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ROLA FAZY ORGANICZNEJ W PROCESACH EKSTRAKCYJNYCH

РОЛЬ ОРГАНИЧЕСКОЙ ФАЗЫ В ЭКСТРАКЦИОННЫХ ПРОЦЕССАХ

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Abstract

The effect of diluent on the activity coefficients of
the extracted complex and of the extractant in the orga-
nic phase has been discussed on the basis of the regular
solutions theory. The dependence of the extraction coef-
ficients of the $Co(\gamma-picoline)_4(NCS)_2$ complex on the so-
lubility parameters of inert organic diluents is parabo-
lic, as predicted by the theory. Rather a small effect of
diluent on the extraction coefficients of the complex at
a constant concentration of the extractant in the organic
phase in due to the partial compensation of the interac-
tions of the complex and of the extractant with the di-
luents. Deviations from the parabolic function of the ex-
traction coefficient values for some diluents result from
the specific molecular interactions between the diluents
and the extracted species.

Streszczenie

Na podstawie teorii roztworów regularnych przedysku -
towano wpływ rozcieńczalnika na wielkości współczynników
aktywności ekstrahowanego kompleksu i ekstrahenta w fazie
organicznej. Wykazano istnienie zgodnej z teorią parabo-
liczną zależności współczynników ekstrakcji kompleksu
$Co(\gamma-pikolina)_4(NCS)_2$ od parametru rozpuszczalności obo-
jętnych rozpuszczalników organicznych. Przy stałym stę-
żeniu ekstrahenta w fazie organicznej stosunkowo niezna-
czny wpływ rozcieńczalnika na współczynniki ekstrakcji
kompleksu spowodowany jest częściową kompensacją oddzia-
ływań kompleksu i ekstrahenta z rozcieńczalnikiem. Odchyle-
nia współczynników ekstrakcji od paraboli dla niektórych

rozpuszczalników są wynikiem istnienia specyficznych od-
działywań cząsteczkowych pomiędzy rozpuszczalnikiem a
substancjami ekstrahowanymi.

Резюме

На основании теории регулярных растворов продискути-
ровано влияние разбавителя на величины коэффициентов ак-
тивности экстрагированного комплекса и экстрагента в ор-
ганической фазе. Показано существование, согласной с те-
орией, параболической зависимости коэффициентов экстракции
комплекса $Co(\gamma\text{-пиколин})_4(NCS)_2$ от параметра растворимости
инертных органических растворителей. Относительно неболь-
шое влияние разбавителя на коэффициенты экстракции комп-
лекса, в условиях постоянной концентрации экстрагента в
органической фазе, является результатом частичной компен-
сации взаимодействий комплекса и экстрагента с разбавите-
лем. Отклонения коэффициентов экстракции от параболы для
некоторых растворителей являются эффектом существования
специфических взаимодействий между растворителем и экс-
трагируемыми соединениями.

Distribution coefficient of a substance in the system
of two immiscible phases - aqueous and organic - depends
in a different way on their physico-chemical properties.
Standard free energy of the solvent extraction process is
mainly determined by the entropy effect in the aqueous
phase. Weak intermolecular interactions in the organic
phase affect in a much lower extent the extraction, ne -
vertheless its role cannot be neglected when considering
a real extraction system.

The present state of the theoretical chemistry creates
no possibilities of determining a priori the values of the
distribution coefficients, provided the physico-chemical
properties of the pure components of the extraction system
are merely known. Only the influence of some parameters of
a real extraction system on the value of the distribution
coefficient can be anticipated; the value of the distribu-
tion coefficient can be estimated if its standard value has
been empirically measured. Problems connected with the ef -
fects of the aqueous phase were discussed in a previous
communication[1]. Let us consider now the role of some pa-
rameters concerning the organic phase.

The process of the extraction of an inert molecule of
a metal complex can be described by the equation:

$$Me^{m+}_{aq} + mR^-_{aq} + nE_{org} \rightleftharpoons MeR_mE_{n,org} \qquad /1/$$
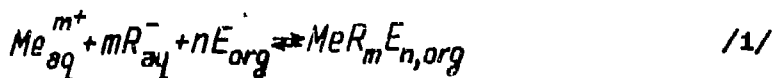
where Me^{m+}, R^- and E denote metal, anion and extractant, resp.,
m and n are stoichiometry coefficients, indexes aq and org re-
late to the aqueous and organic phases, resp. If the composition
of the aqueous phase is considered to be constant, the distri-
bution coefficient can be expressed by the following equation:

$$D = K\frac{a^n_E}{\gamma_C} = K\frac{X^n_E \cdot \partial^n_E}{\partial_C} \qquad /2/$$

where K is a constant /for a given complex, composition of the
aqueous phase and temperature/, a_E and x_E are the thermodynamic
activity and the concentration of the extractant in the organic
phase, resp., γ_E and γ_C are the activity coefficients of the
extractant and complex, resp. Thus, the distribution coeffi-
cient for the extraction of a complex from the defined aqueous
phase depends under defined conditions on: 1° - the concentra-
tion of the extractant in the solvent /diluent/; 2° - the
values of the activity coefficients of the extractant and com-
plex in this diluent.

The power dependence of D on the concentration of the ex-
tractant is a simple consequence of the law of mass action.
/Hereby one has to remember that for high concentrations of the
extractant and complex their variations cause also changes in
the values of the corresponding activity coefficients/. In
some cases, however, a change in the extractant concentration
can also in a different way affect the D-value. The solvation

number, n, of some complexes depends on the extractant concentration. A change in this number and a consequent drift of the configuration equilibrium of the complex can cause a drastic change in the distribution coefficient. In such cases, formula /2/ can be applied only for a definite range of the extractant concentration[2/].

The values of the activity coefficients, γ_E and γ_c, represent quantitatively the intermolecular interaction of the extracted substance with the diluent in solutions sufficiently dilute. For a constant value of the extractant concentration the ratio γ_E^n/γ_c is a measure of the effect of the diluent on the solvent extraction process.

Hildebrand-Scatchard's theory of regular solutions[3/] makes possible the calculation of values of the activity coefficients from the knowledge of the physico-chemical properties of the components of the solution. Assuming that the interaction of the solute and diluent can be reduced to non-specific dispersion forces, and that the distribution of the molecules in the solution is random /the ideal entropy of mixing/, the activity coefficient of the solute /γ_A/ can be expressed as follows:

$$RT \ln \gamma_A = V_A \, \varphi_d^2 (\hat{\delta}_A - \delta_d)^2 \qquad /3/$$

where V_A is the molar volume of the solute in the solution, φ_d is the volume fraction of the diluent in the solution, δ_A and δ_d are the solubility parameters of the solute and diluent, resp. The value of the solubility parameter at a tem-

perature T can be calculated from the value of its heat of vaporisation /ΔH_T/ and molar volume /V_T/:

$$\delta = \sqrt{\frac{\Delta H_T - RT}{V_T}} \qquad /4/$$

In this simple case of extraction by a physical mechanism /when the extraction system does not contain the extractant/, equation /2/ can be expressed as $D = K/\gamma_A$. If the activity coefficient of the solute is expressed using equation /3/, a parabolic dependence of log D on the solubility parameter /δ_d/ of the diluent is obtained, with a maximum for $\delta_d = \delta_A$:

$$\log D \sim \log \frac{1}{\delta_A} = -\frac{V_A}{2.3RT}\delta_d^2 + \frac{2V_A \delta_A}{2.3RT}\delta_d + const. \qquad /5/$$

The substance is then best extracted by solvents /diluents/ whose solubility parameters are equal to the solubility parameters of the extracted substance. The slope of the parabola /5/ is proportional to the molar volume of the extracted substance. This has been observed by Siekierski and Olszer[4] while extracting germanium halides into inert organic solvents.

A similar relation can be applied to the extraction of the free molecules of extractant: di- and tri-butylphosphate[5,6], γ-picoline[7] and other.

To express the functional effect of the diluent on the extraction of solvated salt molecules /in the system: aqueous phase - extractant - diluent/, equation /3/ applies both for the complex and extractant. One obtains as a result:

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$$LogD \sim Log \frac{\gamma_E^n}{\gamma_C} = -\frac{V_C - nV_E}{2.3\,RT}\,\delta_d^2 + \frac{2V_C\,\delta_C - nV_E\,\delta_E}{2.3\,RT}\,\delta_d + const. \qquad /6/$$

The slope of this parabola is proportional to the difference of the molar volumes of the complex and n molecules of the extractant, its maximum corresponds to the solubility parameter of the diluent $\delta_d = \dfrac{V_C\,\delta_C - nV_E\,\delta_E}{V_C - nV_E}$. In this case, a partial or even complete compensation of effects of interaction of the complex and extractant with the diluent occurs; the parabola /6/ has a much less steep shape than the /5/, and the dependence of the distribution coefficient on the solubility parameter of the diluent is much less pronounced. The comparition of such two parabolas for the solvent extraction of $Co(\gamma\text{-picoline})_4(NCS)_2$ complex into inert organic solvents can be seen from Figs.1 and 2. Fig.1 presents a plot of the magnitude $log\dfrac{\partial_E}{\partial_C}$, proportional to the distribution coefficient of the complex at a constant concentration of the extractant /γ-picoline/ in the organic phase.

Fig.2. presents a plot of $log\dfrac{1}{\delta_C}$, proportional to the distribution coefficient at a constant thermodynamic activity of the extractant in the organic phase, i.e. the constant concentration of the extractant in the aqueous phase at equilibrium. This corresponds to the case of extraction of the solvated complex by a simple physical mechanism. It can be seen that the dependence of the distribution coefficient on the solubility parameter of the diluent is very significant in the latter case. It is only slightly marked in the former case, as a result of the discussed compensation. It must be pointed out that all these considerations

pertain extraction from an aqueous phase of a constant composition into diluents of equal concentration of the extractant and of no specific interaction with the extracted substance.

If specific interactions occur between molecules of the extracted substance and diluent, equation /3/ cannot be applied, and experimental values of the activity coefficients /and distribution coefficients/ do not correspond to the theoretical parabola. Specific interactions are usually of chemical character. Thus, the much greater than anticipated extraction of the di-butylphosphate or γ-picoline into chloroform or bromoform can be explained as being due to the formation of hydrogen bonds between molecules of the extracted substance and the diluent[6,7]. A more efficient extraction of arsenic and antimony halides into aromatic hydrocarbons is due to their mutual electronic interaction which results in the formation of complexes /metal halide - aromatic hydrocarbon/ of charge-transfer character[8]. Specific effects due to the structure of the diluent molecule were also found. Thus, the extraction of the $Co\left(\gamma\text{-picoline}\right)_4\left(NCS\right)_2$ complex into mono-substituted benzene derivatives can be described by the equation of the regular solution theory /Fig.2/. An increasing of the number of substituents in the aromatic ring of the diluent molecule to two or, especially, three leads to pronounced reduction of the extraction power of the solvent, independently of the chemical character of the substituents[16].

In the case where the tendency of the diluent to specific interactions with the extractant and the complex is different,

considerable deviations of the experimental values of log D from the parabola /6/ can be observed /Fig.1/. Specific inter-actions of the chemical character are, as a rule, stronger in the diluent–extractant system than in the diluent–complex one. To given an example, both the free electron pair of the hetero – atom /nitrogene/ of picoline and the π-electrons of its aromatic ring can participate in the formation of the hydrogen bond be-tween the molecules of chloroform and picoline. In a coordination complex the pair of electrons of nitrogene is already bonded and cannot participate in the formation of a supplementary hydrogen bond. The interaction of chloroform with picoline coordinated in a complex is, therefore, much weaker than that with free picoline. The pronounced decrease of the activity coefficient of the ex-tractant cannot be fully compensated for by the corresponding change of the complex. This effect causes a relative /with res-pect to the constant concentration of the extractant/ reduction of the extraction power of this diluent, although the solubility of the complex in this diluent is higher.

The described above dependence of the distribution coeffi-cient on the solubility parameter of the diluents was stated experimentally in many laboratories for numerous metals in the form of such species as non–solvated molecules, inert solvated salts, chelates and ion–pairs. Most frequently such extractants as phosphoroorganic acids and their salts[5,6,11], β -diketones[10,14,15], aliphatic and heterocyclic amines[7,9,12] and other[13] have been applied.

Analysis of the results of these papers implies that the
considerations and results presented here are of general
character.

R e f e r e n c e s

1. S.Siekierski: Physical Chemistry of Extraction Processes",
    INR, Report "P" No. 1339/V/C, 1971.

2. S.Siekierski, J.Narbutt: unpublished data.

3. J.H.Hildebrand, R.L.Scott: The Solubility of Nonelectro-
    lytes. New York, 1950.

4. S.Siekierski, R.Olszer: J.inorg.nucl.Chem., 25, 1351 /1963/.

5. S.Siekierski: ibid, 24, 205 /1962/.

6. S.Siekierski: Nukleonika, 9, 601 /1964/.

7. S.Siekierski, J.Narbutt: to be published.

8. R.Olszer, S.Siekierski: J.inorg.nucl.Chem., 28, 1991 /1966/.

9. W.Smułek, S.Siekierski: ibid, 24, 1651 /1962/.

10. T.Wakabayashi, S.Oki, T.Omori, N.Suzuki: ibid, 26, 2265
    /1964/.

11. W.M.Wdowienko, T.W.Kowalewa, M.A.Rjazanow: Radiochimija,
    7, 133 /1965/.

12. H.A.Mottola, H.Freiser: Talanta, 13, 55 /1966/.

13. B.Skytte-Jensen: in "Progress in Coordination Chemistry",
    Amsterdam 1968, p.737.

14. J.W.Mitchel, C.V.Banks: J.inorg.nucl.Chem., 31, 2105 /1969/.

15. K.Akiba, N.Suzuki, T.Kanno: Bull.Chem.Soc.Japan, 42, 2537
    /1969/.

16. J.Narbutt: Proc.Int.Solv.Extr.Conf., Hague, 1971
    /in press/.
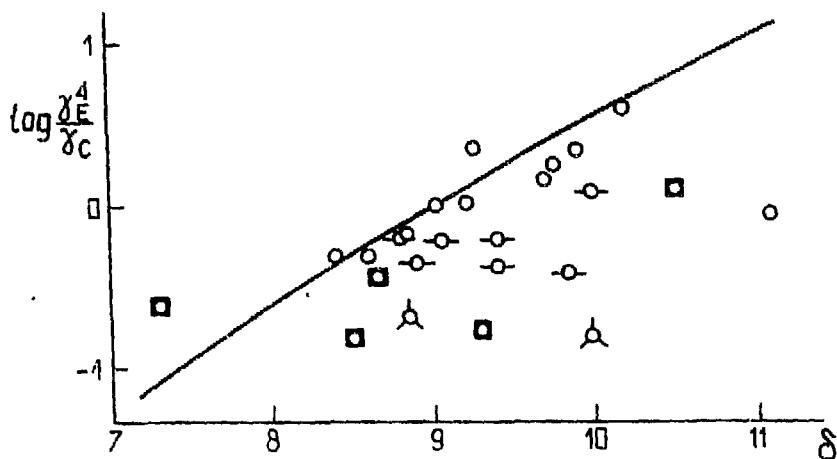
Fig.1. The dependence of $\log \dfrac{\gamma_E^4}{\gamma_C}$ of the $Co\left(\gamma\text{-picoline}\right)_4\left(NCS\right)_2$ on the solubility parameter of the diluent. Curve – a calculated part of the parabola /6/; toluene being chosen as the standard solvent.
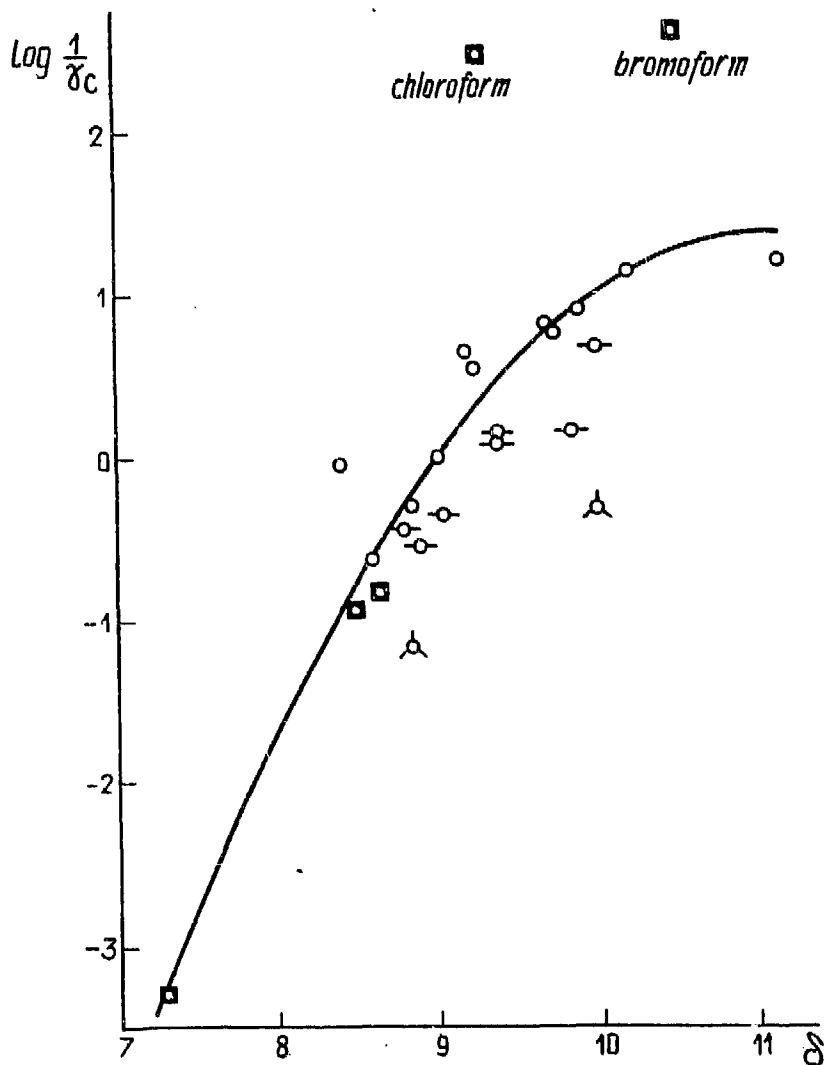
Experimental points were marked as in Fig.2.

Fig.2. The dependence of log $\frac{1}{\gamma_c}$ of the Co$\left(\gamma\text{-picoline}\right)_4\left(\text{NCS}\right)_2$
complex on the solubility parameter of the diluent.
Parabola has been calculated from equation /5/, using
toluene as the standard solvent /$\gamma_{c,tol}$ = 1/.
Marks for the experimental points:
Circles - aromatic solvents: o - benzene and mono-
            -substituted, -o- - di-substituted /o-, m-
            and p-/, △ - tri-substituted /sym- and as-/
            benzenes;
Squares - aliphatic and halogenated aliphatic solvents.