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Electrokinetic Studies in Disperse Systems. VIII. The Electrokinetic Potential of Nonstoichiometric Uranium Oxides in Aqueous Media

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The electrokinetic potential was measured for uranium oxide samples of different atomic ratios O/U, ranging from 2.00 to 2.45. It was found that the differences in the oxidation states correspond to small but significant differences of the electrokinetic potential, with higher values for lower oxidation states. The reversal of sign has been observed for positive suspensions at $pH = 3.3$ by the phosphate counter ion. The electrokinetic potential was found to be independent of the U^{6+}/U^{4+} ratio in the solution, indicating that these ions are not potential determining.

INTRODUCTION

In reactor fuel technology there is considerable interest in uranium oxides of the lower oxidation states (uranium dioxide in particular) as fuel element and as intermediaes in uranium metal production and reprocessing. Uranium(IV) is of special interest because of its reduced solubility in aqueous media. The knowledge of electrical forces on surfaces is of interest with respect to precipitation phenomena and to aggregation and caking of suspensions in pipe flow systems.

The consequences of oxidation, or oxygen adsorption by the disperse uranium oxide material with respect to the electrokinetic potential (EKP) are at present unknown. As many of the phase relationships and other physical properties in the system uranium — oxygen are quite well understood[1-4] several samples of different O/U ratios and with different modes of preparation were taken ,and the EKP was measured in dependence of the ionic concentration in the solution.

EXPERIMENTAL

Samples of various uranium oxides have been prepared by thermic reduction of ammonium diuranate (ADU). Special care was taken to stabilize the prepared product by appropriate coling and deactivation. Table I. summarizes the characteristics of the uranium oxide samples used in experiments.

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* Experimental material taken in part from the Chem. Eng. Thesis presented to the Faculty of Technology, University of Zagreb, 1963.

TABLE I

Characterization of Uranium Oxide Samples Used

Sample No.	Method of preparation	Analysis O/U	X-ray characterization
1	ADU,H_2+0.4%H_2O, 600°C H_2 coling, 3hr.	2.00	pure cubic
2	ADU, H_2, 600°C hot, water quenched	2.00	pure cubic
3	ADU, H_2, 600°C	2.08	cubic
4	ADU+air, 900°C to U_3O_8+H_2, 600°C, CO_2 cooled	2.11	predominantly cubic
5	ADU, H_2+H_2O vapor	2.33	inhomogeneous
6	UO_2(No. 1) 800°C, air to U_3O_8, 1300°C, N_2 N_2 — cooled.	2.45	inhomogeneous
7	Electrochemical, Hg cathode electrolysis, NH_4-carbonate solution; pptd. at 50°C, washed	2.00— —2.04	unknown in wet; dried: predominantly cubic

A portion of the sample for the test was pulverized, sieved through a 270 Mesh standard sieve and suspended in the solution to be measured. Fine colloidal particles were removed by repeated decantation. The sediment was used to form the diafragm in the streaming cell. All solutions were prepared from analytical grade chemicals and tripple distilled CO_2-free water.

Analyses on the O/U ratio were performed by the controlled potential coulometric method.[5] For this purpose a servoanalytical instrument was used, composed of an all-electronic potentiostat, a strip chart recorder and a low inertia motor integrator. The calibration was performed by the method proposed by Lingane.[6] In experiments with an electrolytic sample of uranium oxide the same equipment and an appropriate cell was used for the cathodic reduction of uranyl-carbonate in 1 *M* ammonium carbonate.

The solutions with varying $[U^{6+}] / [U^{4+}]$ ratios were prepared by electrolysis of $1 \times 10^{-3} M$ uranyl carbonate in 1 *M* sodium carbonate-bicarbonate solution at —1.25 volts *vs.* saturated calomel electrode. The extent of reduction was controlled coulometrically supposing an overall current efficiency of 90%.[7]

Measurements of the EKP were made by the streaming potential technique[8] at lower ionic strengths (Fig. 1 and 2), and by the streaming current technique[9] in all other instances. Purified, CO_2-free nitrogen was used for the driving pressure.

RESULTS

The results of the measurements are expressed in terms of the EKP in mV computed from the simple form of the Helmholtz-Smoluchowski equation,[8-10] taking 80.4 for the dielectric constant of water, and 0.01 poise for the viscosity of the liquid phase. All conductances were measured at 25°C. No correction for surface conductance was applied since most of the measurements were performed in solutions of high electrolyte concentrations.

In Fig. 1 the EKP of the samples No. 3 and 5 is shown *vs.* *p*H of the solution. The ionic strength is variable since the volume required for the measurements was titrated with hydrochloric acid or sodium hydroxide to the *p*H value indicated. It is obvious that the EKP is *p*H dependent; thus

H^+ and OH^- are the potential determining ions for the EKP in this system. The isoelectric region is found to be between *p*H 6 and 7. It is shifted towards lower *p*H values for the higher oxidation state. At the negative side, in alkaline solutions from *p*H 7 to 11 the EKP is practically constant. It is also shown that, in general, the uranium oxide sample No. 3 (lower oxidation state) shows higher values of the EKP.

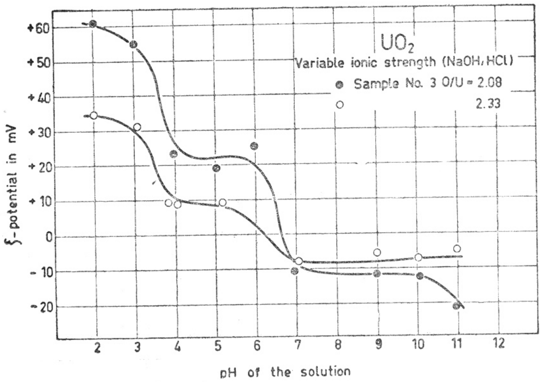

Fig. 1. The dependence of the EKP of uranium oxides on the *p*H of solutions at variable ionic strength: sodium hydroxide or hydrochloric acid added to the *p*H indicated. Samples Nos. 3 and 5.

Working at variable ionic strength complicates the interpretation of the EKP with respect to the change in the conductivity of the liquid phase. This difficulty was overcome by keeping the sum of the concentrations of acetic acid and sodium hydroxide constant at $10^{-2}M$. These results (given in Fig. 2. (for the same samples as before), indicate that the dependence of the EKP on *p*H is the same as in Fig. 1. The isoelectric region (point of zero EKP) is shifted slightly to lower *p*H values. For positive EKP sample No. 5 shows again lower values.

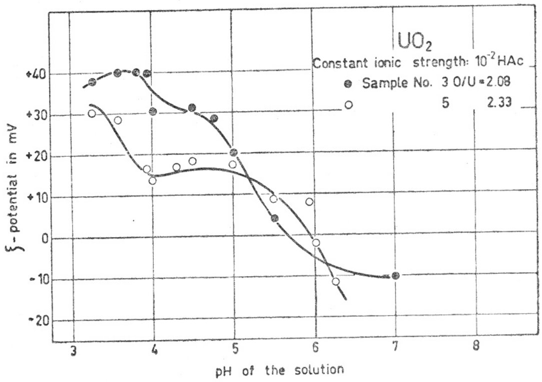

Fig. 2. The dependence of the EKP on the *p*H at constant ionic strength of the solutions: acetic acid + sodium hydroxide, $1 \times 10^{-2}M$. Samples Nos. 3 and 5.

In Fig. 3. comparative experiments in the isoelectric region for the samples Nos. 1, 2 and 6 are shown. The graphs indicate the EKP *vs.* *p*H relation for solutions which were $1 \times 10^{-2} M$ in NaCl + HCl. The results indicate a shift of the position of the zero point of the EKP to lower *p*H values with oxidation. Even the samples which should be equal according to the overall O/U analysis (samples No. 1 and 2) show different values. As indicated in Table I sample No. 2 was prepared under conditions which presume that surface oxidation occured during the cooling by the water quenching procedure. Sample No. 6 is a typical »acid« sample, the zero point being at *p*H = 4.5.

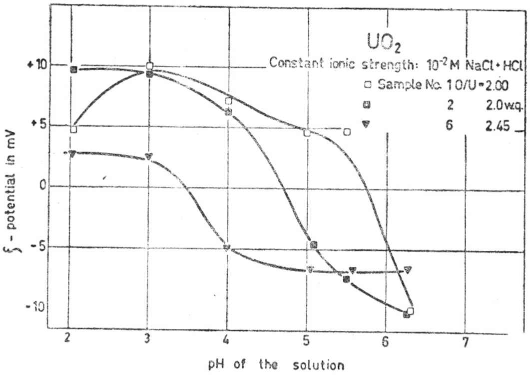

Fig. 3. The EKP of samples Nos. 1, 2, and 6 *vs.* *p*H for systems of constant ionic strength: sodium chloride + hydrochloric acid, $1 \times 10^{-2} M$.

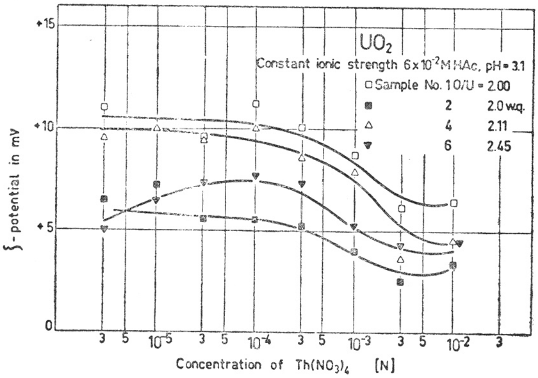

Fig. 4. The EKP of uranium oxide (samples Nos. 1, 2, 4, and 6) at *p*H 3.0 in dependence on the concentration of $Th(NO_3)_4$.

The influence of $Th(NO_3)_4$ concentration at *p*H = 3.0 on the EKP of samples No. 1, 2, 4, and 6 is shown in Fig. 4. There is no significant change in the EKP with increasing $Th(NO_3)_4$ concentration. However, it is clearly seen that lower oxidation states show higher EKP.

In Fig. 5 the EKP *vs.* concentration of Na_3HPO_4 of the same samples at $pH = 3.3$ is shown. On increasing its concentration in the solution the phosphate ion is being adsorbed at the surface in amounts beyond the coulombic equivalency, causing thus the reversal of sign. The concentration for the reversal of sign of the EKP is almost the same for all the samples studied. The initial state at low concentrations of the phosphate ion shows again the higher EKP for samples with lower oxidation states.

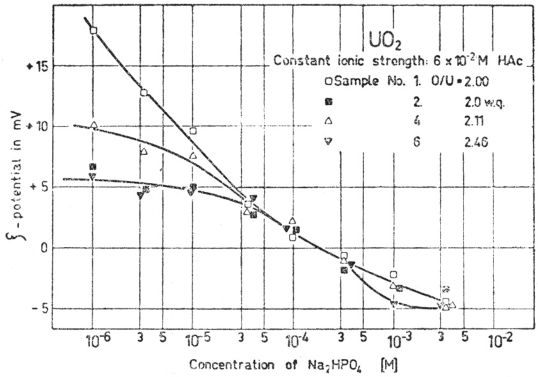

Fig. 5. The EKP of uranium oxide (samples Nos. 1, 2, 4, and 6) at $pH = 3.3$ in dependence on the concentration of Na_2HPO_4.

The EKP potential of uranium dioxide in sodium carbonate-bicarbonate solutions was of interest in view of the proposed preparation of it by cathodic reduction and subsequent precipitation.[7] Fig. 6. shows the results of measurements of EKP on the electrolytically reduced and precipitated sample (sample No. 7) in sodium carbonate-bicarbonate solutions at $pH = 9.7$. There is a maximum in the concentration of $3 \times 10^{-2} M$, but otherwise there is no significant change in the low values of the EKP.

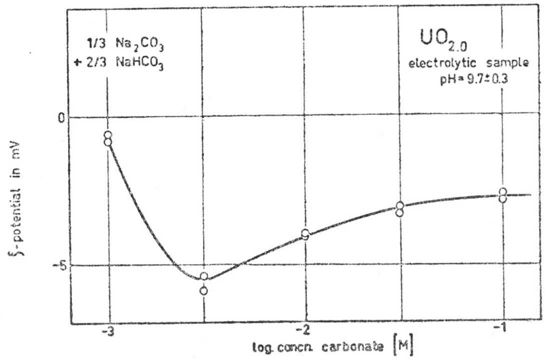

Fig. 6. The EKP of the »electrolytic« sample of uranium oxide in dependence on the concentratian of carbonate in solution at $pH = 9.7 \pm 0.3$.

Fig. 7 shows the results of a measurement of the EKP for an identical electrolytic sample at 0.1 M total carbonate and 1×10^{-3} gion/l total uranium, but with varying ratio of the oxidized to the reduced form. The measurements were performed immediately after the coulometrically controlled reduction has been brought to the degree required. The results indicate that uranium ions UO_2^{2+}, U^{4+}, and probably UO_2^{+} are not EKP determining. This is an indication of the independent electrokinetic and redox potential function.

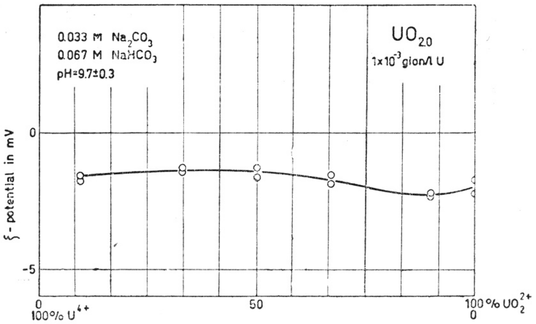

Fig. 7. The EKP of the »electrolytic« sample of uranium oxide in 0.1 *M* total carbonate, *p*H = 9.7 ± 0.3, in dependence on the ratio of concentrations of UO_2^{2+} and U^{4+} at the total uranium concentration of 1×10^{-3} gion/l.

DISCUSSION

Oxide systems have often been studied and the results interpreted in the sense of an adsorption-dissociation type of interfaces.[14] For the uranium oxide systems the same type of surface was proposed[13] anologously to ferric oxide[11] and quartz.[12] The aspect of nonstoichiometric continuous transitions from UO_2 to U_3O_8 was an additional feature which should help in understanding this model of interfaces. The adsorption-dissociation picture supposes active spots for adsorption locating them at the surface oxygen atoms. If one considers the initial lattice of uranium dioxide the incorporation of oxygen (whether by interstitial adsorption or by surface oxidation) should result in increased surface (or interface) charge. An increase of EKP is a result one would expect therefrom. The hypothesis of metal deficiency as the cause of nonstoichiometry[1] requires also at least no change in the charge density and EKP. In the samples studied, especially the example of samples No. 1 and 2 (equal volume O/U ratio but different surfaces) indicates differences which are contrary to the hypothesis of simple adsorption-dissociation as origin of the EKP.

The second interesting feature of the results is the shift in the zero point of the EKP. Therefore, the streaming methods prove as a tool in determining relative acidities of oxidic surfaces. If dissociation is the only process considered for the origin of EKP, the *p*H of the zero point of EKP should represent the *p*K, the logarithm of the dissociation constant. The problem of interaction of counter ions with the surface has been studied in detail for the AgI precipitates.[8,15] In this respect the present experiments with a 4:1 electrolyte [$Th(NO_3)_4$] and a 1:3 (Na_2HPO_4) electrolyte are considered important.The *p*H was chosen in the positive region. The influence of the counter ion is considerable: in the case of phosphate a reversal of the charge is the result of specific adsorption and complex formation. As Th^{4+} represents a cation which is often specifically adsorbed, it is interesting to note that two possibilities are to be considered: either there is no specific adsorption due to coulombic repulsion, or, if there is any, it has no influence upon the structure of the diffuse double layer.

The identical (within the experimental error) zero points for the reversal of charge at $2\times10^{-4}M$ phosphate for all four samples studied indicates that this is a case of complex formation.[16] There is no need to consider oxygen spots on the surface, but only uranium atoms (ions). As the density of these should be approximately equal in all the samples, the same concentration for the reversal of the EKP could be expected.

The carbonate system is interesting in view of the problems associated with precipitation of uranium dioxide from carbonate solutions. The results indicate that there is no significant dependence of the EKP neither on the carbonate concentration nor on the $[U^{6+}] / [U^{4+}]$ ratio. In addition, this latter statement is yet another experimental proof for the indifferent electrolyte role of uranium ions with respect to the uranium oxide surface. This is in accordance with the experimental results on precipitation from carbonate solutions[17] where no influence was found whether the solution was completely reduced or not, for any fraction above 50%. From the theoretical point of view this demonstrates the independence of the EKP and the redox potential: it was found constant when the redox potential was changed for more than 120 mV.

The complex situation indicated by: a) the dependence of the EKP on the oxidation state of the surface; b) the independence of the zero point of the EKP for the reversal of sign by phosphate; and c) the independence on the redox potential in the solution, requires more detailed formulation of the relations governing the mechanism of interface electrical phenomena in electrolyte solutions.

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IZVOD

Elektrokinetičke studije u disperznim sistemima. VIII. Elektrokinetički potencijal uranovih oksida u vodenim otopinama

V. Pravdić i S. Šotman

Mjeren je elektrokinetički potencijal uranovih oksida, različitog stupnja oksidacije, u vodenim otopinama. Pokazano je, da je potencijal viši za okside sa nižim oksidacionim stupnjem, a kao potencijalno-determinantni ioni djeluju H^+ i OH^-. Nul tačka elektrokinetičkoga potencijala pomiče se s porastom oksidacionog stepena oksida prema nižim *p*H vrijednostima, indicirajući na taj način porast kiselosti oksida. U otopinama torijeva nitrata, uz konstantni $pH = 3.0$, ne dolazi do promjene elektrokinetičkog potencijala. Na_2HPO_4 u koncentraciji $2 \times 10^{-4} M$ pokazuje efekt prenabijanja, koji je neovisan o oksidacionom stupnju. Mjeren je također i utjecaj redoks potencijala U^{6+} / U^{4+} u karbonatnoj otopini na EKP i pokazano je, da ne postoji direktna veza.

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ZAGREB

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