomena and diffusion pathways in the solid-phase of the resin, for a more incisive description of experimental findings (1,2,3,4).

Autoradiography coupled to simple light microscopy observation of equatorial sections of the single resin bead allows to interpret transient phenomena in the solid-phase during exchange reaction.

In this paper experimental data for chloride/sulfate forward and reverse exchange, as well as for sulfate isotopic exchange at high solution concentration ($C=1.8N$), when reaction rate is likely to be particle diffusion controlled, are reported, in reference to an acrylic based resin (Kastel A102) with weak functionality.

Experimental

Transient phenomena in the resin bead are studied by light microscopy and autoradiography. A single bead, partially converted at a fixed degree of conversion in labelled form, is sliced and the equatorial sections (~ 10 μm thick), after observation in light microscopy, are tightly faced to a nuclear photographic emulsion obtaining a visual map of diffusional pathways in the solid-phase.

Results & discussion

In Fig.1 a typical result referring to reverse exchange (i.e., resin initially in labelled sulfate form picking up chloride from solution) at a total solution concentration of 1.8N, is reported.

Unusual concentric diffusional pathways are detected. Theoretical speculations based on Nernst-Planck p.d.c. kinetic model allow a good interpretation of the observed phenomena. Comments and discussions follow in the paper.

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1) Streat M.; Kinetics of slow diffusing species in ion exchange; Reactive Polym.,2(1984)79-91.
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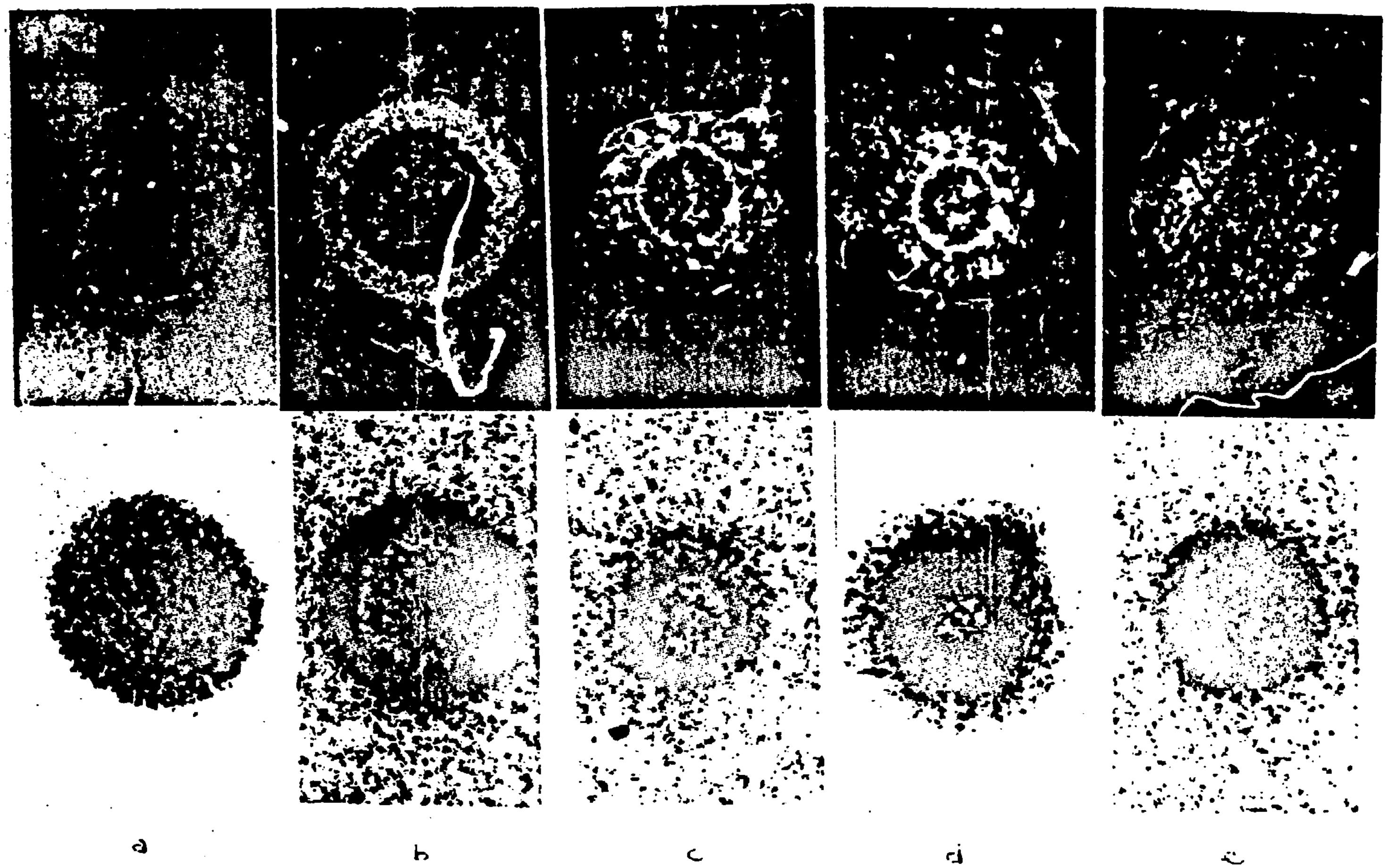

Fig.1.: Polarized light microscopic observations of equatorial sections and corresponding autoradiography for resin Amberlite IRA 458 submitted to reverse exchange. ($C=1.8N$, pH 3, 25°C, 20/30 mesh)
a) $U=0$; b) $U=0.25$; c) $U=0.50$; d) $U=0.75$; e) $U=1.0$

AP-20

TRACE ANALYSIS OF HEAVY METALS AND ALKALINE EARTH BY ION CHROMATOGRAPHY WITH POST-CHROMATOGRAPHIC DERIVATISATION

H. Bauer, D. Yan and H. Boekhoff
Biotronik, Frankfurt/Main, 6457 Maintal 1, POB 1330, Germany

The adaptabilities of the cation exchange columns BT V TM series have been investigated on the system BIOTRONIK IC 1000 for the rapid and complete separations of metals. Fe(III), Cu, Zn, Co Fe(II) and Mn can be baseline separated on a glass column 100 x 3 mm in 2.5 min. 11 common heavy metals and alkaline earth were separated to baseline on the column 200 x 4 mm with 0.1 mol/l tartrat eluent pH 3.05 in 24 min.

The stability of the PAR and PAR-Zn-EDTA solutions was investigated. It depends on the concentration and mainly on the pH-value of the reagent. An optimal detection system was optained by the systematic investigations of the kinetic factors involved (such as concentration, composition, pH-value, length of reaction coil and temperature). By this system the sensitivity of Fe(III), Pb, Cd and Fe(II) was enhanced about a factor 300, 10, 8.3 and 8.3 respectively in comparison with the system used before. The reproducibility of these ions was determined with a relative standard deviation better than 1 %. A detection limit of 1 ppb was obtained for Fe(III), Zn, Ni, Co, Ca, Mg and 2 ppb for Pb, Cd Fe(II), Mn and Cu. By means of concentration it is possible to determine metal ions at low ppt levels, which occur in demineralized water. The analyses of 10 different real samples show that this method can be applied to the multi-element-analysis down to trace levels with a concentration difference of 10^5.

REMOVAL OF IRON FROM IRON-RICH SOLUTIONS OF NICKEL AND CADMIUM SULPHATE.

Gábor Sinka, Mihály Vigvári

HUNGALU Engineering and Development Centre, Budapest,
Hungary

This work is part of a project sponsored jointly by the National Committee for Industrial Development and the Ministry of the Industry.

Introduction

Environment friendly and energy effective, hydrometallurgy is an expedient method for the reclamation of nonferrous metal wastes. Leach solutions of such wastes are often concentrated and almost always contain iron.

Precipitation of $Fe(OH)_3$ is a frequent method for the separation of the valueless iron from the valuable components.

Solutions bearing higher amounts of iron (above 10 g/dm^3), when treated this way will, however, suffer significant losses of valuables due to adsorption on the precipitate surface.

During the hydrometallurgical processing of scrap Ni-Cd batteries as developed at ALUTERV-FKI, a solution of the following composition is reached after the initial dissolution of scrap (g/dm^3):

Ni	Cd	Fe	H_2SO_4
28	28	30	5

Fe^{2+} makes up for more than 90% of all dissolved iron. On oxidation with H_2O_2, a complex anion of the formula $[Fe(SO_4)_2]^-$ is formed, displaying a stability constant of 17000 in a solution of an ionic strength of 1.2 /1/. Neither nickel nor cadmium formes such a complex. This fact opens up an alternative path for the selective removal of iron, using synthetic anion exchange resin.

Experimental

The equilibrium adsorption isotherms, together with the time required to reach equilibrium, were measurod for a Varion AT 660 resin in the bi-sulphate form, at 25° C.

Optimum number of cascades were determined graphically on the basis of the above data. Using countercurrent cascade decantation, the iron content of the solution may be reduced below 10 g/dm^3.

Results

According to the adsorption isotherms, the Varion AT 660 resin in the bi-sulphate form is selective for the complex anion $[Fe(SO_4)_2]^-$, with a maximal separation factor of about 2. Equilibrium is reached in 2 hours.

Using a three stage countercurrent cascade decantation setup with equal volumes of solution and resin, the iron content of the solution was reduced below 10 g/dm^3 from the original 30 g/dm^3.

Following such a preliminary treatment, the traditional $Fe(OH)_3$ precipitation for final iron removal causes only acceptable losses of the other valuables.

Literature

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SYNTHESIS AND INVESTIGATION OF ANION EXCHANGE MEMBRANES

MP-12

E.E.ERGOZHIN, B.A.UTKELOV and K.N.NURAKHMETOV

The Kirov Kazakh State University, Alma-Ata (USSR)

The modification of polyethylene, polypropylene, polyvinylchloride films of different specific surfaces by gamma ray grafting of styrene was studied. To obtain copolymers of the required physical, mechanical and chemical characteristics the effect of irradiation rate and dose, the influence of the nature of a solvent, of the method of copolymerization (in air, in the vacuum and in the inert gas atmosphere) and of the relation of primary components on the amount of the styrene-grafted links were studied.

Chlormethylated copolymers with the amount of chlorine up to 24% were obtained by treating the films with monochlordimethyl ether in presence of Friedel-Krafts catalysts. The reaction kinetics was studied and the chlormethylation of film copolymers was found to proceed with a greater reaction velocity and a greater fractional conversion compared with the granulated macroporous copolymers of styrene and divinylbenzene.

The weak basic anion exchange films with the exchange capacity up to 9,5 meqv/g were obtained by aminating chlormethylated copolymers with the different aliphatic low molecular and polymer amines. The influence of the nature of the alkyl substituents on the acid-base behaviour of anion exchangers was studied. The ionization constants of ion exchangers were found to be determined by the basicity of the aminating reagents.

The comparative study of the ion exchange kinetics of the film aminopolymers and analogous granulated amine polymers was made showing the ion exchange equilibrium to be established faster in the case of the film ion exchangers.

THE WATER-SOLUBLE ANIONITS BASED ON POLYSTYRENE AND HYDRAZIDE OF ISONIKOTINIC ACID.

Tausarova B.R.,Ergozhin E.E.,Begezhanov N.K.

Kazakh State University,Alma-Ata,USSR

The new water-soluble polyelectrolytes have been produced by means of the chemical modification of the chloromethylated polystyrene with various molecular mass ($15\cdot10^3-30\cdot10^4$) by hydrozide of isonicotinic acid.

The reaction has been carried out in the medium of dimethylformamide,dioxan and dimethylsulphoxide in the 1:2 proportion of polymer/amine for 1-2 hours in the temperature region 60-90°C. The reaction kinetics was investigated and it was established that the process of polymer amination took place with the neighbour having the slowing effect. The rate constants of polymer formation and their activation energy in comprasion with their low-molecular analogue-bensyl chloride were calculated.It was established that the rates of reactions in the studied solvents decreased in the order of DO<DMFA<DMSO. Thermodynamic characteristics of the process of amination:free energy,enthalpy and entropy are estimated. The structure and properties of polymers were studied by means of the chemical analysis of pothentiometric titration,conductometric titration, viscosimetry and IR-spectroscopy. Dissociation constants of the functional groups were obtained from the curves of the potentiometric titration, $pK_\alpha=9.9$. Exchange capacity to the 0.1 N solution of HCl=3.61 meq/g.

The investigation of specific and equivalent conductivity confirmed the availability of ionogenic groups in the synthesized polymers.

The effect of the molecular mass,the nature and concentration of the complexing metal,and the medium pH on the liberation of the metal ions from their aqueous solutions. It is shown that synthetized polymers can be used for the formation and precipitation of Cu^{2+},Ni^{2+}, Co^{2+}, Pb^{2+}, MoO_4^-, VO_3^-, WO_4^{2-} ions.

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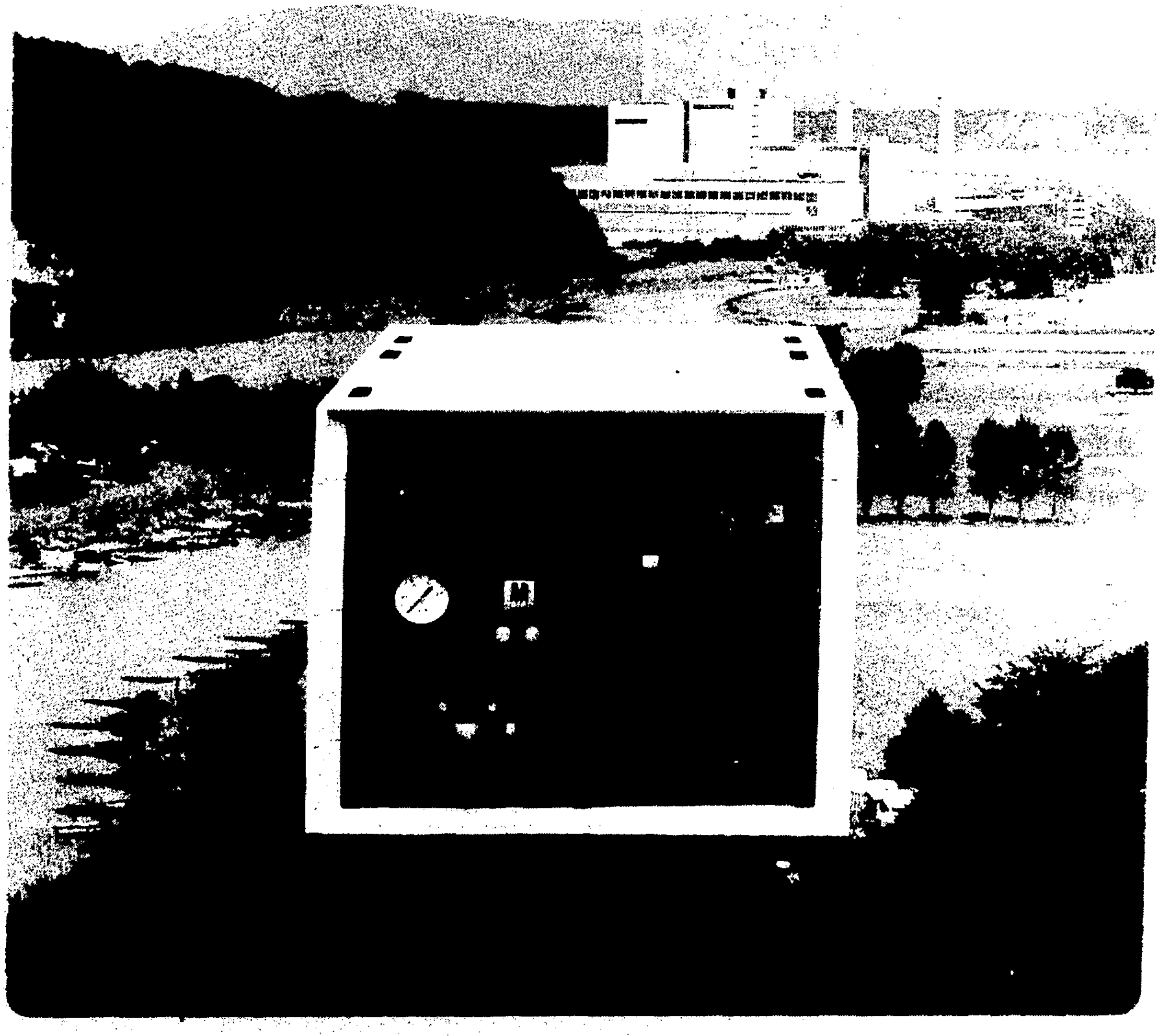

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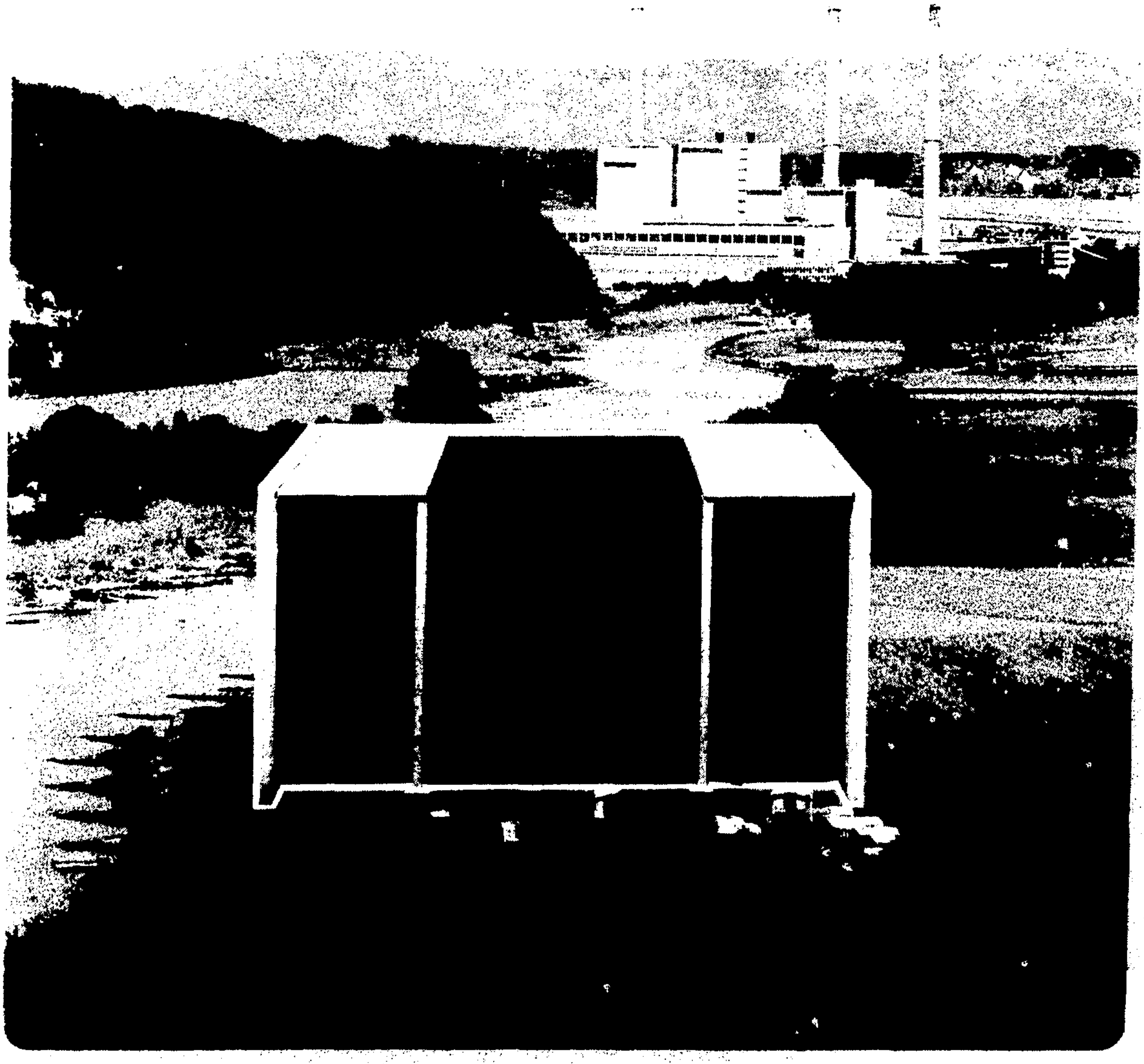
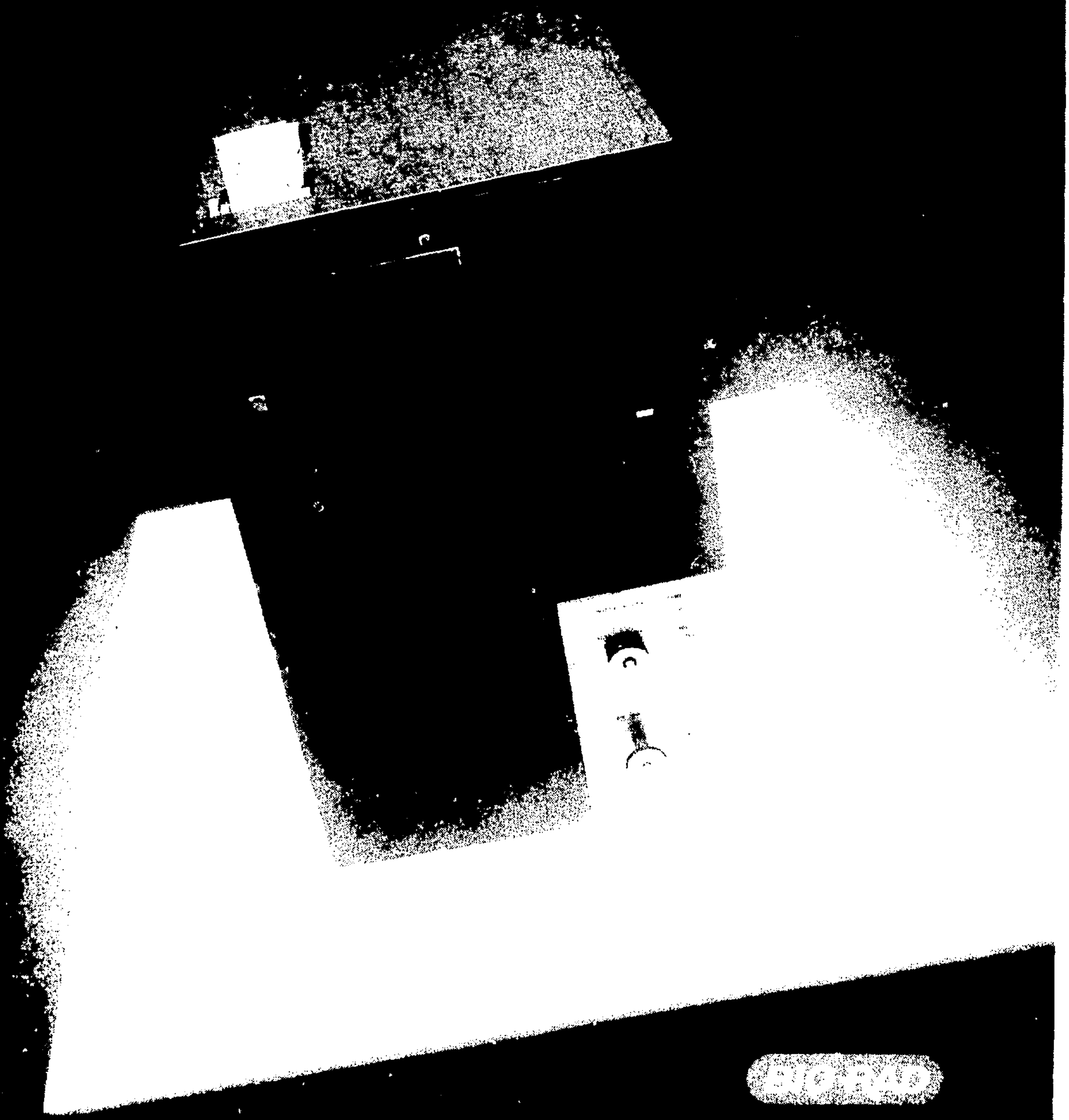


The First Nonsuppressed Ion Chromatograph for High Sensitivity Analysis of Complex Samples



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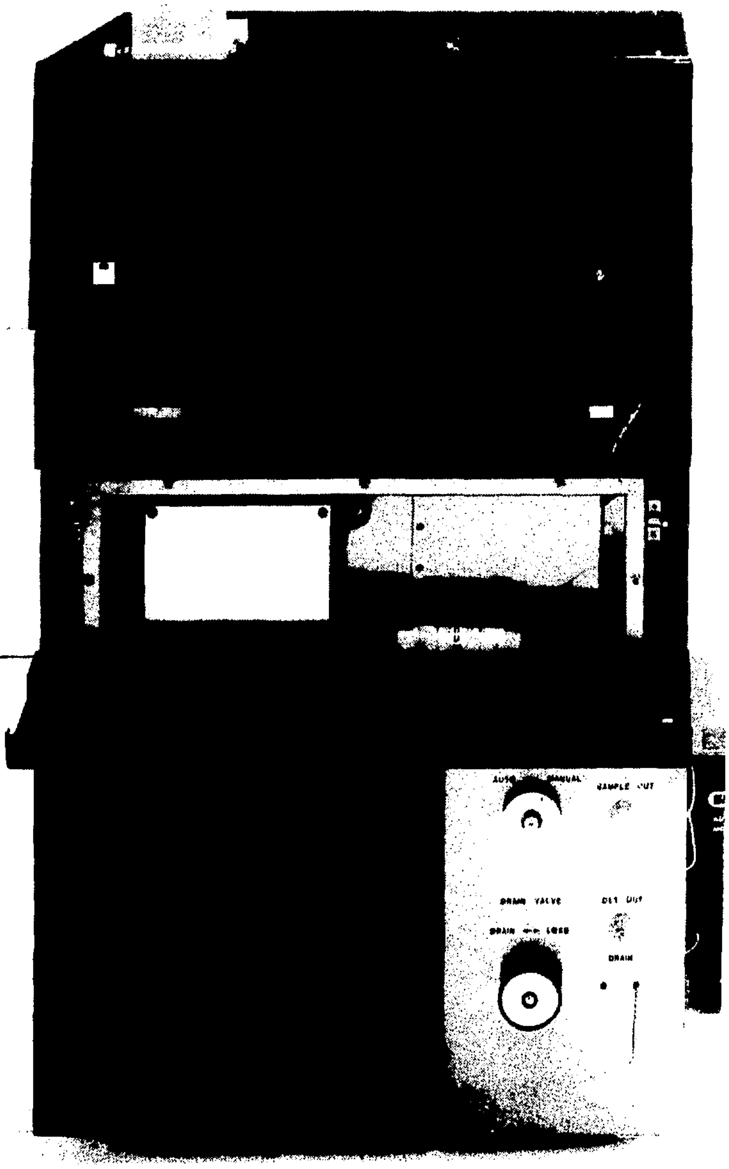

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