the amount of soap. From the fact that the amount of soap hardly affects the length of the induction period we conclude that mainly the styrene molecules dissolved in the water are activated by the persulfate during the induction period and that the solubilized styrene in the soap micelles plays a subordinate role during this period. Hence the locus of the activation of the styrene is mainly the "pure" aqueous phase, and, to a considerably smaller extent, the soap micelles.

It should be realized that the rate of polymerization of the styrene after the induction period depends on the soap concentration. From the experiments given in Fig. 4 we conclude that the rate of polymerization of styrene is proportional to the square root of the soap present in the charge. This matter is being studied further.

Acknowledgment.—The authors acknowledge the help of Miss Julie M. Schott, who assisted in the experiments.

Summary

1. The induction period caused by oxygen in the emulsion polymerization of styrene using persulfate as "catalyst" is inversely proportional to the persulfate concentration, and, provided that the initial partial pressure of oxygen is constant, the induction period is found proportional to the amount of oxygen. Under these conditions the disappearance of oxygen is determined by the rate of activation of styrene molecules, which is proportional to the concentration of persulfate. It has been established that under the experimental conditions the disappearance of oxygen is not a zero order reaction when the initial pressure of oxygen is varied.

2. The length of the induction period is hardly dependent upon the amount of soap in the charge. This indicates that during the induction period mainly styrene molecules dissolved in the "pure" water are being activated by persulfate and that the styrene solubilized in the soap micelles plays a subordinate part in the reaction during the induction period.

3. The rate of polymerization is proportional to the square root of the amount of soap in the recipe.

4. Oxygen acts like a temporary shortstop.

MINNEAPOLIS, MINNESOTA RECEIVED MAY 8, 1946

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Polarography of Uranium. III. Polarography in Very Weakly Acid, Neutral or Basic Solution[1]

BY W. E. HARRIS AND I. M. KOLTHOFF

In moderately acid solution there are two polarographic reductions of uranium,[2] the first corresponding quantitatively to the reduction of hexavalent uranium to the pentavalent state and the second to the reduction to the trivalent state. This paper will be confined to a discussion of the polarography of uranyl in solutions containing only slight traces of free acid, no free acid or slight amounts of alkali, and to the polarography of uranyl in carbonate solutions.

Early work[3] on the polarography of uranium in slightly acid or neutral solution is scanty and inconclusive.

A recent note by Heal[4] on the polarography of uranium in weakly acid medium is in substantial agreement with our work reported previously and in the present paper.

Strubl[5] investigated the polarography of the complex formed between uranyl and a large excess of ammonium carbonate. He found two reduction waves of uranium of equal magnitude at about −0.8 and −1.4 v. *vs.* the saturated calomel electrode. Without conclusive evidence he states that the first wave is due to the reduction of the uranyl carbonate complex to the tetravalent state and that the second wave is due to reduction to the bivalent state.

In this paper it is shown that the polarographic reduction waves of nearly neutral uranyl solutions are strongly affected by hydrolysis of the uranyl ion.

$$UO_2^{++} + H_2O \longrightarrow UO_2OH^+ + H^+ \qquad (1)$$

At all acidities[2] the reduction corresponding to the first wave with a half-wave potential of −0.18 v. is

$$UO_2^{++} + e^- \longrightarrow UO_2^+ \qquad (2)$$

If the reduction according to equation (2) is more rapid than the re-establishment of hydrolysis equilibrium according to equation (1) the magnitude of the first wave should correspond to the amount of unhydrolyzed UO_2^{++} present in the original solution. Actually this has been found to be true.

In solutions of uranyl chloride without excess of free acid and in solutions of uranyl chloride to which small amounts of alkali have been added, UO_2^+, formed during the first reduction, and UO_2OH^+ are reduced (equations 3 and 4) to-

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[1] From a thesis submitted by W. E. Harris to the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the Ph.D. degree, June, 1944.

[2] W. E. Harris and I. M. Kolthoff, THIS JOURNAL, **67**, 1484 (1945).

[3] P. Herasymenko, *Trans. Faraday Soc.*, **24**, 272 (1928).

[4] H. G. Heal, *Nature*, **157**, 225 (1946).

[5] R. Strubl, *Coll. Czechoslov. Chem. Commun.*, **10**, 466 (1938).

gether giving a second single wave with a half-wave potential of about −0.6 v. From the results presented in Table II it is evident that in the absence of free acid the height of the second wave does not correspond to complete reduction of U^{VI} to U^{IV}, but to reduction to a mixture of U^{IV} and U^{V}. To explain this it is assumed that under the specified conditions the reduction products of UO_2^+ and UO_2OH^+ form an insoluble layer on the surface of the dropping mercury

$$UO_2^+ + e^- \longrightarrow UO_2 \qquad (3)$$

$$UO_2OH^+ + e^- \longrightarrow UO_2OH \qquad (4)$$

Under the above conditions the sum of UO_2^{++} and UO_2OH^+ is independent of the extent of hydrolysis. If the polarographic reduction of UO_2^{++} is more rapid than the re-establishment of the hydrolysis equilibrium the total amount of uranium, in a given solution, reduced at the second wave also should be independent of the amount of hydrolysis. It is found experimentally that the diffusion current per millimole per liter of the first wave decreases with decreasing concentration, corresponding to increasing hydrolysis with dilution. However, the diffusion current constant (i_d/c) of the second wave is found to increase slightly with increasing dilution, whereas according to our postulates it should be independent of the dilution. It may be possible that the hydrolysis product UO_2OH^+ undergoes association to non-reducible ions. Such an association should increase rapidly with increasing concentration. This explanation is purely hypothetical and needs further substantiation.

In moderately or strongly acidic solution the reduction product UO_2 from (3) does not separate at the electrode, but redissolves

$$UO_2 + H^+ \longrightarrow UOOH^+ \qquad (5a)$$

or

$$UO_2 + 2H^+ \longrightarrow UO^{++} + H_2O \qquad (5b)$$

The tetravalent uranium from (5) is reduced at the dropping electrode at about −1.2 v. to give trivalent uranium

$$UOOH^+ + e^- \longrightarrow UOOH \qquad (6a)$$

or

$$UO^{++} + e^- \longrightarrow UO^+ \qquad (6b)$$

In moderately or strongly acid solutions reduction (6) occurs at about −0.92 v.[2] In moderately or strongly acid solution the fraction of uranium present as UO_2OH^+ is very small and the polarographic current resulting from reduction (4) is negligible.

In basic non-complexing media the uranium is precipitated as the hydroxide. In basic complexing media the uranium is not reduced beyond the tetravalent state.

Experimental

The apparatus, materials and technique used in making polarographic measurements have been described previously.[2] All diffusion currents have been corrected for the residual current of the medium. Unless stated otherwise, the temperature was maintained at 25 ± 0.1°. All values of the potential refer to the saturated calomel electrode (S.C.E.).

The potassium chloride used was twice recrystallized from conductance water.

Current Voltage Curves of Uranyl Chloride Solutions in the Presence and Absence of Small Amounts of Free Acid.—Figure 1 shows the

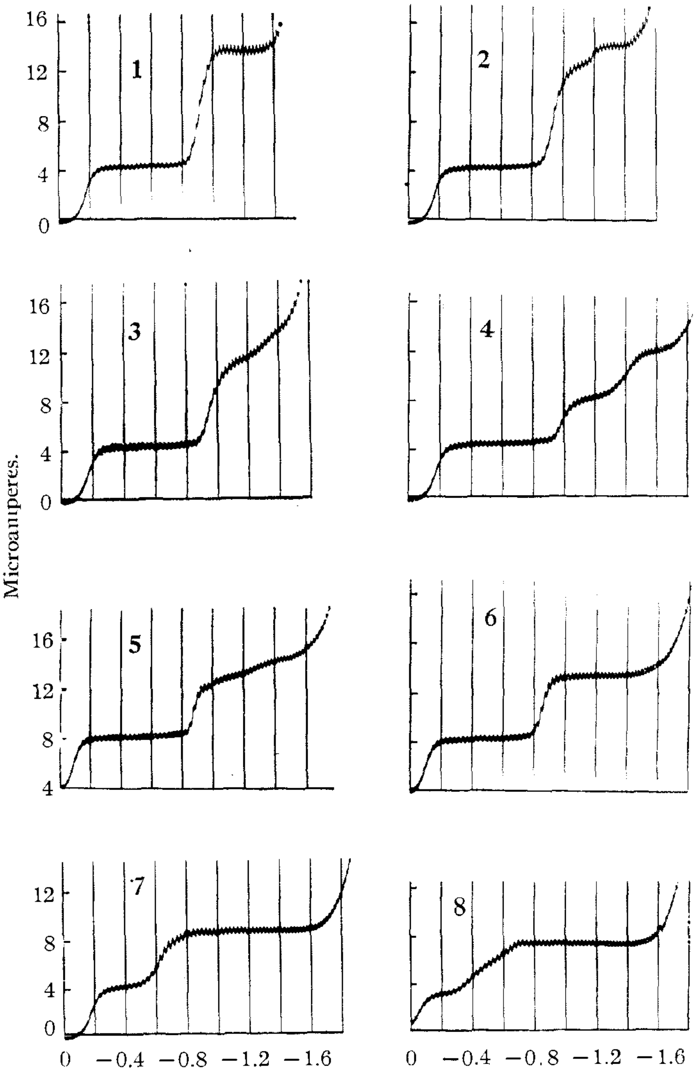

Fig. 1.—Polarograms of 10^{-3} M UO_2Cl_2 in 0.1 M KCl, 2 × 10^{-4}% thymol and varying amounts of hydrochloric acid: 1, 3.42 × 10^{-3} M HCl; 2, 2.00 × 10^{-3} M HCl; 3, 1.48 × 10^{-3} M HCl; 4, 7.28 × 10^{-4} M HCl; 5, 6.03 × 10^{-4} M HCl; 6, 4.79 × 10^{-4} M HCl; 7, 2.37 × 10^{-4} M HCl; 8, 0 HCl.

polarograms obtained when the excess of hydrochloric acid in uranyl chloride solutions is gradually decreased to zero. Solutions of 10^{-3} *M* uranyl chloride which are 3×10^{-3} *M* in hydrochloric acid yield a polarogram which is identical with that obtained in moderately acid (0.1 *M* hydrogen chloride solutions[2]). The first polarographic wave corresponds to reduction (2) and the second wave corresponds to reductions (3) and (6). As the hydrochloric acid concentration is decreased below 3×10^{-3} *M* the second reduction breaks up into two separate ill-defined waves. Thus uranyl gives three reduction waves before the hydrogen discharge wave. Between about 3×10^{-3} *M* hydrochloric acid and about 5×10^{-4} *M* hydrochloric acid the third wave gradually disappears.

In 4.8×10^{-4} *M* hydrochloric acid the third wave disappears completely. The second reduction wave in 4.8×10^{-4} *M* hydrochloric acid is well defined and equal in magnitude to the first one. The second reduction wave then corresponds to reduction (3). No reduction to trivalent uranium occurs since the tetravalent oxide does not dissolve readily in solutions of this or lower acidity. As the excess hydrochloric acid is decreased still further the diffusion current of the first wave decreases due to hydrolysis of the UO_2^{++}. The decrease of the first wave is accompanied by a shift of the half wave potential of the second wave to more positive potentials in the range between 5×10^{-4} *M* excess hydrochloric acid to no excess hydrochloric acid. For instance in 4.79×10^{-4} *M* hydrochloric acid the second half wave potential is about -0.86 v. while in 2.37×10^{-4} *M* excess hydrochloric acid the half wave potential is about -0.62 v.

Polarograms of uranyl chloride solutions with or without added sodium hydroxide in 0.1 *N* potassium chloride as indifferent electrolyte show two waves quite close together. Due to overlapping of the two reduction waves it is difficult to obtain accurate measurements of the first diffusion current. The half wave potential of the first reduction wave is about -0.2 v. *vs.* S.C.E. while that of the second is about -0.6 v. No other polarographic waves of uranyl in solutions without excess free acid or in alkaline non-complex forming solutions have been obtained to a potential of at least -1.7 v. From the two diffusion currents and from the degree of hydrolysis of the uranyl ion calculated from the hydrolysis constant (*v.i.*) it may be inferred that the first reduction wave corresponds to reaction (2) and the second probably to a combination of reactions (3) and (4).

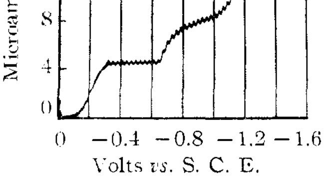

Fig. 2.—Polarogram of 10^{-3} *M* UO_2Cl_2 in 0.2 *M* acetic acid, 5×10^{-4}% thymol.

Well defined second and third uranium waves are obtained only within a narrow range of hydrogen chloride concentrations. Apparently the characteristics of these waves is determined not only by the hydrogen ion concentration of the solution, but also by the type of acid present. For example, in 0.2 *M* acetic acid (Fig. 2) the waves are similar to those obtained in 0.001 *M* hydrochloric acid, although the hydrogen ion concentration in 0.2 *M* acetic acid is about 0.002.

Relation between Diffusion Current and Concentration of Uranyl Chloride in Solutions without Added Acid or Base.—In order to verify the assumptions made in the previous sections regarding the nature of the reduction at the dropping electrode in solutions of uranyl chloride with 0.1 *M* potassium chloride as supporting electrolyte it was necessary to calculate the concentration of UO_2^{++} and its hydrolysis product UO_2OH^+. For this reason it is necessary to know the hydrolysis constant of the UO_2^{++}. This constant was estimated by measuring the hydrogen ion activity of 25° in uranyl chloride solutions with the aid of the quinhydrone electrode. The hydrolysis constant is given by the equation where *C* stands for the concentration

$$\frac{C_{H_3O^+} \times C_{UO_2OH^+} \times \gamma_{H_3O^+}\,\gamma_{UO_2OH^+}}{C_{UO_2^{++}} \times \gamma_{UO_2^{++}}} = K_{\text{Hydrolysis}} = K_w/K_{b1} \qquad (7)$$

and γ for the activity coefficient of the particular ion in solution. The activity coefficients of UO_2^{++} or of UO_2OH^+ were estimated by assuming that the activity coefficient of UO_2^{++} is the same as that of barium ion at the same ionic strength, and that the activity coefficient of UO_2OH^+ is the same as that of potassium ion also at the same ionic strength. The data given by Latimer[6] were used in the estimation of activity coefficients of barium and potassium ions assuming that the activity coefficient of the potassium ion is equal to the activity coefficient of

Table I

Hydrolysis of Uranyl Chloride Solutions at 25°

Concn. UO_2Cl_2, moles/liter	$a_{H_3O^+}$	Concn. H_3O^+ calcd., moles/liter	$K_{\text{hydrolysis}}$
1.25×10^{-3}	2.63×10^{-4}	2.83×10^{-4}	8.7×10^{-5}
2×10^{-3}	2.95×10^{-4}	3.21×10^{-4}	6.5×10^{-5}
4×10^{-3}	4.47×10^{-4}	4.97×10^{-4}	7.6×10^{-5}
5×10^{-3}	4.78×10^{-4}	5.37×10^{-4}	7.0×10^{-5}
6×10^{-3}	5.77×10^{-4}	6.54×10^{-4}	8.9×10^{-5}
1.0×10^{-2}	7.78×10^{-4}	8.99×10^{-4}	9.9×10^{-5}

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(6) W. M. Latimer, "Oxidation Potentials," Prentice-Hall Publishing Co., New York, N. Y.

the chloride ion in solutions of potassium chloride. The results are given in Table I.

The average value of the hydrolysis constant of 8.1×10^{-5} is equal to the ionization constant of the aquo uranyl ion in water as an acid. It is calculated that the first ionization constant of the uranyl hydroxide $K_{b_1} = 1.2 \times 10^{-10}$ which value is in fair agreement with that of 2×10^{-10} reported by Heidt.[7]

Table II gives the values of diffusion currents of uranyl chloride in 0.1 *M* potassium chloride as supporting electrolyte. The concentrations of UO_2^{++} and UO_2OH^+ were calculated from the above hydrolysis constant making the same assumptions with regard to activity coefficients as described earlier. In making the calculations it was assumed that the diffusion currents per millimole per liter of UO_2^{++} and UO_2OH^+ are equal.

TABLE II

DIFFUSION CURRENTS OF URANYL CHLORIDE *vs.* CONCENTRATION IN 0.1 *M* POTASSIUM CHLORIDE

Uranyl chloride, moles/liter	First diffusion current at −0.4 v. *vs.* S.C.E., microamperes Obsd.	Calcd.	Total diffusion current, microamperes Obsd.	Calcd.
2.17×10^{-4}	0.60	0.5	1.55	1.4
4.05×10^{-4}	1.21	1.1	2.88	2.7
5.96×10^{-4}	1.82	1.7	4.18	4.1
7.83×10^{-4}	2.38	2.4	5.41	5.5
9.66×10^{-4}	2.96	3.0	6.60	6.9
1.828×10^{-3}	5.98	6.1	12.30	13.6
2.638×10^{-3}	8.68	9.2	17.50	19.9

In a previous study it was found with a capillary of the characteristics used in the present work that the diffusion current at 25° of the uranyl ion per millimole per liter is equal to 4.08 microamperes. The calculated value of the first diffusion current at −0.4 v. then is equal to 4.08 × concentration UO_2^{++} and the calculated diffusion current at −1.0 v. is equal to

$$4.08\ (C_{UO_2^{++}} \times 2 + C_{UO_2OH^+})$$

The calculated and experimental values of the diffusion currents given in Table II are in reasonable agreement, substantiating the assumption that only UO_2^{++} is reduced at −0.4 v. and that at −1.0 v. UO_2OH^+ is not reduced beyond the pentavalent state.

The experiments described in Table II have been repeated in 0.05 and 0.85 *M* potassium chloride instead of 0.1 *M* potassium chloride. Results very similar to those in Table II were obtained. We do not confirm Herasymenko's statement that the potential of the second reduction of the uranyl is shifted to more positive values with an increase of the potassium chloride concentration.

Polarographic Study of Precipitation of Uranyl Chloride with Sodium Hydroxide.—In order to further verify the assumptions made in previous sections, diffusion currents were measured in solutions of uranyl chloride to which varying slight amounts of hydrochloric acid or sodium hydroxide were added. The solutions used were made air-free and measurements of diffusion currents were made five minutes after the addition of acid or base. The results are given in Table III. The calculated values were estimated in the manner described previously.

TABLE III

AMPEROMETRIC TITRATION OF 100 ML. OF 10^{-3} *M* UO_2Cl_2 IN 0.1 *M* KCl WITH 0.1079 *M* NaOH OR 0.1 *N* HCl

Acid or base added, moles/liter	First diffusion current at −0.4 v. *vs.* S.C.E., microamperes Obsd.	Calcd.	Total diffusion current at −1.0 v. *vs.* S.C.E., microamperes Obsd.	Calcd.
4.79×10^{-4} HCl	3.98	3.7	7.96	7.8
2.37×10^{-4} HCl	3.66	3.5	7.89	7.6
1.18×10^{-4} HCl	3.38	3.4	7.49	7.5
0	3.07	3.2	6.66	7.2
1.89×10^{-4} NaOH	2.64	2.7	6.03	6.7
3.07×10^{-4} NaOH	2.18	2.4	5.26	6.4
5.40×10^{-4} NaOH	1.64	1.7	4.39	5.6
7.24×10^{-4} NaOH	1.19	1.0	3.52	4.9
9.44×10^{-4} NaOH	0.66		2.68	
1.052[a] $\times 10^{-3}$ NaOH	.49		2.15	
1.235×10^{-3} NaOH	.28		1.59	
1.395×10^{-3} NaOH	.04		0.90	
1.576×10^{-3} NaOH	.00		.09	
1.690×10^{-3} NaOH	.00		.00	

[a] Precipitation noticeable.

The calculated and experimental values of the first diffusion current agree substantially. In the presence of excess of base the experimental value of the total diffusion current is smaller than the calculated value. After a period of six weeks of standing the mixtures listed in Table III gave the same diffusion currents as were found originally. A probable explanation of the difference between the calculated and experimental values of the second diffusion current is that part of the UO_2OH^+ hydrolyzes to $UO_2(OH)_2$ and that this is not reducible at the dropping mercury electrode.

Visible precipitation of uranyl begins when about 1.0 mole of sodium hydroxide has been added per mole of uranyl chloride. Precipitation of all the UO_2^{++} and UO_2OH^+ is complete long before the composition $UO_2(OH)_2$ is reached because polarographically detectable amounts of uranium are no longer found in solution after 1.6 mole of sodium hydroxide per mole of uranyl chloride has been added. Further experiments have shown that visible precipitation occurs earlier with increasing concentration of uranyl chloride, increasing concentration of potassium chloride and decreasing speed of titration. Furthermore complete precipitation of all the uranium is found earlier with increasing concentration of uranyl and speed of titration. Our observations are in qualitative but not in quantita-

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(7) L. I. Heidt, *J. Phys. Chem.*, **46**, 624 (1942).

tive agreement with those of Britton and Young[8] who titrated 0.00895 *M* uranyl chloride with sodium hydroxide using quinhydrone as indicator electrode. They found that first precipitation corresponded to the composition $UO_2(OH)_{1.4}Cl_{0.6}$ and precipitation was complete slightly before the composition $UO_2(OH)_2$ was reached.

Polarography of Uranium in Basic Complex Forming Media.—When a solution of 10^{-3} *M* uranyl chloride in 0.1 *M* potassium chloride is titrated amperometrically with ammonium carbonate solution the diffusion current at −1.0 v. *vs.* S.C.E. decreases steadily as ammonium carbonate is added and finally drops to zero. The current voltage curves obtained up to this point are exactly similar to those obtained in the amperometric titration with sodium hydroxide. With the addition of excess ammonium carbonate the precipitated uranium redissolves with the formation of a fairly stable carbonate uranate complex. As the precipitated uranium dissolves a small single polarographic reduction wave appears at about −1.2 v. The polarogram obtained in a mixture which is 0.001 *M* in uranyl chloride and 0.01 *M* in ammonium carbonate is reproduced in Fig. 3. It shows a well-defined first wave and an ill-defined second reduction wave. In 0.1 *M* ammonium carbonate solution both waves are well defined and the second wave becomes almost equal in height to the first (Fig. 3). In 0.5 *M* ammonium carbonate both waves become poorly defined and appear to be about equal in magnitude (Fig. 3). It should be noted that the half wave potential of the first reduction is shifted to more positive values with increasing ammonium carbonate concentration (Table IV). If the reductions were reversible a shift of half wave potential toward more negative values with an increase in concentration of the complexing forming agent should be found.

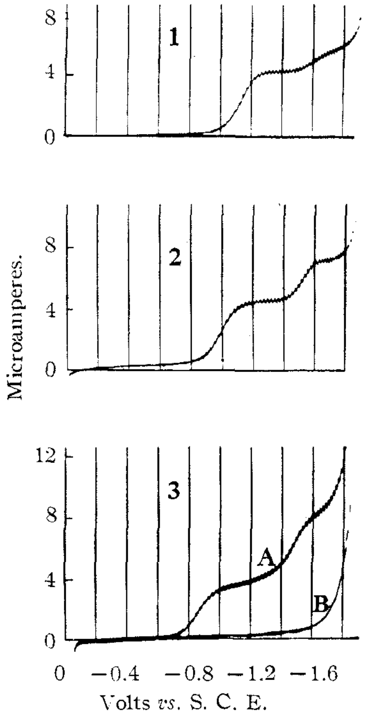

Fig. 3.—Polarograms of 10^{-3} *M* UO_2Cl_2 in ammonium carbonate medium: 1, 0.01 *M* $(NH_4)_2CO_3$, 0.1 *M* KCl; 2, 0.1 *M* $(NH_4)_2CO_3$; 3, 0.5 *M* $(NH_4)_2CO_3$.

Table IV

Effect of Ammonium Carbonate Concentration upon the Half Wave Potential of the First Reduction of U^{VI}

Ammonium carbonate, moles/liter	Half-wave potential volts *vs.* S.C.E.
0.01	−1.1
.1	−1.0
.5	−0.9

In 0.1 *M* ammonium carbonate millimolar uranyl chloride gives a diffusion current of 4.32 microamperes at −1.3 v. *vs.* S.C.E. This value is almost identical with the value of 4.08 microamperes per millimole obtained in moderately acid solution for the first reduction of uranyl.[2] The first reduction wave in moderately acid solution corresponds to an electron transfer of one and it may be postulated that in ammonium carbonate solution the first wave also involves an electron transfer of one for each U^{VI}. If the reduction in ammonium carbonate would correspond to an electron transfer of 2 the diffusion coefficient of carbonate uranate ion should be approximately four times as small as that for the aquo uranyl ion. Such a large difference in diffusion coefficients of the two types of uranyl ions is very improbable. The above conclusion is further substantiated by the behavior of the tetravalent uranium in ammonium carbonate solution.

Tetravalent uranium also forms a stable complex with ammonium carbonate and uranous sulfate is freely soluble in ammonium carbonate solution. However, uranous sulfate dissolved in ammonium carbonate gives no reduction wave up to a potential of at least −1.8 v. This is further evidence that the reduction of uranium in ammonium carbonate does not go beyond the tetravalent state. No anodic or oxidation wave at the dropping mercury electrode was observed with uranous sulfate in ammonium carbonate medium. The foregoing results do not agree

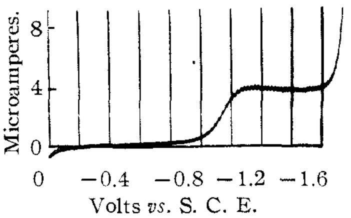

Fig. 4.—Polarogram of 10^{-3} *M* UO_2Cl_2 in 0.1 *M* Na_2CO_3.

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[8] H. T. S. Britton and A. E. Young, *J. Chem. Soc.*, 2467 (1932).

with Strubl's conclusion that each wave in ammonium carbonate solution corresponds to an electron transfer of 2.

The diffusion current of uranyl chloride in ammonium carbonate medium is not proportional to the concentration of uranium. The diffusion current constant at −1.4 v. decreases quite markedly as the concentration of uranium is increased. For example, in 1 *M* ammonium carbonate solution the diffusion current decreased from 5.0 to 3.62 microampere millimole liter when the concentration of uranyl chloride was increased from 2.6×10^{-5} to 3.07×10^{-3} *M*. For this reason we do not recommend ammonium carbonate as supporting electrolyte for the polarographic determination of U^{VI}. We recommend for this purpose approximately 0.1 *M* hydrochloric acid in which medium the diffusion current is proportional to the uranyl concentration.[2]

Instead of ammonium carbonate as the complex forming agent sodium carbonate can be used. In 0.1 *M* sodium carbonate the polarographic reduction wave of uranium appears to be well defined (see Fig. 4). There is no indication of a second reduction similar to that found when ammonium carbonate is used. Although the reduction wave appears to be well defined in 0.1 *M* sodium carbonate the diffusion current again is not proportional to concentration of uranium.

Summary

1. From polarograms obtained in solutions of uranyl chloride containing 0.1 *M* potassium chloride, either without or with small amounts of acid or alkali it is concluded that the first wave corresponds to the reduction of UO_2^{++}. The hydrolysis product UO_2OH^+ from UO_2^{++} is not reduced at the first wave, but is reduced at the second wave together with U^V. The UO_2OH^+ is reduced to pentavalent and not to tetravalent uranium. It is assumed that under the specified conditions UO_2 and UO_2OH separate as insoluble films at the surface of the dropping mercury.

2. The hydrolysis constant of the uranyl ion at 25° is 8.1×10^{-5}.

3. Amperometric titration of uranyl chloride with sodium hydroxide yields complete precipitation long before the stoichiometric end point $UO_2(OH)_2$ is reached.

4. At the proper concentration of ammonium carbonate two well-defined waves of U^{VI} are found. Contrary to statements in the literature each reduction wave corresponds to an electron transfer of one. Carbonate is not recommended as supporting electrolyte for the polarographic determination of U^{VI} because the diffusion current is not proportional to the concentration.

MINNEAPOLIS, MINNESOTA RECEIVED JUNE 24, 1946

[CONTRIBUTION FROM THE METCALF RESEARCH LABORATORY OF BROWN UNIVERSITY]

Properties of Electrolytic Solutions. XXIII. Conductance of Several Quaternary Onium Salts in Ethylene Chloride at 25°[1]

BY LELAND F. GLEYSTEEN[2] AND CHARLES A. KRAUS

I. Introduction

Earlier papers of this series have served to elucidate the interaction between ions in solution as a function of their dimensions, on the one hand, and of the dielectric constant of the solvent medium, on the other. There are, however, specific factors that remain to be examined, more particularly, the detailed structure and constitution of the ions, the constitution of the molecule of the solvent medium and the interaction of ions with molecules of a third component.

This is the first of a series of papers in which will be presented the results of investigations intended to elucidate how the factors mentioned above influence the ionic equilibria in several solvents. The solvents chosen are ethylene chloride, pyridine, nitrobenzene and benzene. The dielectric constants of the first three solvents (10.23, 12.01 and 34.5, respectively) are sufficiently high to permit direct evaluation of the limiting conductance for all but very weak electrolytes. One of these solvents, pyridine, is a basic solvent while the others have neither acidic nor basic properties.

The dielectric constants for pyridine and ethylene chloride differ but little and afford a favorable opportunity for studying the influence of solvent constitution on ionic equilibria. The higher dielectric constant of nitrobenzene and its larger molecules, with respect to ethylene chloride, permits of a study of these factors for two inactive solvents otherwise very similar. Numerous inorganic salts may be studied in pyridine and a few are sufficiently soluble in nitrobenzene to permit of their investigation.

Limiting conductances cannot be reliably evaluated in benzene; however, the behavior of concentrated solutions of electrolytes in benzene is of great interest because of the light that these solutions throw on the problem of concentrated solutions of electrolytes. The molecular weights of electrolytes in benzene have likewise been investigated up to fairly high concentrations and

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[1] This paper is based on a portion of a thesis presented by L. F. Gleysteen in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Brown University, May, 1936.

[2] University Fellow at Brown University, 1934–1936.