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POTENTIAL CHARACTERISTICS OF A PSEUDOLIQUID MEMBRANE ELECTRODE INCLUDING COORDINATIVELY SOLVATED $UO_2(NO_3)_2 \cdot 2TBP$ COMPLEXES

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Summary—Mechanisms of formation of electrode potential with a pseudoliquid membrane phase including uranyl nitrate complexes coordinatively solvated by tri-n-butyl phosphate were investigated. It was stated that the electrode function of these membranes could be of cationic or anionic character depending on concentration $UO_2(NO_3)_2$ in an aqueous phase. The influence of extraction and salting out on membrane phase composition and the slope of calibration curve was studied. It was shown that in the concentration range $c > 0.1M$ the electrode potential depends on value of salt distribution coefficient between aqueous and organic phases. The dependence describing the electrode function in this concentration range was derived.

Mechanism of potential formation of the electrodes including liquid or pseudoliquid membranes is explained by a few theories in the papers by Sandblom *et al.*,[1] Morf[2] and Kamo *et al.*[3] The equations given by these authors which describe the value of membrane potential, show that its formation is influenced both by ion-exchange and extraction processes. The equations describing this potential were mainly verified in the concentration range 10^{-5}–$10^{-1}M$, typical for ion-selective electrode application. Properties of these electrodes in the range of high concentrations have rarely been the subject of more detailed studies.[4,5] For this reason the role of extraction processes in the mechanisms determining electrode potential formation is not shown.

It may be supposed that in the case of well-extracted salts and using a plasticizer membrane of high extractive properties for the preparation, extraction processes causing changes of quantitative composition of the membrane surface phase will affect the membrane potential formation mechanisms.

The above extraction processes are probably a reason for non-typical behaviour of liquid electrodes of uranyl function reported by many authors[6–9] but not yet fully explained. To explain the influence of extraction and ion exchange processes on the membrane potential formation mechanism of uranyl function membrane, properties of electrodes whose membrane phase was constituted by a typical extraction system $UO_2(NO_3)_2$–H_2O–TBP without an ion-exchanger were studied. In this system the mechanism conditioning membrane potential formation is very clear which makes interpretation of the results easier.

THEORY

Neutral extractants possessing electronegative groups capable of replacing water in the first coordination sphere of cation [10] form readily extractable complexes coordinatively solvated with ionic compounds. The most commonly used extractant of this group is tri-n-butyl phosphate (TBP).

Extraction of $UO_2(NO_3)_2$ by means of TBP[11] takes places according to the reaction:

$$UO^{2+}_{2(w)} + 2NO^-_{3(w)} + 2TBP_{(o)} \rightleftarrows UO_2(NO_3)_2 \,.\, 2TBP_{(o)}. \quad (1)$$

The equilibrium constant of this equation can be determined from the dependence:

$$K_u = \frac{[UO_2(NO_3)_2 \,.\, 2TBP]_o}{[UO_2^{2+}]_{(w)}[NO_3^-]^2_{(w)}[TBP]^2_{(o)}} \cdot \frac{\gamma_s}{\gamma^3_\pm \gamma^2_{TBP}}, \quad (2)$$

where $\gamma_\pm$ is the mean activity coefficient[18].

In practice to estimate the extraction efficiency the distribution coefficient of the substance between the aqueous and organic phases is often used:

$$D = \frac{\Sigma[\mathrm{A}]_o}{\Sigma[\mathrm{A}]_w} = \frac{c_o}{c_w}, \qquad (3)$$

where $\Sigma[\mathrm{A}]$ is total the concentration of substance A in the organic and aqueous solutions.

In the case of extraction of the substance into a liquid or pseudoliquid membrane phase, assuming the value of solvate activity coefficient in the membrane phase to be constant, it can be written:

$$D = \frac{c_o}{a_w} \cdot \text{const.}, \qquad (4)$$

where c_o is the solvate concentration in the surface layer of phase membrane and a_w is the salt activity in the aqueous phase.

The interfacial potential of the system: liquid (pseudoliquid) membrane-aqueous solution is described by the equation:

$$E = E_{st} + \frac{RT}{nF} \ln \frac{a_w}{a_o}, \qquad (5)$$

where a_w is the activity of complexes in the aqueous phase and a_o is the activity of complexes in the organic phase.

For aqueous solutions of $UO_2(NO_3)_2$, concentrations $c < 0.1M$, in which solvate extraction into a membrane phase has little effect (composition of membrane phase remain almost unchanged) and the anion influence is insignificant, the electrode potential is determined by the equation:

$$E = E_{st} + \frac{RT}{2F} \ln a_{UO_{2(w)}^{2+}}. \qquad (6)$$

For higher concentrations, $c > 0.1M$, the extraction process of uranyl nitrate into an organic phase is determined by the anion concentrations[12,13] in the aqueous phase. Thus equation (5) can be written:

$$E = E_{st} + \frac{RT}{F} \ln \frac{a_o}{a_w}. \qquad (7)$$

Due to an advantageous equilibrium constant of reaction (1) $K_u = 2.65 \,.\, 10^3$, the dependence between the concentration of uranyl and nitrate ions given in equation 2 means a 10-fold change of UO_2^{2+} activity causes a 10^2-fold change of nitrate ion activity. Taking dependences (4) and (7) into account it can be written:

$$E = E'_{st} + 2\frac{RT}{F} \ln D \text{ or } \Delta E = 2\frac{RT}{F} \ln D. \qquad (8)$$

It follows from the dependences that in the concentration range $c > 0.1M$, the electrode potential in the first approximation depends on the distribution coefficient D of uranyl nitrate. The slope of electrode characteristics is $2(-2.3026RT/F) = -0.11632$ V (20°C).

It can be said that the electrode potential and direction factor of the calibration curve depend on the quantitative composition of the complexes extraced from the organic phases. In the cases of using a salting out agent of high concentrations (1.0–3.0M), when the complex $Na[UO_2(NO_3)_3] \cdot 2TBP$ can be formed, the slope of the electrode characteristics may be $3(-2.3026RT/F) = -0.17448$ V.

The above dependences were experimentally verified and the results obtained are presented in this paper.

EXPERIMENTAL

Preparation of electrodes

Pseudoliquid membranes including coordinatively solvated complexes constituting a membrane phase of the studied electrodes were made by gelation of a suitable mixture at 373–393 K including 30% polyvinyl chloride (PVC) by weight and 70% solution of $UO_2(NO_3)_2 \cdot 2TBP$ complex by weight in TBP(organic phase). Concentrations of $UO_2(NO_3)_2 \cdot 2TBP$ in the organic phase of electrodes were El.1, $0.0M$; El.2, $0.1M$; El.3, $0.3M$; El.4, $0.5M$; El.5, $0.7M$; El.6, $1.0M$. The method of membrane phase preparation was given in earlier papers.[14,15] The organic solutions of complexes $UO_2(NO_3)_2 \,.\, 2TBP$ of concentrations 0.1, 0.3, 0.5 and 0.7M were made by dilution of $1.0M$ solution of $UO_2(NO_3)_2 \,.\, 2TBP$ obtained by dissolution of a suitable, weighed amount of $UO_2(NO_3)_2 \,.\, 6H_2O$ in TBP.

Solutions

The aqueous solutions of uranyl nitrate of concentrations 10^{-5}–$1.0M$ were made by dilution of $1.0M$ of stock solution. Redistilled water was used in dilution.

The solutions were kept in dark at 277 K.

Measurements and electromotive force

Electromotive force of the studied cells (electrode with a pseudoliquid membrane, the reference electrode was Orion 90-02 with Orion solution 90-00-01 of composition: $1.70M$ $KNO_3 + 0.64M$ $KCl + 0.06M$ $NaCl + 1.0$ ml/l. of 37% HCHO) was measured by means of a

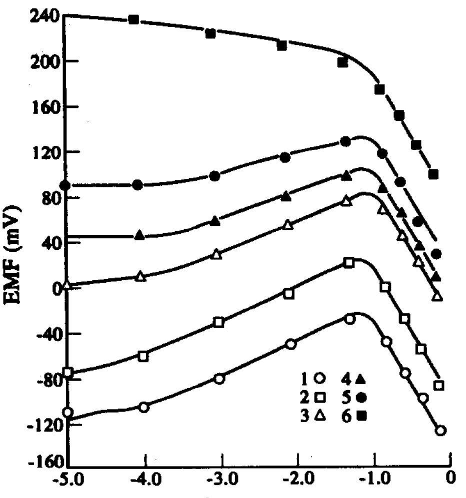

Fig. 1. Calibration curves of the electrodes in the solutions $UO_2(NO_3)_2$, pH = 2.75. (Number of curves correspond to numbers of electrodes given in the experimental part.)

multivoltmeter–pH-meter Radiometer PHM 85 Precision pH Meter.

Electromotive force changes were registered by a BAS Recorder MF 8051F.

RESULTS AND DISCUSSION

The above assumptions concerning potential formation in membranes including coordinatively solvated $UO_2(NO_3)_2 \cdot 2TBP$ complexes were verified by studying the properties of electrodes with pseudoliquid membranes including these complexes. The calibration curves of the tested electrodes are shown in Figs 1 and 2.

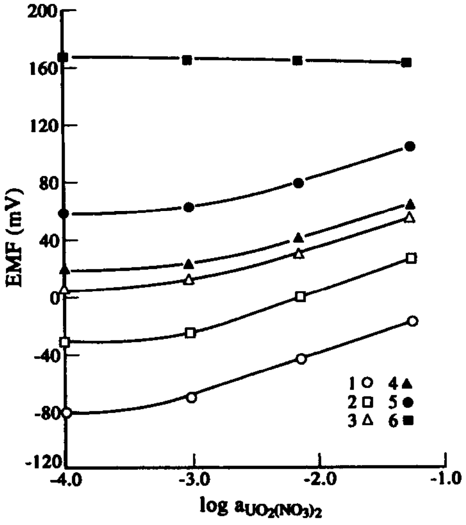

Fig. 2. Calibration curves of the electrodes in the solutions $UO_2(NO_3)_2$, pH 4.32. (Numbers of curves correspond to numbers of electrodes given in the experimental part.)

Table 1. Parameters characterizing electrodes of various solvate contents in uranyl nitrate solutions (pH 2.75)

Electrode number	mV/pa		$E_{st}(mV)$		L.D. pa.
	I range	II range	I range	II range	
1	+29	−116	+8	−142	4.4
2	+29	−116	+56	−107	4.6
3	+27	−116	+118	−27	4.0
4	+22	−116	+123	−16	3.8
5	+17	−116	+148	+9	3.6
6	−16	−116	+165	+79	4.0

Some parameters characterizing the tested electrodes are presented in Tables 1 and 2.

It follows from Fig. 1 that the electrode calibration curves are characterized by a non-typical course. They consist of two parts: in solutions $10^{-5} < c_{UO_2(NO_3)_2} < 0.1M$ (concentration range I) curves 1–5 were characteristic for electrodes of cation function with the characteristics slope decreasing with the increase of complex concentration in the membrane phase. In solutions of concentration $c \approx 0.1M$ all curves changed direction rapidly. In solutions $c_{UO_2(NO_3)_2} > 0.1M$ (concentration range II) the electrodes were characterized by anion function slope-116 mV/pa$_{UO_2(NO_3)_2}$.

The calibration curves obtained in $UO_2(NO_3)_2$ solutions of pH 4.32 were similar to those obtained in concentration ranges of the solutions of pH 2.75. A distinct shift of limit of detection (LD) towards higher concentrations of uranyl nitrate can be seen. At this pH in solutions of concentrations $c_{UO_2(NO_3)_2} > 0.1M$, precipitation of $UO_2(OH)_2$ took place.

Decrease of the electrode characteristics slope in the concentration range I in the solutions of pH 2.75 with an increase of solvate concentration in the membrane phase resulted from the establishment of extraction and ion-exchanging equilibria in which NO_3^- ions start to play a decisive role. In solutions of pH 4.32 in which NO_3^- ion concentration was smaller this influence was less visible.

Table 2. Parameters characterizing electrodes of various solvate contents in uranyl nitrate solutions (pH 4.32)

Electrode number	mV/pa	E_{st} (mV)	L.D. pa.
1	+29	−10	3.6
2	+29	+37	3.4
3	+28	+58	3.0
4	+27	+65	3.0
5	+27	+110	2.7
6	−4	+164	

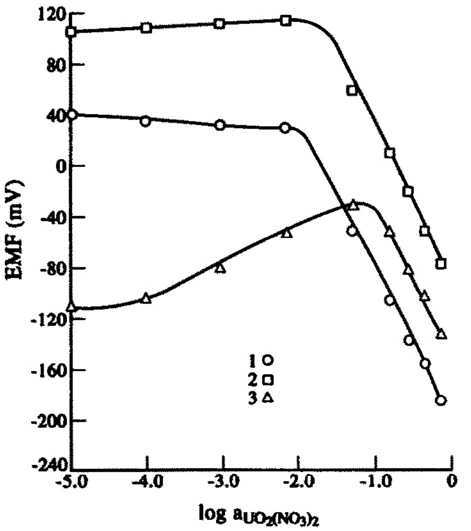

Fig. 3. Comparison of equilibrium potential of "free interface" $UO_2(NO_3)_{2(w)} \| UO_2(NO_3)_2 \cdot 2TBP_{(o)}$ with the potential of electrodes with "immobilized" organic phase. Curve: 1—free interface; 2—organic phase "suspended" in porous teflon (TBP without solvate $UO_2(NO_3)_2 \cdot 2TBP$); 3—electrode with a pseudoliquid membrane phase El.1.

It follows from the course of calibration curves presented in Fig. 1 that the change of mechanisms responsible for membrane potential formation takes place in solutions of concentration $c_{UO_2(NO_3)_2} \approx 0.1M$. In solutions of $c_{UO_2(NO_3)_2} > 0.1M$ the extraction process of uranyl nitrate into the electrode membrane phase had a decisive effect on the membrane potential value. To verify this hypothesis the potential was measured at the interface $a_{UO_2(NO_3)_2(w)} \| a_{UO_2(NO_3)_2 \cdot 2TBP_{(o)}}$. The $UO_2(NO_3)_2$ aqueous and organic solutions of equilibrium concentrations were prepared according to the method of Davis and Mrochek.[16] The reference electrode was a silver wire covered with AgCl and immersed in TBP saturated with water (Fig. 3).

The obtained dependence, EMF = $f(a_{UO_2(NO_3)_{2(w)}})$, is shown by curve 1 in Fig. 3. For comparison Fig. 3 also gives the dependence EMF $= f(a_{UO_2(NO_3)_{2(w)}})$ for the electrodes with an organic phase immobilized in a matrix of porous teflon as well as for the electrode with a pseudoliquid membrane phase. It follows from Fig. 3 that in concentration range II, EMF $= f(a_{UO_2(NO_3)_{2(w)}})$ was very similar for all electrodes tested. The curves had the same slope (-116.3 mV/pa) but differ only in standard potential.

In concentration range I, the free interface as well as the organic phase 'suspended' in porous teflon did not show the dependence EMF = $f(a_{UO_2(NO_3)_{2(w)}})$. The electrode potential did not depend on aqueous phase activity, owing to the fact that 'potential creating centres' in the organic phase are mobile. With increasing concentration of $UO_2(NO_3)_2 \cdot 2TBP$ in the organic phase, density and viscosity of the phase increased and mobility of 'active centres' decreased as a result of which the electrode function developed in concentration range II.

It follows from equation (8) that the potential of the electrodes studied depends on the partition coefficient of uranyl nitrate between the aqueous and organic phases. The dependence was checked by determination of distribution coefficient values from the extraction experimental data, calculation of ΔE from equation (8) and plotting the dependence $\Delta E = f(a_{UO_2(NO_3)_{2(w)}})$. The function was compared with the calibration curves obtained in solutions of $UO_2(NO_3)_2$ of $c > 0.1M$. D values were determined from equation (4) based on the values gives in Ref. 16. The obtained results are presented in Table 3. The values of $\Delta e = f(a_{UO_2(NO_3)_{2(w)}})$ and the calibration curve El.1 as $\Delta E = E - E_{st}$ on $UO_2(NO_3)_2$ activity in the aqueous phase are given in Fig. 4. The curve obtained from equation (8) is characterized by the slope equal to -110 mV/p$a_{UO_2(NO_3)_2}$ which constitutes 95% of the theoretical characteristics slope value.

The potential, E_{st}, of the curve calculated from equation (8) was shifted by 20 mV towards

Table 3. Values of distribution coefficients $UO_2(NO_3)_2$ and corresponding ΔE values

$c_{UO_2(NO_3)_{2(w)}}$ (M)	0.3	0.5	0.7	1.0	1.3
$\gamma_{\pm}$	0.512	0.530	0.610	0.730	1.010
$a_{UO_2(NO_3)_{2(w)}}$	0.154	0.265	0.427	0.730	1.313
$c_{UO_2(NO_3)_{2(o)}}$	0.985	1.310	1.370	1.470	1.530
$D = c_o/a_w$	6.41	4.94	3.21	2.01	1.16
$\lg D$	0.8070	0.6940	0.5063	0.3039	0.0664
$\Delta E = 116.3 \lg D$ (mV)	93.8	80.7	58.8	35.3	7.7

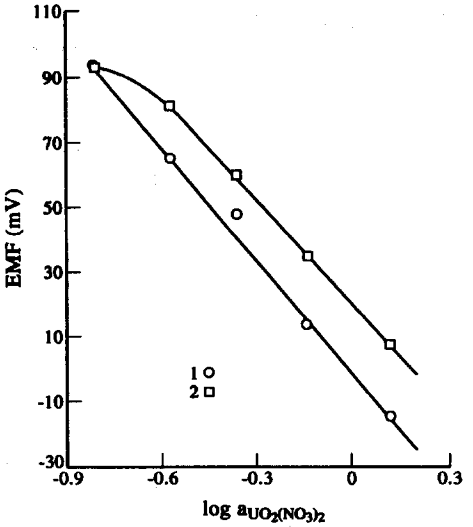

Fig. 4. Dependence of membrane potential calculated from equation "8" and determined experimentally on $UO_2(NO_3)_{2(w)}$ activity. 1—experimental data; 2—data calculated from equation "8".

positive values compared with the potential determined experimentally. Physicochemical and extraction properties of a pseudoliquid membrane phase cause the values of the partition coefficient proper for this phase to differ from the D values determined for the liquid phase which accounts for the discrepancies. The values of partition coefficients determined from the electrode calibration curves are given in Table 4.

The smaller D_{pot} values are due to the decrease in TBP concentration in the surface layer of the pseudoliquid membrane phase and differences in the physicochemical properties of the membrane surface and the interior. The coefficient $W = D_{ext}/D_{pot}$ allows for the rapid determination of D_{ext} values from potentiometric data.

Further evidence for dependence of the electrode potential in the concentration range $c_{UO_2(NO_3)_{2(w)}} > 0.1M$ on the distribution coefficient value D_{ext} and composition of solvate in the surface layer of pseudoliquid membrane phase is provided by potentiometric data characterizing the salting out effect. The results of electrode potential measurements in mixed solutions $UO_2(NO_3)_2 + NaNO_3$ in which $c_{UO_2(NO_3)_2} =$ const., but $NaNO_3$ is changed are shown in Fig. 5.

The slope of electrode characteristics for the $0.05M$ $UO_2(NO_3)_2 + NaNO_3$ solutions was -116.32 mV/pa_{NaNO_3}. From the curves the distribution coefficient D_{ext} was not constant which was caused by the change of quantitative composition of membrane phase surface layer. The negative value of the characteristic slope indicates the dependence of electrode potential on NO_3^- ion activity. In the case of $0.3M UO_2(NO_3)_2 + NaNO_3$ solutions the characteristic slope was $3(-58.16)$ mV/$pa_{NO_3^-}$. In this case the value of the characteristics slope points to saturation of a membrane phase surface layer by the solvate of composition $Na[UO_2(NO_3)_3) \cdot 2TBP$.[17]

CONCLUSIONS

The studies show that the potential of pseudoliquid membrane including complexes solvated coordinately depends on ion-exchange and extraction processes occurring in a given membrane system. These processes take place simultaneously and domination of one of them depends mainly on uranyl nitrate concentration.

In solutions of $c < 0.1$M concentrations in which transfer of mass into a pseudoliquid

Table 4. Comparison of D values calculated from extraction and potentiometric data

$c_{UO_2(NO_3)_{2(w)}}$ (M)	D_{pot}	D_{xt}	$W = \frac{D_{ext}}{D_{pot}}$
0.3	6.43	6.41	0.997
0.5	3.62	4.94	1.364
0.7	2.25	3.2	1.422
1.0	1.35	2.01	1.488
1.3	0.75	1.16	1.546

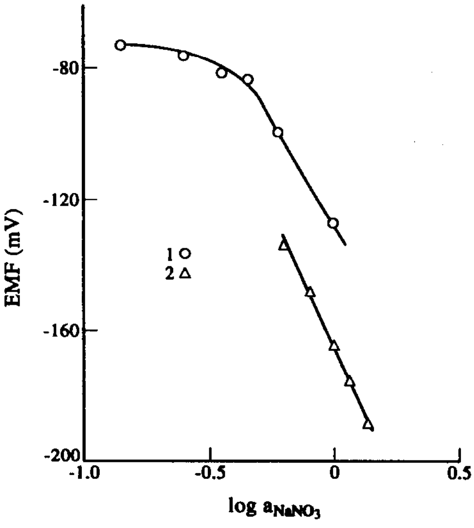

Fig. 5. Influence of salting out agent on potential of electrodes with a pseudoliquid membrane phase. El.1. Curve 1—aqueous solution composition $0.05M$ $UO_2(NO_3)_2 + NaNO_3$; Curve 2—aqueous solution composition $0.03M$ $UO_2(NO_3)_2 + NaNO_3$. Curves were plotted as $EMF = f(pa_{NaNO_3})$.

membrane phase by extraction is slight, ion-exchange processes are predominant. The electrode potential is determined by equation (6).

In the aqueous solutions of concentrations $c > 0.1M$, development of electrode function depends on extraction properties of the pseudoliquid membrane phase and the value of the reaction equilibrium constant causing formation of coordinatively solvated complexes in the organic phase. In such a case the electrode function is dependent on concentration of anions in the aqueous phase through the reaction equilibrium constant. It is also dependent on the value of distribution coefficient of the extracted compound and quantitative composition of complexes in a membrane phase. The electrode potential is determined from equation (8). The application of a pseudoliquid membrane of polyvinyl chloride plasticized with tri-n-butyl phosphate enabled us to explain the mechanism influencing the course of the uranyl nitrate extraction process in the system.

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