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A Polarographic Study of Uranyl-Salicylate and Uranyl-Phthalate Complex Formation in Acidic Solutions

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The d. c. and a. c. polarography and cyclic voltammetry were applied to the study of uranyl-salicylate and uranyl-phthalate complexes. The study was limited to the pH range <5, because insoluble uranyl-hydroxydes are formed above this pH value. Uranyl-salicylate and -phthalate are irreversibly reduced. The electrode process is preceded by the chemical reaction of the complex with protons. By this reaction the electroactive species with the charge $z = +2$ is formed, which was connected with the charge of the »free« uranyl-ion.

INTRODUCTION

In the present times man turns to the sea, among other natural resources a significant source of food and minerals. The most recent investigations have shown that humic material is a possible substrate for an efficient recovery of uranium from seawater[1–5].

Humic substances are mixtures of different highmolecular organic compounds (molecular weight in the range from 10^3 to 10^6) containing various proteins, polysaccharides, phenols and aliphatic hydrocarbon chains bound to the polyaromatic skeleton through oxygen bridges of carboxyl, carbonyl, and hydroxyl functional groups. These groups are proton-donors and, together with various phosphorous, nitrogen and sulphur groups, have a very important role in the complexing of metal ions with humic substances[6,7].

The metal ion interaction with humic substances was investigated using various ligands as model systems. Most frequently EDTA[8,9], NTA[9,10], intramolecular hydroquinones[11] and some simpler aminoacids were used to elucidate the uranyl-ion interaction with humic substances.

Polyfunctional model systems, based on randomly positioned functional groups and aromatic rings, have been recently investigated. They can be used to deduce the type of the metal-ion interaction with active chelating sites. The results have shown that the predominant bidentate sites are likely to be phthalate and salicylate-type sites with a significant proportion of aromatic carbonyl and phenolic hydroxyl, which practically do not participate as active chelating sites. Therefore, the interaction of uranyl-ion with salicylic

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and phthalic acid in the homogeneous electrolyte solution has been investigated. The basic electrochemical characteristics of these complexes were studied using various polarographic techniques.

The formation and stability of uranyl-salicylate and uranyl-phthalate complexes were investigated by several authors[13–17], mainly by potentiometric and spectrophotometric methods. Polarography was not used extensively in stability studies of these complexes. Difficulties arised because of their aromatic character, which causes adsorption phenomena on the mercury electrode and renders the simple analysis of the results quite difficult. In this laboratory the electrochemistry of uranyl-ion[18,19] and its inorganic[20–23] and organic[24–27] compounds was polarographically investigated in a broad concentration and pH range·

EXPERIMENTAL

Instruments

All d. c. polarographic and cyclic voltammetric measurements were performed with the PAR-174 polarograph connected to a Hewlett-Packard X-Y recorder, Model 7045A. A. c. polarographic measurements were performed with a PAR-170 polarograph. A. c. measurements were performed at the frequencies of 230 Hz and by in-phase mode, respectively.

The pH of solutions was measured by an Iskra MA 5723 pH-Meter.

Cells and Electrodes

All the measurements were performed in a standard polarographic cell (50 cm^3) using the three electrode system: a dropping mercury electrode (DME) (or hanging mercury drop electrode (HMDE)) as the working electrode, a saturated calomel electrode (SCE) as the reference electrode and a platinum wire as an auxiliary electrode.

Chemicals and Solutions

All the solutions were prepared from analytical grade chemicals and doubly distilled water. Supporting electrolytes, sodium perchlorate and sodium chloride, were prepared by dissolving the appropriate amounts of salts in bidistilled water. The uranyl perchlorate stock solution was prepared from uranyl nitrate, as described in Gmelins Handbuch der Anorganischen Chemie[28]. The uranium content was gravimetrically standardized[29]. Stock solutions of the disodium salts of acids were prepared by dissolving salicylic and phthalic acid in bidistilled water with addition of appropriate amounts of NaOH.

The solutions were deaerated before measurements by bubbling the extra pure nitrogen for 20 minutes.

RESULTS

Uranyl-Salycilate

The a. c. polarogram presented in Figure 1 indicates the complexation of uranyl-ion with salicylic acid at pH 3.6 in perchlorate solution (0.7 mol dm^{-3}). By increasing the concentration of salicylic acid the original uranyl reduction peak (E_p = — 0.18 V vs. SCE) (curve 1) diminishes and practically disappears at a higher ligand to uranyl-ion ratio. The corresponding reduction peak of the uranyl complex appears at a more negative potential (curve 2).

The influence of pH on the complex reduction was examined by the measurements carried out in perchlorate solutions with a constant metal to ligand ratio (1 : 2) at various pH values. With the increasing pH the reduction peak

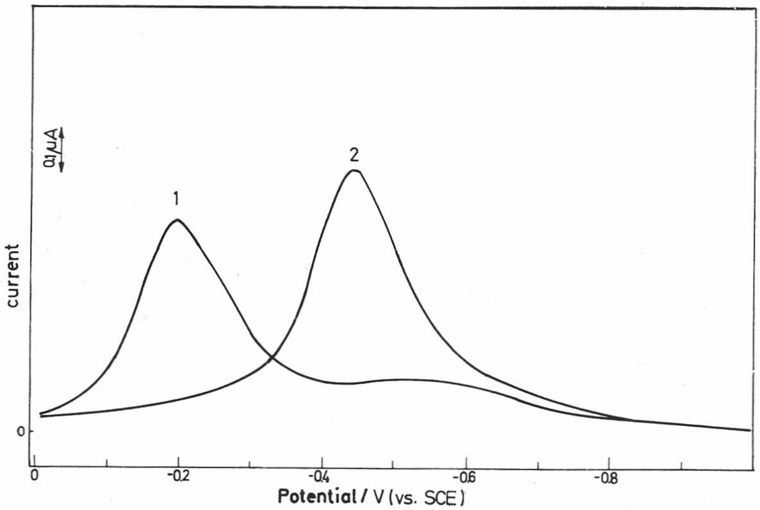

Figure 1. A. C. polarogram (in-phase mode) of 2.4×10^{-4} mol dm^{-3} UO_2^{2+} in 0.7 mol dm^{-3} $NaClO_4$ at pH 3.6 and various concentrations of salicylic acid; (1) 0; (2) 10^{-3} mol dm^{-3}. Frequency 230 Hz; amplitude of a. c. voltage 10 mV; scan rate 5 mVs^{-1}.

of uranyl-salicylate complex moves towards more negative potentials. By the cyclic voltammetry it was noted that in the pH range between 3.4 and 3.8 on the cathodic side, a discontinuity at $E_p = -0.25$ V was recorded. By increasing the pH this discontinuity moves to more negative potentials. At higher uranyl concentrations, in the solution with a constant pH (3.5) and salicylic acid concentration, the discontinuity becomes more distinct (Figure 2), and appears even at a slow scan rate (5 mV s^{-1}).

A discontinuity was also observed on d. c. polarograms at a dropping time of 2 seconds. At a certain molar ratio of uranyl-ion and salicylic acid, the discontinuity appears at about — 0.30 V. With a further increase in the ligand concentration, the current exaltation on the reduction wave moves to more negative potentials. The phenomenon was studied separately in the solution with constant concentration of salicylic acid and varying concentration of uranyl-ion. It was observed that once the discontinuity appears, it becomes more distinct with the increasing concentrations of uranyl-ion and it appears in the polarograms even at a dropping time of 0.5 seconds. At dropping times between 0.2 and 0.1 seconds this surface phenomenon was not noticed and the uranyl-ion reduction waves had the regular shape (Figure 3). With increasing the concentration of salicylic acid at pH 3.6, the d. c. reduction wave moves towards the negative potentials. From the logarithmic analysis of uranyl-ion reduction wave in perchlorate solution without addition of the complexing reagents, the reversible one-electron reduction of the free uranyl-ion with $E_{1/2} = -0.18$ V was confirmed. The reduction process of the complexed uranyl-ion by logarithmic analysis was also found to be a single electron, but an irreversible one, with the transfer coefficient $\alpha_n = 0.58$ and $E_{1/2} = -0.4$ V vs. SCE.

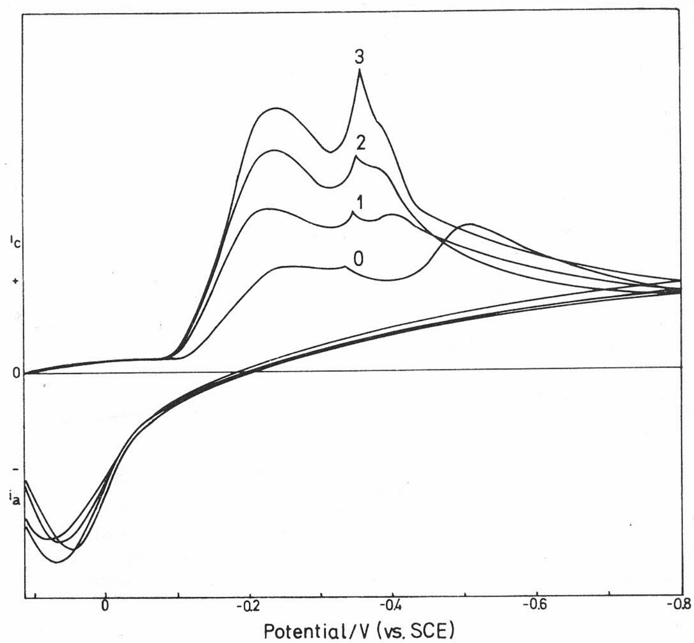

Figure 2. Cyclic voltammograms of (0) 4.8×10^{-4} mol dm^{-3}; (1) 7.2×10^{-4} mol dm^{-3}; (2) 9.5×10^{-4} mol dm^{-3}; (3) 1.1×10^{-3} mol dm^{-3} UO_2^{2+} in 0.7 mol dm^{-3} $NaClO_4$ and 1.4×10^{-3} mol dm^{-3} salicylic acid at pH 3.6. Scan rate 20 mVs^{-1}.

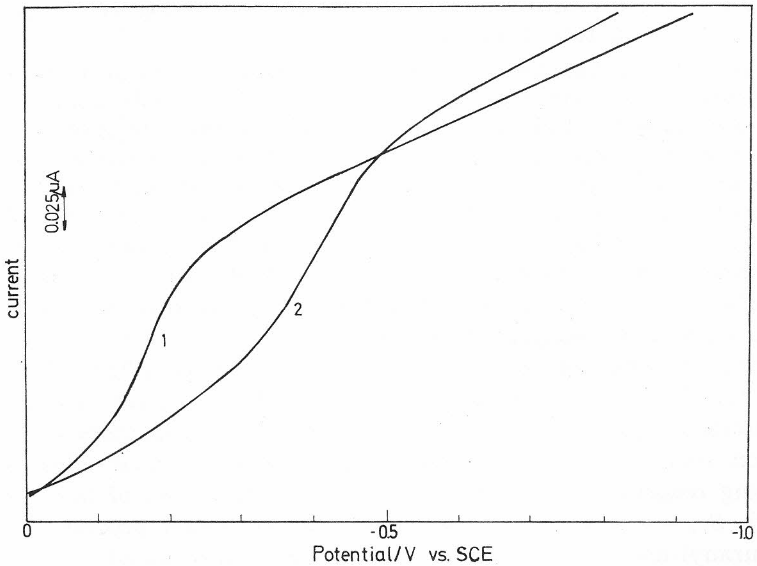

Figure 3. D. C. polarographic curves of 2.4×10^{-4} mol dm^{-3} UO_2^{2+} in 0.7 mol dm^{-3} $NaClO_4$ at pH = 3.6. (1) no salicylic acid present; (2) 10^{-2} mol dm^{-3} salicylic acid. Drop time 0.2 s; Scan rate 5 mVs^{-1}.

In order to estimate the charge of the electroactive species, the method of Hush and Scarrott[30] was applied. By that method parameters of the chemical reaction were determined under the conditions where the contribution to the limiting current, owing to kinetics and diffusion, is comparable.

The relationship between Koutecky's kinetic parameter χ_1 and the potential of the outer Helmholtz plane (the ϕ_2-potential, taken from Russell's tables[31]) was estimated in solutions of various concentrations of sodium chloride (0.1, 0,2, 0.3, 0.5, 0.75 and 1.0 mol dm^{-3}). The χ_1 parameter incorporates the ratio of the rate constants for the forward and backward chemical reactions in the following manner:

$$\chi_1 = (12/7)^{1/2}\, k_f/(k_b\, t_1)^{1/2} \tag{1}$$

χ_1 values were graphically estimated, as shown in Figure 4. The limiting current was measured as the potential — 0.65 V, the dropping time varied (0.1, 0.14, 0.17, 0.18 and 0.2 s), while the mercury flow rate was kept constant.

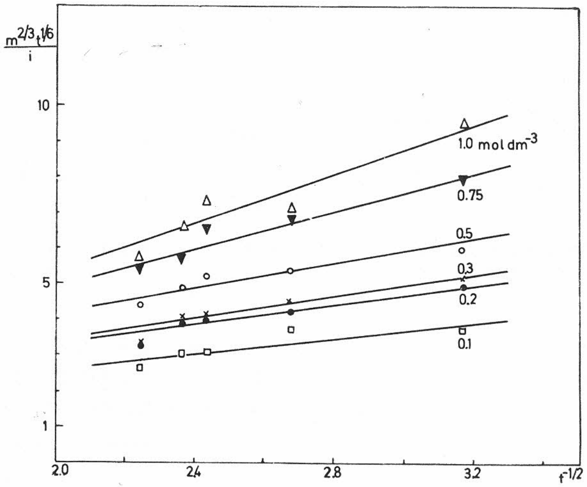

Figure 4. Evaluation of χ_1 values by the method of Hush and Scarrott[30] in a solution of 2.4 × 10^{-4} mol dm^{-3} UO_2^{2+}, 9.4 × 10^{-4} mol dm^{-3} salicylic acid and various concentrations of NaCl. (□) 0.1 mol dm^{-3}; (●) 0.2 mol dm^{-3}; (×) 0.3 mol dm^{-3}; (○) 0.5 mol dm^{-3}; (▲) 0.75 mol dm^{-3}; (△) 1.0 mol dm^{-3}. Drop time varied while the flow rate was kept constant.

The relationship between the logarithm of the kinetic parameter χ_1 and the ϕ_2-potential gives a linear dependence. From the slope of that straight line, the charge of the reducible particle z, using equation (2), was evaluated·

$$\frac{\log \chi_1}{\Phi_2} = z\,\frac{F}{2.3\,RT} \tag{2}$$

For uranyl-salicylate complex the value of + 2 was obtained.

Uranyl-Phthalate

Phthalic acid is an electroactive compound by itself. In perchlorate solution it reduces in the three a. c. polarographic steps (Figure 5) and its electrochemical behaviour depends upon the pH of the solution. This dependence is examined in the range from pH 2.2 to 4.6. The first reduction peak of phthalic acid is at the potential — 1.24 V, the second at — 1.47 V and the third at — 1.7 V vs. SCE. Their heights depend upon the pH of the solution. The first reduction peak is registered up to pH 3.5. The second and the third reduction peaks are registered up to pH 4.6.

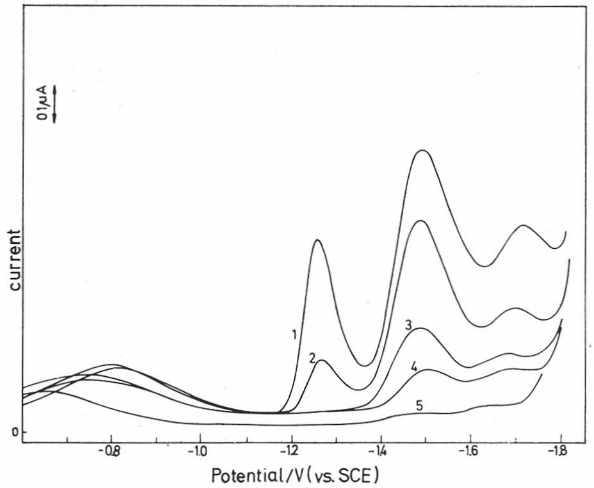

Figure 5. A. c. polarograms of 3.4×10^{-3} mol dm^{-3} phthalic acid in 0.7 mol dm^{-3} $NaClO_4$ at various pH; (1) 2.8; (3) 3.5; (4) 4.2; (5) 4.6. All recording conditions as in Figure 1.

Phthalic acid forms a complex with uranyl-ion, too. The complexation was studied by in-phase a. c. polarographic measurements. Two separate reduction peaks were obtained in the a. c. polarograms (Figure 6). The first

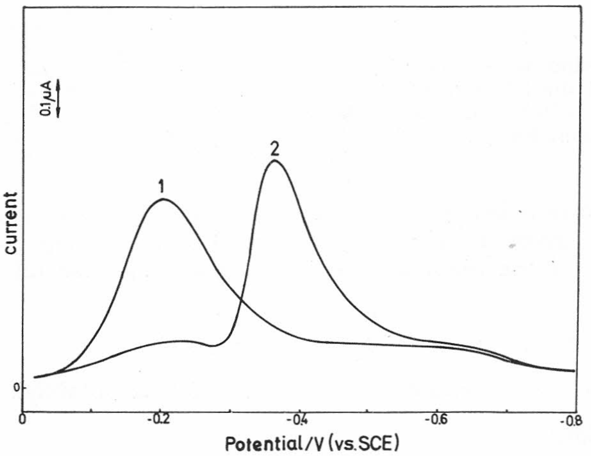

Figure 6. A. c. polarographic reduction curves of 2.4×10^{-4} mol dm^{-3} UO_2^{2+} in 0.7 mol dm^{-3} $NaClO_4$ at pH 3.8. (1) no phthalic acid present; (2) 3.4×10^{-4} mol dm^{-3} phthalic acid. All recording conditions as in Figure 1.

peak corresponds to the reduction of the »free« uranyl-ion ($E_p = — 0.18$ V). The second one corresponds to the reduction of the uranyl-phthalate complex ($E_p = — 0.35$ V). At more negative potentials none of the phthalic and reduction peaks was recorded.

The influence of pH on the reduction of the uranyl-phthalate complex was studied, too. The measurements were carried out in sodium perchlorate solution of the ionic strength 0.7 mol dm^{-3}, with a constant concentration of uranyl-ion and phthalic acid. The pH was varied in the range of 2.5 to 5.4. In the range of a lower pH (2.5 to 2.9) only one reduction peak was recorded moving to more negative potentials as pH rose. At pH 3.2 two separate peaks were registered. The first peak corresponds to the reduction of the uranyl-ion and the second one to the reduction of the uranyl-phthalate complex. As the pH increased from 3.2 to 4.0, the second reduction peak moved towards a more negative potential. Furthermore, at pH 4.8 and 5.4 insoluble uranyl hydroxydes are formed, which are reduced at the potential of — 0.55 V and — 0.65 V vs. SCE.

D. c. polarographic measurements were performed with the dropping times of 2 to 0.2 seconds. With the dropping time of 2 seconds ill-defined waves were recorded and could not be used for further analysis (Figure 7). With the dropping time of 0.2 seconds, the adsorption phenomena are avoided. With the increasing concentration level of 1.8×10^{-4} and 2.9×10^{-4} mol dm^{-3} of phthalic acid, two separate waves are registered. Logarithmic analysis of the reduction wave of the complexed uranyl-ion shows that it is an irreversible single-electron process with the transfer coefficient $\alpha_n = 0.51$ and $E_{1/2} = — 0.35$ V vs. SCE.

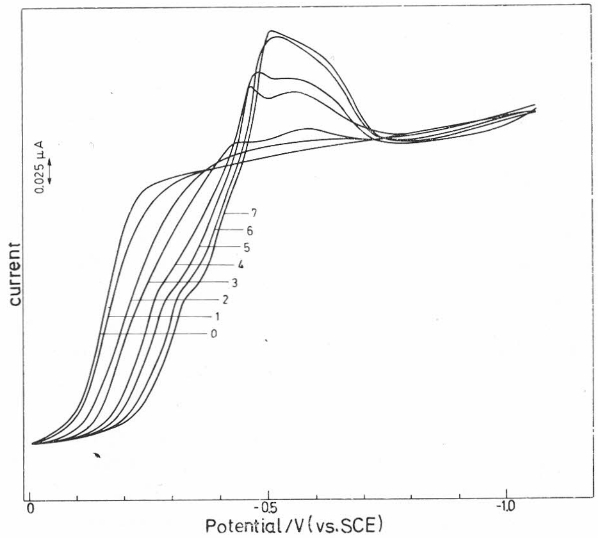

Figure 7. D. c. polarographic curves of 2.4×10^{-4} mol dm^{-3} UO_2^{2+} in 0.7 mol dm^{-3} $NaClO_4$ at pH 3.8 and various concentrations of phthalic acid. (0) 0; (1) 6×10^{-5} mol dm^{-3}; (2) 1.8×10^{-4} mol dm^{-3}; (3) 3×10^{-4} mol dm^{-3}; (4) 5.8×10^{-4} mol dm^{-3}; (5) 1.2×10^{-3} mol dm^{-3}; (6) 1.7×10^{-3} mol dm^{-3}; (7) 2.2×10^{-3} mol dm^{-3}. Drop time 2 s; scan rate 2 mVs^{-1}.

The charge of the electroactive species was determined by the method of Hush and Scarrott[30], like for the uranyl-salicylate complex. Solutions of various concentrations of NaCl (0.1, 0.2, 0.3, 0.5, 0.75 and 1.0 mol dm^{-3}) were used as the supporting electrolyte. The relationship between log χ_1 and the potential of the Helmholtz outer plane ϕ_2 gives a straight line· From the slope of that linear dependence, using the equation (2), the charge of the reducible particle z was evaluated as + 2.

DISCUSSION

In this work the formation and the electrochemical behaviour of uranyl-salicylate and uranyl-phthalate complexes are illustrated by polarographic measurements.

By a. c. polarography separate reduction peaks of the »free« uranyl-ion and uranyl-salicylate ($E_p = -0.45$ V) and uranyl-phthalate ($E_p = -0.35$ V) complexes are registered (Figures 1 and 6). The formation of a chelate between UO_2^{2+} and salicylic acid was also indicated by a change in the colour of the solution from faint to deep yellow and to orange as the pH increased from 2.0 to 4.5. At pH 4.5 the solution becomes turbid because insoluble uranyl hydroxydes (uranates) are formed.[32]

The influence of pH on the reduction process of the complexes was extensively studied by a. c. measurements, as well as by the cyclic voltammetry. It was found that for both complexes reduction peaks move towards the more negative potentials with an increase in pH. This indicates proton participation in the chemical reaction preceding the electrode process. By that chemical reaction the H^+ ions are bound to the complex. The reduction was registered in the pH range of 2.8—4.2 in the case of the uranyl-salicylate, and 3.2—4.0 in the case of the uranyl-phthalate complex. This pH range is wider for lower concentrations of uranyl-ion. At the same time this pH range is probably determined by the number of H^+ ions which react with the complex to give electroactive species. Namely, the reduction of the complexes will be observed in the pH range in which there is a sufficient concentration of protons which react with electroinactive uranyl-complex species forming the electroactive one.

However, the theoretical distribution showed that the complexes are formed in the pH range of 2.5—14 for the uranyl-salicylate complex (Figure 8) and of 2—8 for uranyl-phthalate (Figure 9). Such different distributions of uranyl complexes by polarographic measurements were obtained because above a definite pH value uranyl hydroxydes are formed and they accumulate on the mercury electrode and block the regular reduction process. Thus, this distribution shows that complexes are present in a much narrower pH range.

The fact that on the anodic side of the cyclic voltammograms only one oxidation peak was recorded (oxidation of uranium(IV) to uranium (VI) by the irreversible two-electron oxidation), shows that the complex was dissociated at the electrode. To find out when the dissociation occurs the charge of the electroactive species was evaluated.

As already mentioned, the electrode process is preceded by the chemical reaction of complexes with protons. Owing to the irreversible and kinetic character of the reduction process of the complexes, the electrode and chemical reactions are influenced by the structure of the double layer. It may

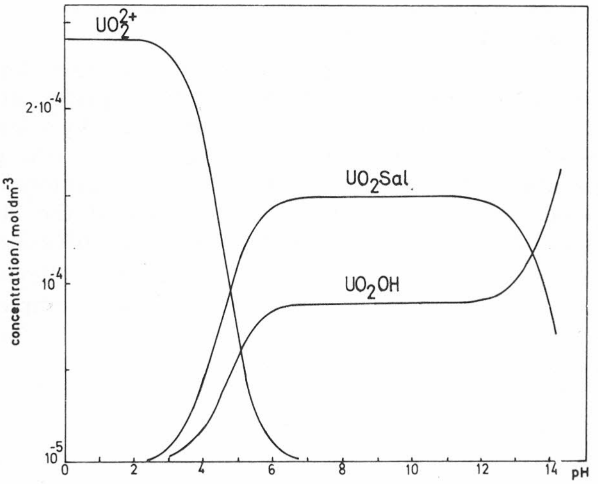

Figure 8. Theoretical distribution of uranyl-salicylate in dependence on pH calculated by using dissociation constants of salicylic acid $K_1 = 1.66 \times 10^{-3}$ and $K_2 = 2.34 \times 10^{-14}$ and the stability constant of uranyl-salicylate complex 1.2×10^{12}.

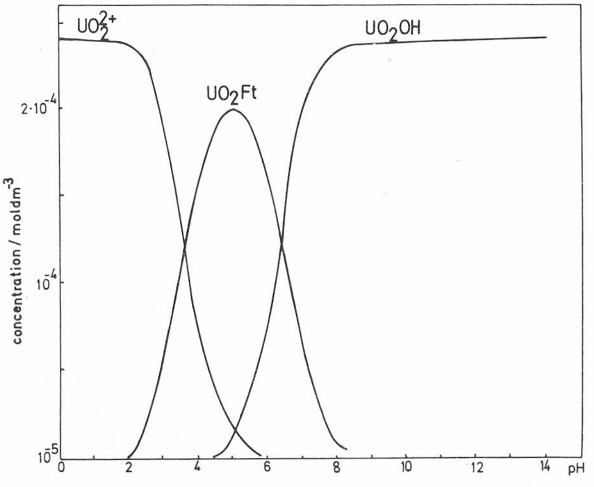

Figure 9. Theoretical distribution of uranyl-phthalate in dependence on pH calculated by using dissociation constants of phthalic acid $K_1 = 1.58 \times 10^{-3}$ and $K_2 = 1.95 \times 10^{-5}$ and the stability constant of uranyl-phthalate complex 6.46×10^4.

be concluded that the electrochemical reduction of uranyl complexes with salicylic and phthalic acid is partly controlled by diffusion and partly by kinetics. Namely, experimentally determined values of the exponents in the expressions $i_d = \text{const.} \times t^{1/6}$ and $i_k = \text{const.} \times t^{2/3}$, which are the slope of the straight line $\log i$ vs. $\log t$ dependence, lie between these two borderline cases, i. e. 1/6 and 2/3, and amount to 0·45 for the uranyl-salicylate and 0.22

for uranyl-phthalate complex. Therefore, this means that these processes are both kinetically and diffusion controlled.

The apparent rate of the reducible species formation depends upon the ϕ_2-potential and the concentration of the inactive species at the electrode. surface. The protonation rate is proportional to Koutecky's kinetic parameter χ_1. On the basis of the linear dependence of log χ_1 vs. ϕ_2 (the potential at the outer Helmholtz plane) it may be concluded that the protonation takes place under the electrode double layer[33,34] in the vicinity of the electrode surface after the transport of the inactive species through the diffusion layer.

The charge z of the reducing species of the uranyl-salicylate and uranyl-phthalate complexes has been evaluated and for both complexes it amounts to +2. This charge was connected with the »free« uranyl-ion so it may be concluded that before the reduction the complex dissociation takes place on the surface of the mercury electrode.

Accordingly, we propose the following electrochemical reduction mechanism of the uranyl-salicylate and uranyl-phthalate complexes. The first reduction peak can be described by the following electrochemical reduction:

$$UO_2^{2+} + e^- \rightleftharpoons UO_2^+ \tag{3}$$

This electron transfer is preceded by two parallel homogeneous reactions:

$$UO_2L \rightleftharpoons UO_2^{2+} + L^{2-} \tag{4}$$

$$UO_2L + 2H^+ \rightleftharpoons UO_2^{2+} + H_2L \tag{5}$$

where L^{2-} is an anion of the salicylic and/or phthalic acid and H_2L is the undissociated form of the acids.

Dissociation of the UO_2L complex, described by the reaction (4) is slower than the reaction (5) which is acid catalyzed. Therefore, the second reduction peak involves the slow rate determining protonation step which determines the overall electron transfer, as shown in the following scheme:

$$UO_2L + 2H^+ + e^- \xrightarrow{\alpha_n} UO_2^+ + H_2L \tag{6}$$

The reduction of the complex is preceded by the rate determining step of protonation. This results in the formation of a »protonized intermediate«. The very unstable intermediate species immediately dissociates and the »free« uranyl-ion is then reduced giving an overall one-electron irreversible reaction.

A. c. technique also proved to be convenient in the study of the electrochemical behaviour of phthalic acid. These reduction peaks are registered (Figure 5) on the a. c. polarograms. According to the literature data[35] the first one, at —1.24 V, is ascribed to the two-electron reduction of the molecule of phthalic acid for one proton richer than its undissociated form. The second one, at —1.47 V, was a response of the four-electron reduction of the undissociated molecule of phthalic acid, and the third ,at —1.7 V, of the reduction of the biphthalate ion. As heights of reduction peaks depend on the pH, it was established that the electrode reaction was preceded by the chemical reaction with protons. Contrary to Ryvolova and Hanuš[36], the three peaks of phthalic acid were registered on a. c. polarograms in approximately the same pH range (the first up to pH 3.5, and the second and third up to pH 4.6). All the peaks were very well defined and therefore further examination of phthalic acid by the a. c. technique will be done.

It should be mentioned that in the uranyl-salicylate system, in the pH range of 3.4—3.8 some electrochemical phase changes are noticed. Namely, on d. c. polarograms and cyclic voltammograms discontinuities on the reduction waves are registered (Figure 2). This may be ascribed to the phase change of adsorbed molecules of the uranyl-salicylate complex on the HMDE. For a more exact evaluation of such an electrochemical phase change further examinations are necessary.

Finally, an effort was made in calculation of apparent stability constants of uranyl-salicylate and uranyl-phthalate complexes. However, by the analysis of the nature of the electrode process, as well as polarograms and voltammograms, it was established that these electrochemical techniques are unsuitable for this purpose, in the first place because by the formation of the complex the electrode process becomes irreversible (the »free« uranyl-ion is reduced reversibly). Furthermore, the diffusion coefficient is probably changed by the complexation. It was also found that the complexes are adsorbed on the surface of the mercury electrode. Because of that, the exact ratio between the »free« and the complexed uranyl-ion could not be determined.

At the same time, the complex concentration on the electrode will be greater then in the bulk of the solution, so that equilibrium conditions are not achieved.

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REFERENCES

1. J. V. Ibarra and J. Osacar, *Fuel* **58** (1979) 827.
2. K. Wagener and D. Heitkamp, *Thal. Jugosl.* **16** (1980) 185.
3. A. Szalay, *Geochim. Cosmochim. Acta* **28** (1964) 1605.
4. H. Kerndorff and M. Schnitzer, *Geochim. Cosmochim. Acta* **44** (1980) 1701.
5. R. F. C. Mantoura, A. Dickson, and J. P. Riley, *Estuarine Coastal Mar. Sci.* **6** (1978) 1.
6. P. Povoledo H. L. Golterman, *Proc. of International Meeting,* Netherlands May 29—31, 1972.
7. M. Schnitzer and S. U. Khan, *Humic Substances in the Environment,* M. Dekker, New York, 1972.
8. T. M. Florence and G. E. Bately, *Talanta* **23** (1976) 179.
9. A. Dixon, R. F. C. Mantoura, and J. P. Riley, *Thal. Jugosl.* May 1976.
10. W. Stumm and D. A. Braunner, *Chemical Oceanography,* J. P. Riley and G. Skirrow, 2nd Ed. Vol. **1**, Acad. Press, London, p. 173.
11. M. Andrzejewski, *Proc. Intl. Meet. Humic Substances,* Neinwershus, 1972, Pudoc, Wageningen.
12. K. Murray and P. W. Linder, *J. Soil Sci.* **34** (1983) 511.
13. G. Courtois, *Bull. Soc. Chim. France* **33** (1923) 1761.
14. D. V. Jahagirdar and D. D. Khanolkar, *J. Inorg. Nucl. Chem.* **35** (1973) 921.
15. R. S. Rajan and A. E. Martell, *J. Inorg. Nucl. Chem.* **26** (1964) 789.
16. S. Hakamori, *Chem. Abstr.* **26** (1932) 2366.

17. 17. N. G. Palaskar, D. V. Jahagirdar, and D. D. Khanolkar, *J. Inorg. Nucl. Chem.* **38** (1976) 1673.
18. V. B. Vouk, M. Branica, and A. O. Weber, *Arhiv Kem.* **25** (1953) 235.
19. O. A. Weber, M. Branica, and V. B. Vouk, *Arhiv Kem.* **25** (1953) 225.
20. V. Pravdić, M. Branica, and Z. Pučar, *Croat. Chem. Acta* **33** (1961) 151.
21. V. Žutić and M. Branica, *J. Electroanal. Chem.* **28** (1970) 187.
22. L. Sipos, Lj. Jeftić, M. Branica, and Z. Galus, *J. Electroanal. Chem.* **32** (1971) 35.
23. V. Žutić and M. Branica, *J. Electroanal. Chem.* **52** (1974) 217.
24. Lj. Jeftić and M. Branica, *Croat. Chem. Acta* **35** (1963) 203.
25. M. Branica and J. Kuta, *Coll. Czech. Chem. Commun.* **31** (1966) 2833.
26. D. Krznarić, B. Ćosović, and M. Branica, *J. Electroanal. Chem.* **33** (1971) 61.
27. B. Ćosović, Lj. Jeftić, M. Branica, and Z. Galus, *Croat. Chem. Acta* **45** (1973) 475.
28. *Gmelins Handbuch der Anorganischen Chemie*, No. 55, Auflag (1963) 136.
29. C. I. Rodden, *Analytical Chemistry of Manhattan Project*, McGraw Hill, New York (1960) 46.
30. N. S. Hush and J. N. Scarrott, *J. Electroanal. Chem.* **7** (1964) 26.
31. C. D. Russell, *Electroanal. Chem.* **6** (1963) 486.
32. B. Tomažič, M. Branica, and B. Težak, *Croat. Chem. Acta* **34** (1962) 41.
33. H. B. Mark, Jr. and L. R. McCoy, *J. Phys. Chem.* **72** (1968) 1083.
34. L. R. McCoy, H. B. Mark, Jr., and L. Gierst, *J. Phys. Chem.* **72** (1968) 4637.
35. A. Ryvolova and V. Hanuš, *Coll. Czech. Chem. Commun.* **21** (1956) 853.

SAŽETAK

Polarografsko ispitivanje tvorbe kompleksa uranil-salicilat i uranil-ftalat u kiselim otopinama

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Kompleksi uranil-sacilat i uranil-ftalat istraživani su d. c. i a. c. polarografijom, te cikličkom voltametrijom pri pH < 5, jer se pri višim pH vrijednostima tvore netopivi uranil-hidroksidi u proučavanom području koncentracija. Oba se kompleksa reduciraju ireverzibilno. Elektrodnom procesu prethodi kemijska reakcija kompleksa s protonima. Tom reakcijom nastaje elektroaktivna vrsta s nabojem $z = +2$, što je povezano s nabojem »slobodnog« uranil-iona.