Pergamon

Talanta, Vol. 41, No. 2, pp. 295–299, 1994
Copyright © 1994 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0039-9140/94 \$6.00 + 0.00

POTENTIOMETRIC PROPERTIES OF MEMBRANE ELECTRODES WITH AN IMMOBILIZED AQUEOUS PHASE IN THE SOLUTIONS OF COMPLEXES COORDINATIVELY SOLVATED BY TRI-*n*-BUTYL PHOSPHATE. (COMPLEXES: $UO_2(NO_3)_2 \cdot 2TBP$, $Co(NO_3)_2 \cdot 3TBP$, $Ca(NO_3)_2 \cdot 6H_2O \cdot 2TBP$)

RYSZARD DUMKIEWICZ
Faculty of Chemistry, M. Curie-Skłodowska University, 20031 Lublin, Poland

(*Received* 31 *March* 1993. *Revised* 7 *June* 1993. *Accepted* 10 *August* 1993)

Summary—The paper presents the results of studies on potential dependent properties of typical extraction systems: $UO_2(NO_3)_2$–H_2O–TBP, $Ca(NO_3)_2$–H_2O–TBP, $Co(NO_3)_2$–H_2O–TBP (TBP–tri-*n*-butyl phosphate) treated as membrane systems with an immobilized aqueous phase. It was shown that the processes influencing on the membrane potential in the studied system depended mainly on extraction constants. The electrode functions of the systems depended on concentration of salts in the immobilized aqueous phase and concentration of solvate in the organic phase. It was found that the activity coefficients could be determined from the dependence describing the electrode potential in the concentrated solvate solutions.

The mechanism of formation of ion-selective electrodes with a liquid membrane phase potential depends on ion-exchange and extraction processes between aqueous and organic phases.[1,2] In typical ion-selective electrodes the liquid (or pseudoliquid) organic phase is immobilized but the aqueous one mobile.

The potential difference at the interface of two immiscible solutions[3–6] is described by the relation:

$$\Delta\phi = \frac{RT}{zF} \ln \frac{a_j(1)}{a_j(2)} \qquad (1)$$

where z is the charge of ions; $a_j(1)$ and $a_j(2)$ are the activities of ions in solutions 1 and 2.

After making assumptions[2] about the influence of pressure, temperature, activity, mobility of species in both solutions, the condition of ion-exchange centre immobilization in the organic phase and establishment of thermodynamic equilibrium at the interface, the membrane potential in the case of interfering ion $a_k(1)$ occurrence is described by the relation:

$$\Delta\phi = \frac{RT}{zF} \ln \frac{a_j(1) + K^{\text{pot}}_{j,k} a_k(1)}{a_j(2)} \qquad (2)$$

The ion-selective electrode potential is determined by the Eisenman–Nikolski equation:

$$E = E_{\text{st}} \pm \frac{RT}{zF} \ln [a_j(1) + K^{\text{pot}}_{j,k} a_k(1)] \qquad (3)$$

Assuming that interfering ions are absent in the solution dependence (3) is as follows:

$$E = E_{\text{st}} \pm \frac{RT}{zF} \ln a_j(1) \qquad (4)$$

in the author's opinion dependence (4) can be used to determine the electrode potential with an immobilized aqueous phase.

While studying the mechanism of electrode function formation of pseudoliquid membrane including $UO_2(NO_3)_2 \cdot 2TBP$ complexes coordinatively solvated, it was stated that inversion of the typical membrane system, *i.e.* immobilization of the aqueous phase and leaving the organic phase as a mobile one leads to preparation of electrodes characterized by dependence of potential on activity (concentration) of the component in the organic phase. The comparative analysis of electrode function of the electrodes with the immobilized organic phase and corresponding electrodes with the immobilized aqueous phase gives more reliable description of processes influencing potential formation at the interface.

The paper presents the results of studies on potential creating properties of the following typical extraction systems: $UO_2(NO_3)_2$–H_2O–TBP, $Ca(NO_3)_2$–H_2O–TBP, $Co(NO_3)_2$–H_2O–TBP treated as membrane systems with the immobilized aqueous phase.

EXPERIMENTAL

Construction of the electrode with the immobilized membrane aqueous phase

The membrane aqueous phase was immobilized in gel prepared from soluble starch. A mixture consisting of 2.5 g soluble starch (POCh—Gliwice) and 5.0 g H_2O or 5.0 g aqueous solution of salt of desired concentration (immobilized membrane aqueous phase—further P_m). The mixtures prepared in this way were heated almost up to boiling point (95°C) and used for filling, *e.g.* syringes (2 ml). The reference electrode Ag/AgCl in direct contact with P_m was fixed into the syringe piston. The electrode could be used when gel was cooled. This construction enables regeneration of membrane active surface by squeezing out of gel. The reference electrode potential stability results from stability of membrane phase quantitative composition.

Solutions

Solutions of $UO_2(NO_3)_2 . 2TBP$, $Ca(NO_3)_2 . 6H_2O$ 2TBP, $Co(NO_3)_2 . 3TBP$ were prepared by dilution of 1.0*M* stock solution obtained by dissolution of weighed amount of salt in TBP. To prepare organic solutions water, saturated TBP was used; for aqueous solutions TBP saturated redistilled water was used. Uranyl nitrate solutions were protected from light.

EMF measurement

The electrode potential with an immobilized membrane aqueous phase was measured with respect to the reference electrode which was a silver wire covered with AgCl and immersed in water saturated with TBP. The electrode was connected with the studied solution by a salt bridge. To measure EMF a PHM-85 Radiometer was used. The mixtures were stirred during measurements.

RESULTS

The characteristic of electrodes containing $UO_2(NO_3)_2$ in P_m

The electrode calibration curves in the solutions including uranyl nitrate solvate were shown in Fig. 1. The parameters characteristic for the studied electrodes are given in Table 1.

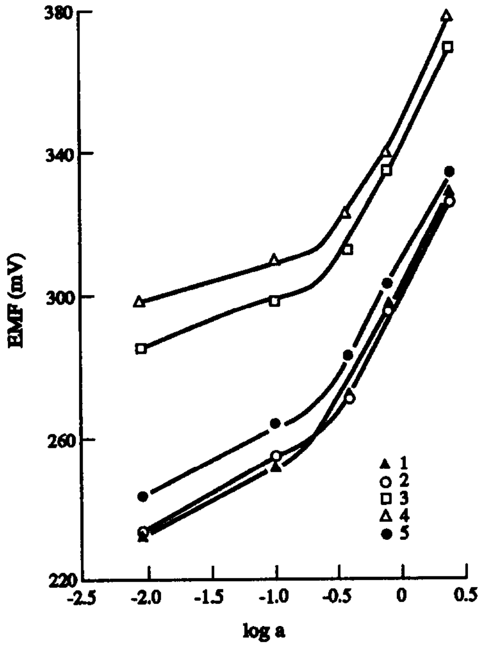

Fig. 1. Calibration curves of electrodes in $UO_2(NO_3)_2 . 2TBP$ solutions. Concentrations of $UO_2(NO_3)_2$ in electrode membrane phases: (1) 0.0*M*; (2) 0.01*M*; (3) 0.25*M*; (4) 0.5*M*; (5) 1.0*M*.

The dependence of activity coefficient of $UO_2(NO_3)_2 . 2TBP$ complex (UN) on its concentration in TBP solutions determined from the data published in the paper by Davis[3] is presented in Fig. 2.

Two segments having different slope values can be seen on calibration curves of the tested electrodes differing in salt concentration in P_m. In concentration range $I (a_{UN} > 0.2M)$ electrodes show a cationic function slope varies in the interval $10 \text{ mV/pa}_{UN} < S < 19 \text{ mV/pa}_{UN}$. In concentration range II $(a_{UN} > 0.2M)$ the slope is stable, $s = +59 \text{ mV/pa}_{UN}$. The time of electrode potential response in the solvate solutions stirred mechanically is ~6 min.

Table 1. Parameters characterizing the electrodes with immobilized solutions of $UO_2(NO_3)_2$. Quantitative composition of MP—see Fig. 1

No.	mV/*pa*		E_{st} (*mV*)	
electrode	I range	II range	I range	II range
1	18	59	269	300
2	19	59	273	297
3	13	59	311	339
4	10	54	318	345
5	18	59	280	308

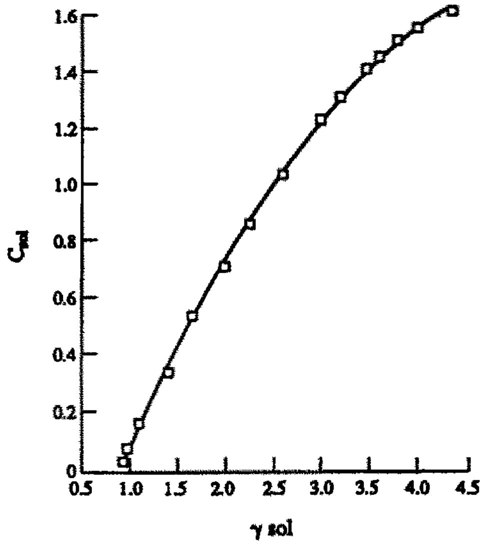

Fig. 2. Dependence of solvate activity coefficients (γ_s) on its concentration (c_{sol}) in pure TBP solutions.

The characteristic of electrodes with $Ca(NO_3)_2$ in P_m

The calibration curves in the solvate solutions $Ca(NO_3)_2 . 6H_2O . 2TBP$ (further—Ca(TBP)) are shown in Fig. 3.

It follows from the diagram that the obtained calibration curves have different slopes dependent both on concentration of the solvate in the organic phase and that of $Ca(NO_3)_2$ in the immobilized aqueous phase. In concentration range *I* ($c_{\mathrm{Ca(TBP)}} < 0.3M$) the slope of electrode response depends on concentration of salt in P_m. In changes the sign from positive (cationic function) for the electrodes of small salt concentration in P_m into negative (anionic function) for El.4 in which the concentration of $Ca(NO_3)_2$ in P_m is 1.0*M*. The slopes in this concentration range are: El.1. $s = +12$ mV/$pa_{\mathrm{Ca(TBP)}}$; El.2. $s = +11$ mV/$pc_{\mathrm{Ca(TBP)}}$; El.3. $s = +0.5$ mV/$pc_{\mathrm{Ca(TBP)}}$; El.4. $s = -6$ mV/$pc_{\mathrm{Ca(TBP)}}$.

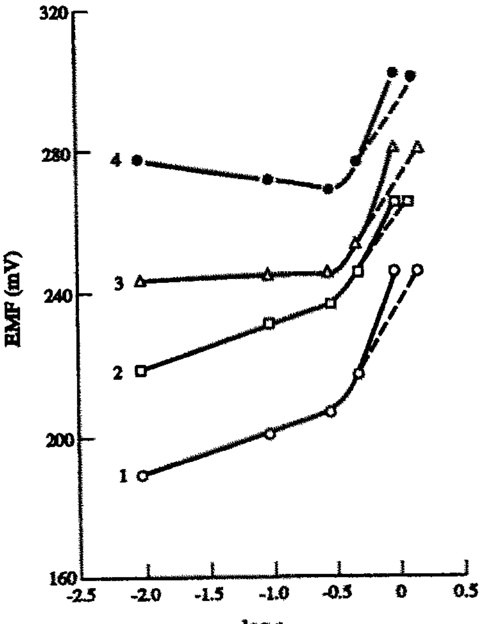

Fig. 3. Calibration curves of electrodes in $Ca(NO_3)_2 . 6H_2O . 2TBP$ solutions. Concentrations of $Ca(NO_3)_2$ in electrode membrane phases. (1) 0.0*M*; (2) 0.01*M*; (3) 0.3*M*; (4) 1.0*M*. --- Hypothetical activity of solvate.

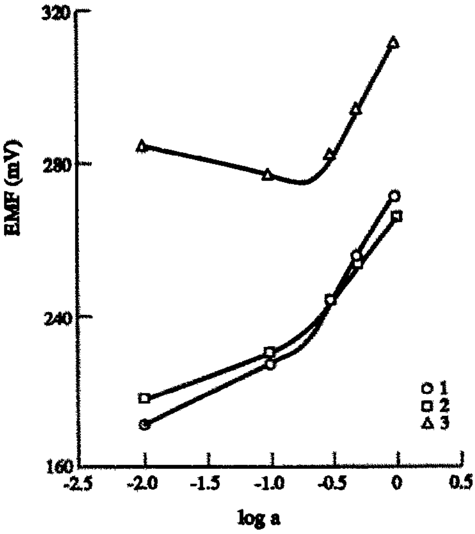

Fig. 4. Calibration curves of electrodes in $Co(NO_3)_2 . 3TBP$ solutions. Concentrations of $Co(NO_3)_2$ in electrode membrane phases. (1) 0.0*M*; (2) 0.01*M*; (3) 1.0*M*.

In concentration range II ($c_{\mathrm{Ca(TBP)}} > 0.3M$) all electrodes possess cationic function. Extrapolated calibration curves of characteristics slope $s = +59$ mV/$pa_{\mathrm{Ca(TBP)}}$, taking into account the calculated activity of solvate in its 1.0*M* solutions in TBP, are marked with broken lines in the diagram.

The characteristic of electrodes including $Co(NO_3)_2$ in P_m

The calibration curves of electrodes in the solutions including cobalt nitrate solvate are shown in Fig. 4. The analytical parameters of the tested electrodes are shown in Table 2.

The electrode calibration curves consist of two segments of different slopes. The change of direction takes place at solvate concentration $Co(NO_3)_2 . 3$ TBP (further—Co(TBP)) $c_{\mathrm{Co(TBP)}} \approx 0.2M$. In the solutions of concentration $c_{\mathrm{Co(TBP)}} < 0.2M$ with the increase of concentration of $Co(NO_3)_2$ in P_m the cationic plot passes into the anionic one for El.3. Slope of characteristics in concentration range II ($C_{Co(TBP)} > 0.2M$) is $s = +57$ mV/$pc_{Co(TBP)}$. The course of characteristics for the tested electrodes is the same as in the previously discussed systems.

The above presented courses of electrode functions show that extraction and re-extraction processes cause potential creation in the studied system depending on concentration of salts in the immobilized aqueous phases. In the case of readily extractable salts into TBP phase, *e.g.* $UO_2(NO_3)_2$ $K_{ext} = 2.23 \times 10^3$,[7] potential creation is dependent re-extraction process. In the studied range of salt concentration in P_m all electrodes are characterized by cationic function both in the first and second concentration ranges of solvate in the organic phase (see Fig. 1). It follows that potential formation in both concentration ranges solvate is due to the same mechanism, *i.e.* re-extraction of ions UN_2^{2+} in concentration range I but in concentration range II to re-extraction or $UO_2NO_3^+$ ions.

In the case of poorly extractable salts of not very good useful extraction constants, *e.g.* $Ca(NO_3)_2$ $K_{ext} = 0.229$[8] and $Co(NO_3)_2$ $K_{ext} = 0.17$[9] the character of electrode function depends on salt concentration in P_m. In concentration range I of cobalt and calcium solvates in the organic phase as well as in the case of low concentration of $Ca(NO_3)_2$ and $Co(NO_3)_2$ in P_m, potential formation depends on re-extraction of the complex into P_m and slopes of characteristic are of cationic character. If salt concentration in P_m is high $c = 1.0M$ in both cases the electrode function is of anionic character which indicates extraction of the salt into the organic phase. (See curves in Figs 3 and 4.) In concentration range II of solvates in the organic phase in both cases the electrode function is of cationic character which points to re-extraction of the salt into P_m.

Solvation complexes of uranyl, calcium and cobalt nitrates with TBP can be slightly dissociated in the organic phase which is shown in the paper by Healy.[9] Solvate complexes and resulting from them solvated ions, ion pairs and water dissociation products can exist in its phase.

Table 2. Parameters characterizing the electrodes with immobilized solutions of $Co(NO_3)_2$. Quantitative composition of electrode membrane phases—see Fig. 4

No. electrode	mV/*pa*		E_{st} (*mV*)	
	I range	II range	I range	II range
1	17	57	243	279
2	12	43	243	266
3	−8	57	267	310

It follows from the results that in concentration range I of solvates in the organic phase in the case of poorly extractable salts by TBP the electrode potential depends on equilibria being established at the interface and can be described by the equation:

$$E = E_{st} \pm \frac{RT}{RF} \ln a_{MeTBP} \qquad (5)$$

where:

the sign "+"—the extraction process—low concentration of the salt in P_m
the sign "−"—the re-extraction process—high concentration of the salt in P_m

In the case of readily extractable salt, *e.g.* $UO_2(NO_3)_2$ in the whole concentration range of the salt in P_m the re-extraction processes are predominant and the calibration curves have a positive slope.

In the organic phase in which $c_{Me(TBP)} > 0.2M$ the solvate dissociation is withdrawn. Then potential formation consists in $MeNO_3^+$ ions transfer through the interface (re-extraction). It would indicate slope of electrode characteristics which is $s = +58$ mV/$pa_{Me(TBP)}$ in this concentration range. The electrode function is shaped by activity of solvate in the organic phase. The electrode potential is described by the equation:

$$E = E_{st} + \frac{RT}{F} \ln a_{meTBP}$$

$$a_{MeTBP} = c_{MeTBP} \times \gamma_{\pm MeTBP} \qquad (6)$$

Assuming similarity in the extractant-salt interaction for the studied salts based on the known activity of uranyl complexes in TBP a hypothetical course of activity for solvation calcium and cobalt complexes can be plotted. Dependence ('6') can be used to determine activity coefficients of uranyl, calcium and cobalt solvates in their concentrated TBP solutions.

RESULTS

The paper presents properties of membrane systems with the immobilized aqueous phase hitherto unknown. It was stated that the processes influencing the membrane potential in the studied system was dependent mainly on the extraction constants and the resultant electrode functions were dependent on concentrations of salt in the immobilized aqueous phase and concentration of solvate in the organic phase. A detailed analysis of these dependences was carried out using them to describe the processes influencing the membrane potential.

REFERENCES

1. W. E Morf, The principles of ion-selective electrodes and of membrane transport. *Akademiai Kiado*, Budapest, 1981.
2. W. W. Jegorow, G. L. Starobiniec and W. A. Repin, *Zur. Anal. Chem.*, 1987, **42**, 78.
3. J. Koryta and K. Stulik, *Jonoselektivnyje Elektrody. Moskva, Mir*, 1989.
4. Le Quoc Hung, *J. Electroanal. Chem.*, 115, **159**, 1980.
5. P. Vanysek and R. P. Buck, *J. Electroanal. Chem.*, 297, **19**, 1991.
6. W. E. Morf, The principles of ion-selective electrodes and membrane transport. *Akademai Kiado*, Budapest, 1981.
7. W. Dawis and J. Mrochek, in *Solvent Extraction Chemistry*. D. Dyrsse (ed.) p. 283. *Proc. of the Inter. Conf. Gothenburg*, Amsterdam, 1967.
8. A. J. Michajliczenko, M. A. Klimienko and W. B. Bułgakowa, *Zur. Nieorg. Chim.* 1971, **16**, 2557.
9. T. V. Healy, J. Kennedy and G. M. Waind, *J. Inorg. Nieel. Chem.*, 1959, **10**, 137.