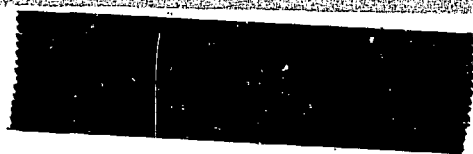


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**AN INVESTIGATION
OF THE URANYL NITRATE-TBP COMPLEXES
IN HEXANE BY THE VAPOUR PRESSURE
LOWERING METHOD**

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WARSZAWA

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INSTITUTE OF NUCLEAR RESEARCH
DEPARTMENT OF NUCLEAR CHEMISTRY ENGINEERING

AN INVESTIGATION OF THE URANYL NITRATE - TBP COMPLEXES
IN HEXANE BY THE VAPOUR PRESSURE LOWERING METHOD

BADANIE KOMPLEKSÓW AZOTANU URANYLU Z TBP W HEKSANIE
METODĄ OBNIŻENIA PRĘŻNOŚCI PAR ROZPUSSZCZALNIKA

ИССЛЕДОВАНИЕ КОМПЛЕКСОВ УРАНИЛНИТРАТА С ТРИБУТИЛФОСФАТОМ
В ГЕКСАНЕ С ПОМОЩЬЮ МЕТОДА ПониЖЕНИЯ ДАВЛЕНИЯ ПАРА
РАСТВОРИТЕЛЯ

Andrzej Poczynaiko

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Abstract

The relative measurements of vapour pressure in the systems TBP - hexane and $UO_2(NO_3)_2$ - TBP - hexane were performed with the help of the Mechrolab 301A osmometer. The partial dimerization of tributylphosphate / $K_{dim} = 1.24 \pm 0.08$ at $25^\circ C$ / and the solvation phenomenon of the $UO_2(NO_3)_2 \cdot 2$ TBP complex with one molecule of free TBP were found. The equilibrium constant of the reaction $UO_2(NO_3)_2 \cdot 2$ TBP + TBP \rightleftharpoons $UO_2(NO_3)_2 \cdot 3$ TBP is equal to 3.7 ± 2.0 at $25^\circ C$.

Streszczenie

Na osmometrze Mechrolab 301A wykonano pomiary względne prężności par układów TBP - heksan i $UO_2(NO_3)_2$ - TBP - heksan. Stwierdzono częściową dimeryzację trójbutylofosforanu / $K_{dim} = 1,24 \pm 0,08$; temp. $25^\circ C$ / oraz występowanie zjawiska solwatacji kompleksu $UO_2(NO_3)_2 \cdot 2$ TBP jedną cząsteczką wolnego TBP. Stała równowagi reakcji $UO_2(NO_3)_2 \cdot 2$ TBP + TBP \rightleftharpoons $UO_2(NO_3)_2 \cdot 3$ TBP jest równa $3,7 \pm 2,0$ w temperaturze $25^\circ C$.

Резюме

На осмометре Mechrolab 301A были произведены относительные измерения давления пара для систем ТБФ-гексан и $UO_2(NO_3)_2$ - ТБФ - гексан. Найдено, что трибутилфосфат частично подвергается димеризации ($K_{dim} = 1,24 \pm 0,08$ при $25^\circ C$) и что комплекс $UO_2(NO_3)_2 \cdot 2$ ТБФ способен сольватироваться одной молекулой свободного ТБФ. Константа равновесия реакции $UO_2(NO_3)_2 \cdot 2$ ТБФ + ТБФ \rightleftharpoons $UO_2(NO_3)_2 \cdot 3$ ТБФ равна $3,7 \pm 2,0$ при $25^\circ C$.

1. INTRODUCTION

The solvation of uranium compounds by organic solvents, in particular of uranium nitrate salts, is long studied. Tributyl phosphate is a solvent of special interest in these investigations because of its practical use in the reprocessing of irradiated nuclear fuel. For example, the technological Purex process, now almost generally applied in the reprocessing of fuel on an industrial scale, is based on the use of TBP.

Such problems as the composition of uranyl nitrate complexes with TBP, their structure and, in particular, the course of extraction of uranyl nitrate from an acidified aqueous phase to the organic phase, composed of TBP in inert diluent, have intensely been studied in the fifties^{1-11/}. The solvation number was determined with the help of various methods, but most frequently from the dependence of uranium distribution ratio on the concentration of TBP in the organic phase^{4,6,7/}, from measurements of the solubility of the nitrate salt in TBP^{4,6/} and from infrared absorption spectra^{4,9,10,11/} of the complexation product. Results of these investigations permitted to define the formula of the complex as $\text{UO}_2(\text{NO}_3)_2 \cdot 2 \text{TBP}$, generally cited in the chemical literature. The complex molecule does not contain molecules of water and is not charged.

The aim of the work was to study the solvation phenomenon of uranyl nitrate by TBP by means of the thermoelectric differential vapour pressure method, usually called the vapour pressure lowering /VPL/ method. The problem of the composition of complexes arose when carrying out experiments on the simultaneous extraction of uranium, plutonium and nitric acid in the system $\text{UO}_2(\text{NO}_3)_2 - \text{Pu}(\text{NO}_3)_4 - \text{HNO}_3/\text{TBP}-n\text{-dodecane}$. Till now in investigations of this type the aggregation of solvent itself was not taken into account, therefore it was

interesting to study the composition of the organic phase in a more complex way. The replacement of n-dodecane with hexane was extorted because of low vapour pressure of n-dodecane. This should not have any influence on the character of complexation processes.

It is note worthy that from the point of view of application of the VPL method the search after several species in the solution with the aim at their identification is inverse to the traditional use of the method. The method is routinely applied for the determination of molecular weights of organic and inorganic substances and aggregation, dissociation phenomena being strong impediments. When molecular weights of substances are known a priori, then it is possible to investigate chemical equilibria in solutions. One can give, as an example, studies of the aggregation equilibria of alkyl-ammonium salts in benzene^{12-14/} and a study of the composition of $ZnCl_2$ complex with trichlorolaurylamine in benzene^{15/}.

2. PRINCIPLES OF THE VPL METHOD

The physical basis of the VPL method consists in a known fact, that the vapour pressure of a pure solvent is always greater than the vapour pressure of a solvent to which a solute was added. The lowering of vapour pressure of solvent is proportional to the molar fraction of the solute in the solution.

When two drops of liquids, one being a pure solvent and the second a solution, are placed side by side in an isothermic chamber, to which previously a large quantity of the solvent /placed on the bottom of a vessel/ has been introduced, then after short time the drop of the solvent will be in equilibrium with the vapour of the solvent in the gaseous phase. The drop of the solution is growing /the rate depends on the concentration

of the solute/ because the number of the solvent molecules condensing on its surface is greater than the number of the evaporating molecules. As a result, the mass transfer occurs connected with the evolution of condensation heat. The temperature of the solution drop is somewhat higher than the temperature of the solvent drop. The latter temperature is equal to the ambient temperature predetermined by a heater control circuit.

One of the best way for continuous measurements of very small temperature differences is to put the drops on matched thermistors, as shown in Fig.1. The change of the thermistor resistance ΔR must be proportional to the change of temperature ΔT . The Mechrolab Osmometer Model 301A belongs to the drop type of VPL osmometers^{16/}. The thermistors are of high resistance small beads with diameter circa 1 mm, mounted on fine wires. They constitute the essential part of a DC Wheatstone bridge circuit, by means of which changes of electrical resistance of the sample bead are measured by compensating on the balancing arm. The scheme of the bridge is shown in Fig.2. It is designed for measuring values of ΔT between the drops equal to 0.0001°C . Of course, the stability of temperature in the chamber must be maintained adequately.

VPL osmometers are operating with good accuracies when solvents, such as benzene, toluene, carbon tetrachloride, demonstrate great volatility at moderate temperatures, and solutes, on the contrary, show very low volatility. Then the content of the solute in the drop of the solution is constant and the evaporation - condensation process is connected almost entirely with the solvent. The per cent of accuracy is comparable with the ratio of vapour pressure of the solute to that of the solvent.

The most characteristic feature of VPL osmometers is that they "count" in the same way all particles in the solution, independently of the chemical nature of species.

Simple molecules of various magnitude, ions, and aggregates /dimers, trimers, multimers/ cause the same effect of vapour pressure lowering of a solvent provided their concentration in solution, expressed in molar fraction, is equal. This gives a possibility of reading the concentrations of various species from one calibration curve, traced for a given solvent. The calibration curve expresses the values ΔR for various concentrations of a standard solute. The molecules of the standard solute should not aggregate or dissociate; then, at correct operation of the osmometer, the calibration curve should be a straight line. As a rule, in the VPL method small concentrations of solutes are used and this makes possible to express them as the molarity instead as the molar fractions /both calibration curve and proper solutions/.

It is desirable that the drops should be of the same magnitude because not whole heat of condensation contribute to the rise of temperature of the drop and thermostat. Part of the heat dissipates from the solution by convection, conduction and radiation^{17/}. In some cases it may cause false readings of ΔR and lack of good reproducibility.

3. AGGREGATION EQUILIBRIUM STUDIES OF TBP IN HEXANE

Benzil, tribenzylamine, biphenyl, 1,2-dichlorobenzene and n-dodecane were used in hexane solutions for the calibration of the Mechrolab VPL osmometer, model 301A. Benzil and tribenzylamine were not useful because of too low solubility in hexane at 25°C. On the contrary, biphenyl and 1,2-dichlorobenzene gave an aggregation effect at concentrations above 0.05 M. Only n-dodecane gave an increase of ΔR values proportional to the rise of concentration in the studied range 0.03-0.25 M. The straight calibration

line for the concentrations of n-dodecane, greater than foreseen as optimal in the benzil - benzene system, led us to work with concentrations of larger range than normally used /0.01 - 0.15 M/.

The drops of hexane and suitable sample solutions were placed by means of syringes on beads and readings of ΔR values were recorded after 2, 4, 6, 8 and 10 minutes. The measurement of ΔR for each concentration of the solution was repeated three times. The graph of ΔR as a function of time has to be constructed from which the values $\Delta \bar{R}_0$ at $t = 0$ were found by extrapolation. In Fig. 3 the determination of $\Delta \bar{R}_0$ for a 0.20 M solution of n-dodecane in hexane is shown. The reproducibility of repeated readings of the ΔR values was about 1%. The reproducibility of the whole operations, including the preparation and measurement of solutions at different times, was within 3%. All measurements were made at 25°C.

The results for the n-dodecane - hexane and TBP-hexane systems are shown in Fig. 4. The points representing the $\Delta \bar{R}_0$ values for the various concentrations of solutes lie, in the case of n-dodecane, on a straight line, and in the case of TBP on a somewhat sloped line. The straight line was used as the calibration curve. The sloping of the TBP curve is caused by the relative decrease in particle concentration with growing total concentration of the solute in hexane. Since tributyl phosphate has the polar phosphoryl group, $P \rightarrow O$, and hexane is a nonpolar solvent, it is obvious to assume the association of TBP molecules. The magnitude of aggregates may vary. In the simplest case they occur as dimers.

When in the solution only monomer and dimer molecules of a solute are present, the aggregation equilibrium is easily described.



Assuming that the activity coefficients are unity, the equilibrium constant then is:

$$\frac{X_2}{X^2} = \beta_2 \quad /1/$$

where x_2 - concentration of dimer in the solution,
 x - concentration of monomer.

It is obvious that x_2 must be equal to the difference between the total concentration of TBP and the concentration of the monomer, divided by a factor of two:

$$X_2 = \frac{(TBP)_{tot.} - X}{2} \quad /2/$$

The value of x can be found from the following equation:

$$E = X + \frac{(TBP)_{tot.} - X}{2} \quad /3/$$

where E - equilibrium concentration of all species in the solution. E is determined from the calibration curve after measuring the ΔR_0 value of solution containing a given total concentration of the solute.

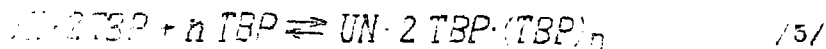
Replacing x in eq./2/, and /1/, by the expression $2E - (TBP)_{tot.}$ we receive:

$$\beta_2 = \frac{(TBP)_{tot.} - E}{(2E - (TBP)_{tot.})^2} \quad /4/$$

Substituting the relative values of $(TBP)_{tot.}$ and E from Fig.4 to eq./4/ a good constancy of β_2 was found in the whole range of the studied concentrations. The calculated value of β_2 is 1.24 ± 0.08 . The small differences between the individual determinations imply that only dimerization of TBP takes place in the hexane solution.

4. SOLVATION OF THE $UO_2(NO_3)_2 \cdot 2$ TBP COMPLEX BY FREE TBP

The general form of the solvation equation can be written as:



where the symbol UN means $UO_2(NO_3)_2$.

Taking into account that two processes occur in the organic solution of TBP and uranyl nitrate, namely, the aggregation of TBP itself and the solvation of the formed $UN \cdot 2 TBP$, the expression for the total concentration of TBP may be written:

$$\begin{aligned} (TBP)_{tot} &= [TBP] + 2[TBP]_2 + 2UN \cdot 2TBP + 3UN \cdot 2TBP(TBP)_1 + 4UN \cdot 2TBP(TBP)_2 + \dots \\ &= [TBP] + 2\beta_2 [TBP]^2 + 2[UN \cdot 2TBP] + 3K_1[UN \cdot 2TBP][TBP] + \\ &\quad + 4K_2[UN \cdot 2TBP][TBP]^2 + 5K_3[UN \cdot 2TBP][TBP]^3 + \dots \end{aligned} \quad /6/$$

or, at $[TBP] = X$:

$$(TBP)_{tot} = X + 2\beta_2 X^2 + [UN \cdot 2TBP](2 + 3K_1 X + 4K_2 X^2 + 5K_3 X^3 + \dots) \quad /7/$$

The total uranium concentration is:

$$\begin{aligned} U_{tot} &= [UN \cdot 2TBP] + K_1[UN \cdot 2TBP] \cdot X + K_2[UN \cdot 2TBP] \cdot X^2 + K_3[UN \cdot 2TBP] \cdot X^3 + \dots = \\ &= [UN \cdot 2TBP](1 + K_1 X + K_2 X^2 + K_3 X^3 + \dots) \end{aligned} \quad /8/$$

The equilibrium concentration of all the species present in the solution is expressed by E:

$$E = X + \beta_2 X^2 + [UN \cdot 2TBP](1 + K_1 X + K_2 X^2 + K_3 X^3 + \dots) \quad /9/$$

By subtraction eq./8/ from /9/ we receive the expression:

$$E - U_{tot.} = X + \beta_2 X^2 \quad /10/$$

from which it is easily to determine the free /monomeric/ concentration of TBP.

The aim of our considerations was to know how many molecules of TBP are combined with one molecule of uranyl nitrate (\bar{n}). The calculation was carried out with the help of the functions:

$$A = [(TBP)_{tot.} - (X + 2\beta_2 X^2)] = [UN \cdot 2TBP] (2 + 3K_1 X + 4K_2 X^2 + 5K_3 X^3 + \dots) \quad /11/$$

$$B = [E - (X + \beta_2 X^2)] = [UN \cdot 2TBP] (1 + K_1 X + K_2 X^2 + K_3 X^3 + \dots) \quad /12/$$

Eq./11/ represents the concentration of TBP combined with uranium, eq./12/ the total concentration of uranium in the system. The relation A to B gives \bar{n} :

$$\bar{n} = \frac{A}{B} = \frac{2 + 3K_1 X + 4K_2 X^2 + 5K_3 X^3 + \dots}{1 + K_1 X + K_2 X^2 + K_3 X^3 + \dots} \quad /13/$$

with $\lim_{X \rightarrow 0} \frac{A}{B} = 2$ at $X \rightarrow 0$.

From eq./13/ it is clearly seen that if there is the solvation of the UN.2 TBP complex by free TBP, then the increase of monomer concentration X in the solution must cause an increase of the average solvation number \bar{n} . To be in accordance with the literature, only a complex with solvation number 2 should exist at the saturation concentration of TBP with uranyl nitrate.

The value K_1 can be determined by the following operations:

$$\bar{n}-2 = \frac{2+3K_1X+4K_2X^2+5K_3X^3+\dots-2-2K_1X-2K_2X^2-2K_3X^3}{1+K_1X+K_2X^2+K_3X^3+\dots} =$$

$$= \frac{K_1X+2K_2X^2+3K_3X^3+4K_4X^4+\dots}{1+K_1X+K_2X^2+K_3X^3+\dots} \quad (14)$$

$$\frac{\bar{n}-2}{X} = \frac{K_1+2K_2X+3K_3X^2+4K_4X^3+\dots}{1+K_1X+K_2X^2+K_3X^3+\dots} \quad (15)$$

with $\lim_{X \rightarrow 0} \frac{\bar{n}-2}{X} = K_1$.

By further application of this method of calculation it is possible to find the values of higher solvation constants.

5. EXPERIMENTAL RESULTS

Small amounts of TBP were weighed in 25 ml flasks, 20 ml of hexane were added for dilution, and then adequate quantities of the $(\text{NO}_2(\text{NO}_3))_2 \cdot 6\text{H}_2\text{O}$ salt. The solution was diluted to mark by hexane. The measurements of ΔR values were carried out after 24 hours and after filtration of the solution through a paper filter. The filtration was necessary to separate crystallization water evolving on the walls of the flasks.

The results of experiments are presented in Table I. In the respective columns are given:

- 1 - the total concentration of TBP in solution
- 2 - the total concentration of uranium,
- 3 - the average value of the observed resistance change,
- 4 - the sum of the concentration of all species,
- 5 - the sum of the concentration of monomers and dimers,
- 6 - the monomer concentration,
- 7 - the values of function Λ (eq.11) calculated by

- the substitution of X values from column 6 and $\beta_2 = 1.24$ to the expression: $(\text{TBP})_{\text{tot.}} - (X + 2\beta_2 X^2)$
- 8 - the values of function B /eq.12/. calculated by substituting X and β_2 values, as above, to the expression: $\bar{E} - (X + \beta_2 X^2)$
- 9 - the average value of solvation number,
- 10 - the calculated values of the function given in eq.15.

In Fig.5 are presented the values of \bar{n} /column 9/ vs. the concentration of free, monomeric TBP.

In Fig.6, similarly, are presented the values from column 10 vs. the free TBP concentration.

Chemicals

The following reagents were used:

- n-hexane, RP ACS, Carlo Erba /M.w. 86,17; b.p. $68.7 \pm 1^\circ\text{C}/$,
n-dodecane, free of olefins, purum, Fluka AG Buchs S.G.
/M.w. 170.34; b.p. $216.3^\circ\text{C}/$,
tributyl phosphate, puriss., Fluka AG Buchs S.G.
/M.w. 266,32; b.p. $259^\circ\text{C}/$,
uranyl nitrate hexahydrate, p.a.

6. DISCUSSION

The measurements of average solvation number in the uranyl nitrate - TBP system by the VFL method supplied very interesting results. It is easily seen from column 9 of Table I and from Fig.5 that:

- /I/ the average solvation number depends on the proportion between the concentrations of solvent and the salt,
- /II/ the value of \bar{n} proceeds to a value of 2 parallelly to the saturation of TBP with uranyl nitrate.

Hence we can say the following:

/I/ The dominating and the most stable complex of uranyl nitrate with TBP in the organic phase under the variable chemical conditions is only $UO_2(NO_3)_2 \cdot 2 TBP$. This remains in full accordance with the rich literature on this subject.

/II/ The $UO_2(NO_3)_2 \cdot 2 TBP$ complex undergoes the solvation process in the presence of free TBP.

The nature of the other species, beside the disolvates, present in the solution at $X > 0$, was determined by the stepwise analysis. The application of first mathematical operation /eq.15/ has given the values of $(\bar{n}-2)/X$ function without any trend to systematic change with the monomer concentration. This means, that only the existence of the $UO_2(NO_3)_2 \cdot 3 TBP$ complex can be taken into account. Because of considerable scattering of the results in column 10, it was not possible, as is seen from Fig.6, to make extrapolation to $X = 0$ with the purpose of determining the solvation constant K_1 . On the other side, at larger concentrations of the TBP monomer the expression $(\bar{n}-2)/X$ can very differ from the solvation constant K_1 . For these reasons calculations of the values K_1 were made for each experiment.

Remembering equation /5/ we can write the equilibrium constant of solvation process as:

$$K_1 = \frac{[UN \cdot 2TBP \cdot TBP]}{[UN \cdot 2TBP][TBP]} \quad /16/$$

The proportion of the trisolvate to disolvate in the solution is:

$$\frac{[UN \cdot 2TBP \cdot TBP]}{[UN \cdot 2TBP]} = K_1 \cdot [TBP] \quad /17/$$

The sum of the concentrations of di- and trisolvate is equal to the total concentration of uranium, C_{UN} :

$$[UN \cdot 2TBP] + [UN \cdot 3TBP] = C_{UN} \quad /18/$$

If we denote $[UN \cdot 2 TBP] = y$ and $[UN \cdot 3 TBP] = C_{UN} - y$, then:

$$\frac{2y + 3(C_{UN} - y)}{C_{UN}} = \frac{A}{B} = \bar{n} \quad /19/$$

From eq./19/ we have:

$$y = C_{UN}(3 - \bar{n}) \quad /20/$$

The proportion of the trisolvate to disolvate in terms of \bar{n} is:

$$\frac{[UN \cdot 2TBP \cdot TBP]}{[UN \cdot 2TBP]} = \frac{\bar{n} - 2}{3 - \bar{n}} \quad /21/$$

From the equality of the right hand sides of equations /17/ and /21/ we receive:

$$K_1 = \frac{\bar{n} - 2}{(3 - \bar{n}) \cdot X} \quad /22/$$

where $X = [TBP]$.

The values of the $(\bar{n} - 2)/(3 - \bar{n})$ function and the values of K_1 , calculated by means of eq./22/, are given in columns 11 and 12 of Table I, respectively. By comparison of suitable figures in columns 10 and 12 it is apparent that in many experiments the use of the above method for calculating K_1 was necessary.

After rejecting the result in experiment No 20, the arithmetical mean of the value K_1 is equal to 3.7 and the mean deviation 2.0. Hence $K_1 = 3.7 \pm 2.0$.

The only case of application of the VPL method to study the actinide complexes with tributyl phosphate is the paper of Apelblat and Hornik^{18/}. Results of their experiments on the complexation of thorium nitrate by TBP in CCl₄ solutions are explained by assuming a mixture of two complexes with TBP, the disolvate and trisolvate. The solvation constant of the trisolvate is 30 at 25°. This value is much higher than our value of K₁ for uranyl nitrate in the hexane solution at 25°C.

Our results on the aggregation of TBP are in agreement with those of Petkovic^{19/}. He has found that in hexane solutions only the dimerization process of TBP takes place and that the equilibrium constant β_2 , determined by dielectric constant measurements, is equal to 2.7±0.7 at 20°C.

7. CONCLUSIONS

- a/ Osmometric measurements by the VPL method of the aggregation of TBP in hexane solutions, up to concentration 0.2 M, have indicated that the dimerization of TBP molecules takes place. The equilibrium constant β_2 of the reaction: monomer \rightleftharpoons dimer is equal to 1.24±0.08 at 25°C.
- b/ The results of application of the VPL method for studies of equilibrium in the UO₂(NO₃)₂ - TBP - hexane system has been explained by assuming that the solvation of UO₂(NO₃)₂·2 TBP complex by free TBP takes place. The trisolvates are present in equilibrium with the disolvate:

$$\text{UO}_2(\text{NO}_3)_2 \cdot 2 \text{TBP} + \text{TBP} \xrightleftharpoons{K_1} \text{UO}_2(\text{NO}_3)_2 \cdot 2 \text{TBP} \cdot \text{TBP}$$
The formation constant K₁ is equal to 3.7±2.0 at 25°C.

A c k n o w l e d g e m e n t s

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TABLE 1. The experimental data obtained and the calculated values of the functions presented in the text.

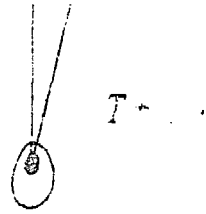
N ^o EXP.	C _{exp} [M]	C _{0H} [M]	ΔR ₀ [ohms]	E [M]	E-C _{0H} [M]	X [M]	A [M]	B [M]	R	$\frac{R-2}{X}$ [M ⁻¹]	$\frac{R-2}{3-R}$	K ₂
	1	2	3	4	5	6	7	8	9	10	11	12
1	0.150	0	30.3	0.1345	0.1315	0.1180						
2	0.150	0.01	56.6	0.1225	0.1125	0.0990	0.0287	0.0114	2.34	3.43	0.315	5.3
3	0.150	0.02	52.3	0.1142	0.0942	0.0840	0.0465	0.0215	2.25	2.97	0.333	4.0
4	0.150	0.03	49.5	0.1050	0.0750	0.0684	0.0697	0.0311	2.24	3.49	0.316	4.8
5	0.150	0.04	17.3	0.1033	0.0832	0.0555	0.0930	0.0405	2.05	0.86	0.062	0.9
6	0.150	0.05	43.0	0.0920	0.0450	0.0402	0.1058	0.0508	1.08	1.90	0.087	2.2
7	0.150	0.06	39.5	0.0855	0.0255	0.0242	0.1244	0.0206	1.05	2.07	0.063	2.1
8	0.150	0.07	78.3	0.0790	0.0090	0.00885	0.14115	0.07015	2.012	1.36	0.012	1.4
9	0.150	0.08 ^{a)}	76.2	0.0790	-0.0004							
10	0.178	0	71.4	0.1545	0.1545	0.1332						
11	0.178	0.01	87.2	0.1455	0.1355	0.1160	0.0286	0.0123	2.23	1.98	0.299	1.8
12	0.178	0.02	63.4	0.1370	0.1170	0.1020	0.0510	0.0226	2.27	2.84	0.370	3.6
13	0.178	0.03	59.3	0.1255	0.0995	0.0850	0.0714	0.0322	2.22	2.50	0.282	3.2
14	0.178	0.04	56.3	0.1225	0.0825	0.0720	0.0918	0.0429	2.14	1.32	0.183	2.2
15	0.178	0.05	52.8	0.1142	0.0642	0.0599	0.1131	0.0533	2.12	2.11	0.138	2.4
16	0.178	0.06	50.0	0.1060	0.0460	0.0435	0.1298	0.0622	2.09	2.07	0.089	2.3
17	0.178	0.07	46.9	0.1015	0.0315	0.0281	0.1450	0.0724	2.05	1.79	0.063	1.9
18	0.178	0.08	43.2	0.0935	0.0135	0.0133	0.1613	0.0800	2.05	1.75	0.092	3.9
19	0.272	0	102.8	0.2222	0.2222	0.1965						
20	0.272	0.03	39.2	0.1932	0.1632	0.1375	0.0876	0.0322	2.73	5.23	2.370	18.0
21	0.272	0.05	34.2	0.1824	0.1324	0.1138	0.1281	0.0525	2.46	3.51	0.870	5.8
22	0.272	0.07	73.4	0.1699	0.0998	0.0939	0.1636	0.0719	2.56	3.38	0.430	4.8
23	0.272	0.09	68.8	0.1450	0.0690	0.0560	0.2082	0.0891	2.34	3.07	0.510	2.1
24	0.272	0.12	65.8	0.1440	0.0548	0.0531	0.2374	0.1112	2.14	4.38	0.183	5.2
25	0.272	0.15	61.5	0.1330	0.0030	0.0028	0.2692	0.1509	2.06	2.14	0.061	2.1
26	0.272	0.15 ^{a)}	80.0	0.1300								
27	0.510	0.2	114.3	0.2485	0.0485	0.0438	0.4618	0.2027	2.25	5.44	0.390	2.9
28	0.5	0.187	119.2	0.2595	0.0925	0.0840	0.3986	0.1668	2.39	4.64	0.630	7.6
29	0.6	0.123	161.1	0.2190	0.0800	0.0780	0.3055	0.1323	2.31	3.92	0.450	5.7
30	0.332	0.1	92.3	0.1928	0.0998	0.0860	0.2315	0.1022	2.27	3.07	0.370	4.2
31	0.336	0.18	78.1	0.1692	0.0192	0.0165	0.3218	0.1523	2.11	6.88	0.123	7.5
32	0.3	0.1	78.3	0.1895	0.0605	0.0645	0.2249	0.0997	2.28	4.03	0.351	5.4
33	0.2	0.087	55.3	0.1200	0.0830	0.0500	0.1138	0.0669	4.15	3.00	0.178	3.6
34	0.1265	0.025	43.2	0.0937	0.0887	0.0525	0.0544	0.0264	2.08	0.96	0.084	1.0
35	0.1285	0.05	35.1	0.0768	0.0258	0.0250	0.1000	0.0500	2.00	0	0	0
36	0.1	0.033	30.3	0.0650	0.0320	0.0306	0.0871	0.0332	2.02	0.48	0.020	0.65
37	0.075	0.025	22.8	0.0490	0.0240	0.0230	0.0507	0.0253	2.00	0	0	0
38	0.0835	0.025	19.0	0.0408	0.0155	0.0152	0.0477	0.0250	1.91			
39	0.05	0.0166	18.3	0.0345	0.0179	0.0173	0.0320	0.0172	1.86			

^{a)} The saturation of Ca^{2+} with uranyl nitrate was observed.

Solvent



Solution



Evaporation	$N, -Q$
Condensation	$N, +Q$

$n, -q$
$N, +Q$

$$\Delta Q = 0$$

$$\Delta Q = (Q - q) \sim C_{\text{solute}}$$

$$\frac{\Delta Q}{m} \sim \Delta T \sim C_{\text{solute}}$$

$$\underline{\Delta R \sim \Delta T \sim C_{\text{solute}}}$$

- N, n - moles of solvent in unit time, ($n < N$)
- Q, q - quantities of heat in unit time, ($q < Q$)
- m - summarized mass of the drop and thermistor,
- \sim - sign of proportionality.

Fig.1. The temperature of thermistors during equilibrium between the liquid and vapour phases.

MODEL 301A VAPOUR PRESSURE OSMOMETER

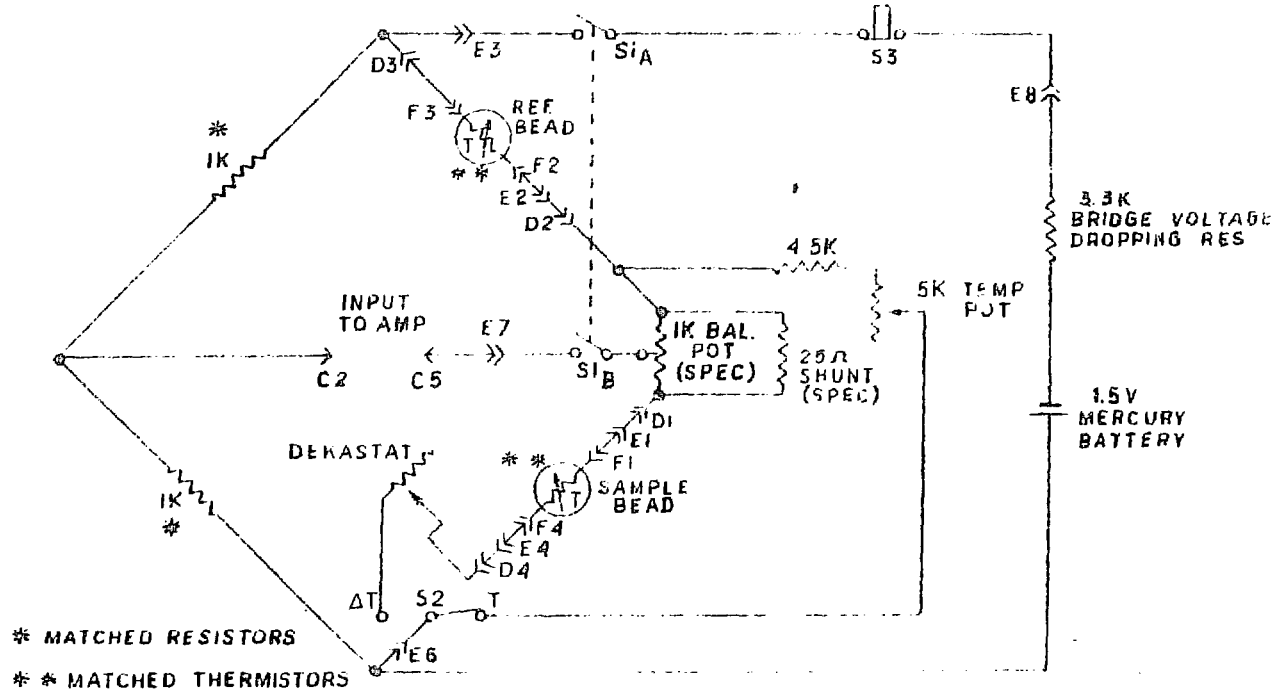


Fig.2. Thermistor bridge circuit.

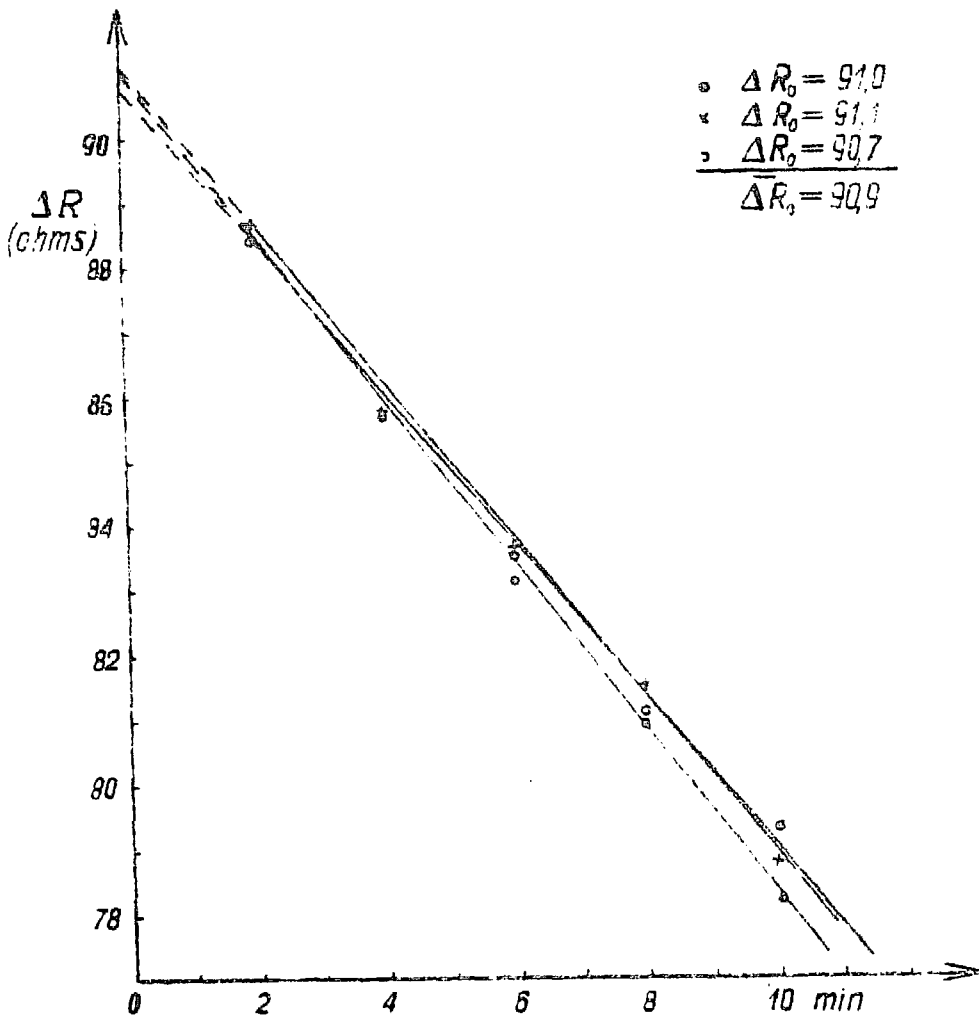


Fig.3. Determination of $\bar{\Delta R}_0$ value from ΔR data by extrapolation. /An example/.

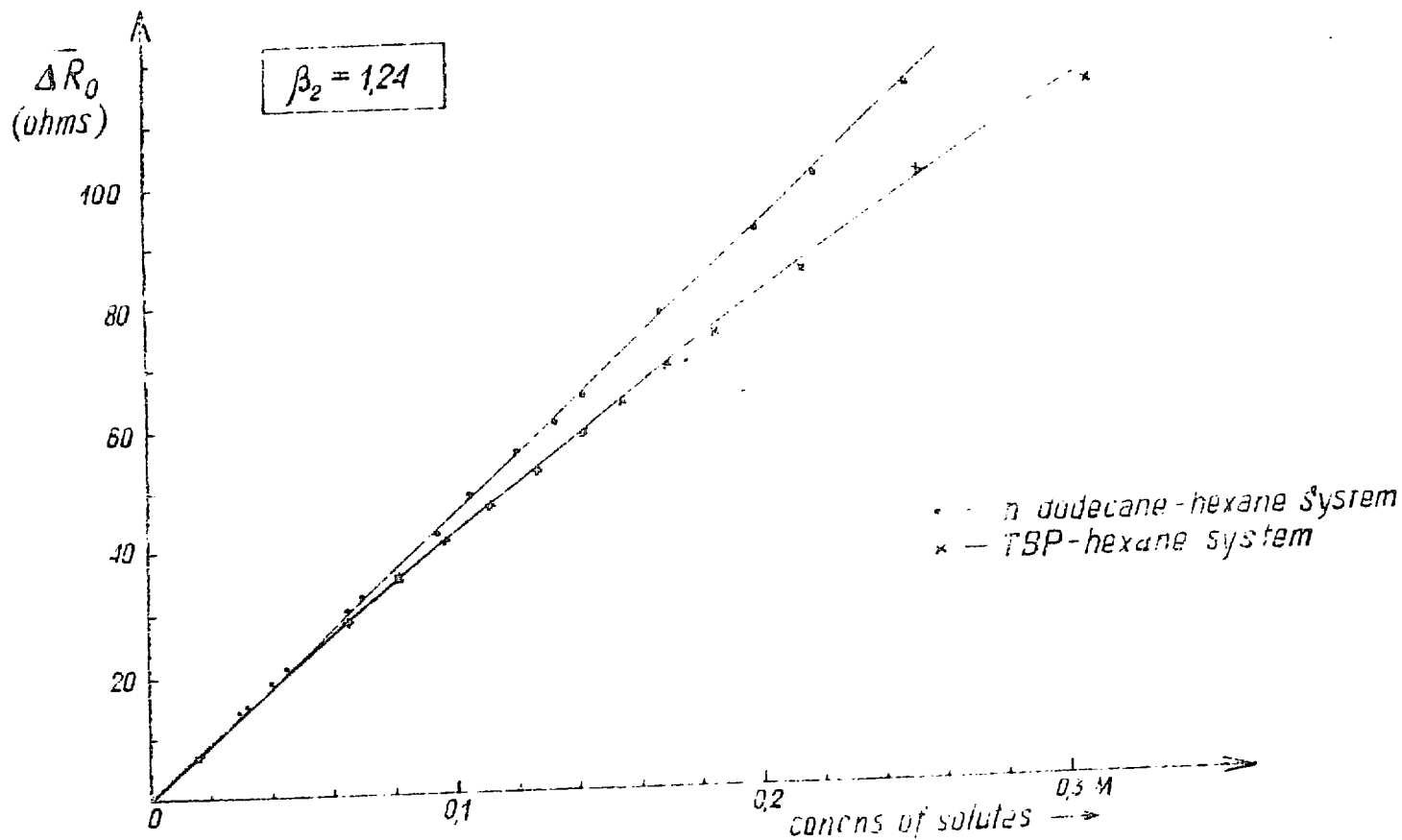


Fig.4. $\Delta \bar{R}_0$ values vs. concentration of solutes for the n-dodecane-hexane system /calibration curve/ and for the TBP - hexane system /aggregation curve/.

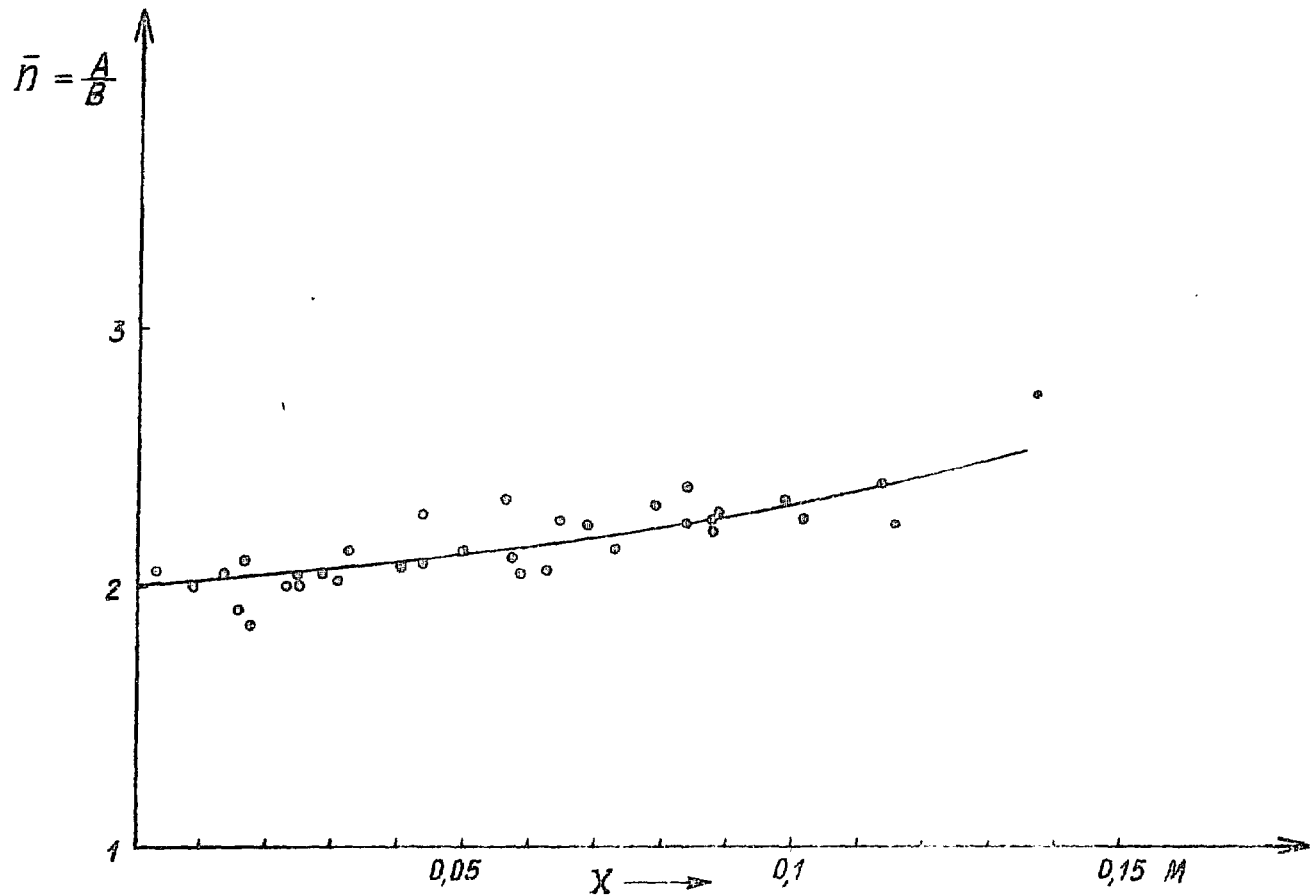


Fig.5. Dependence of the average solvation number in the $\text{UO}_2(\text{NO}_3)_2$ -TBP-hexane system on the concentration of monomeric TBP.

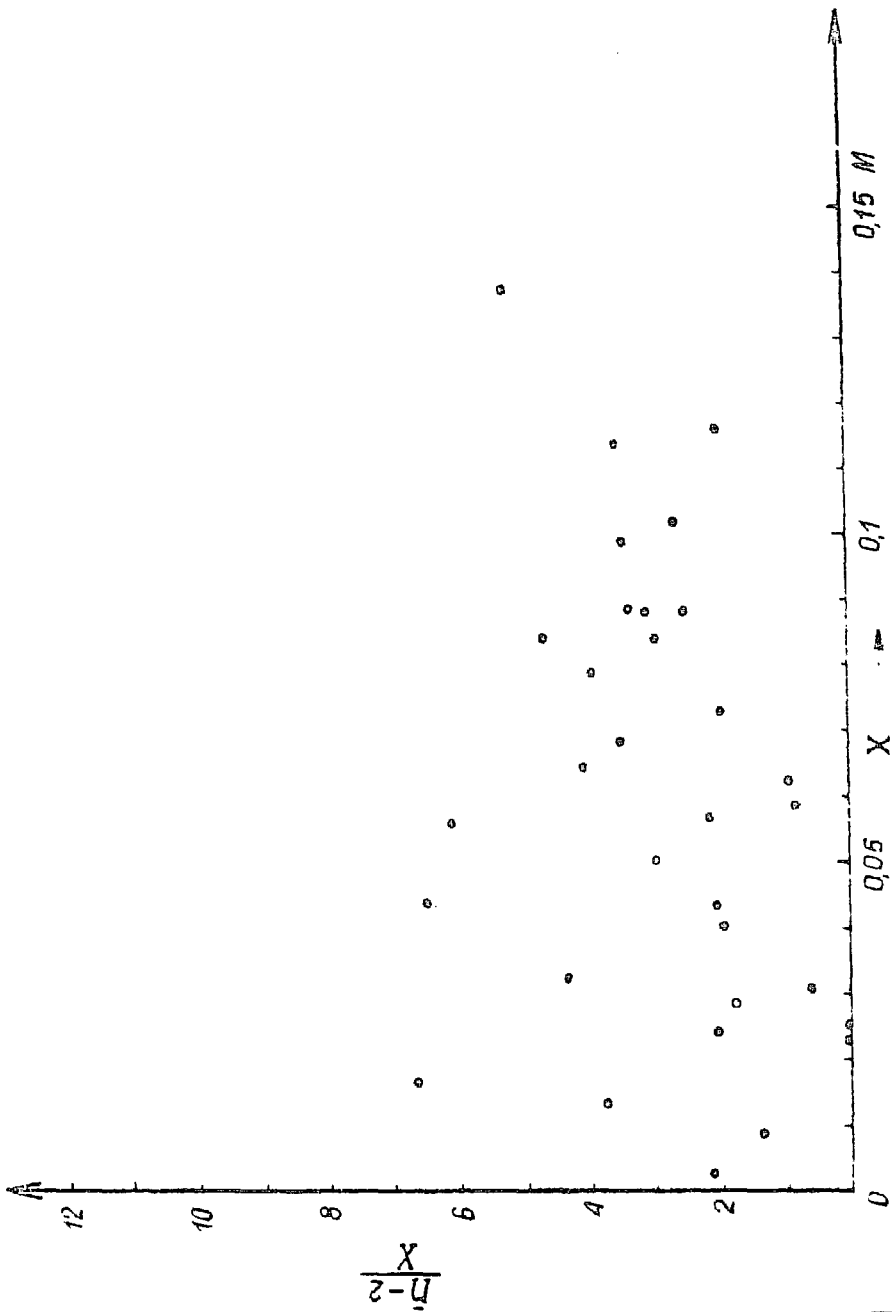


Fig. 6. Values of $(\bar{n} - 2)/X$ function for various concentrations of monomeric TBP.

