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Polarography of Uranyl Complex with *p*-Aminothiophenoxyacetic Acid in Dimethyl Sulfoxide Solution

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The polarography of uranyl ion in dimethyl sulfoxide (DMSO) was investigated in the DMSO concentration range 40—99 vol%. The complex species identified is $UO_2(DMSO)_6^{2+}$; it is transformed into $UO_2(DMSO)_2^+$ and UO_2^+ after the electrode reduction. In the presence of *p*-aminothiophenoxyacetic acid, the uranyl ion in the DMSO medium produces a two-step wave at lower pH and higher concentration of DMSO. The limiting current of the wave is controlled partially by the kinetics of the preceding chemical reaction and partially by the diffusion of the complex. The rate constant and diffusion coefficient of the reduction process were determined. At pH around 4, the formation of binuclear uranyl complexes was confirmed.

Gutman and Shoeber were the first to study the polarography of a number of inorganic ions in dimethyl sulfoxide solution.[1-3] They found that many polarographic reductions appeared to be irreversible in dimethyl sulfoxide. The polarography of uranyl complex with fumarate in a dimethyl sulfoxide concentration up to 40 vol% has been studied.[4]

Because of difficult solubility of *p*-aminothiopenoxyacetic acid in water, dimethyl sulfoxide was chosen as a solvent to study the complex of uranium(VI) with *p*-aminothiophenoxyacetic acid. The concentration range of dimethyl sulfoxide was 40—99 vol%.

Experimental

Apparatus. The polarograph and technique used in this work have been reported.[5] The capillary characteristics were: $m=1.307$ mg/sec and $t=4.88$ sec/drop at $H=67.3$ cm in 1.0 mM $UO_2(ClO_4)_2$, 70 vol% dimethyl sulfoxide, 0.08M *p*-aminothiophenoxyacetic acid, 0.15M $NaClO_4$ and 0.002% Triton X-100 at closed circuit. The hydrogen used for deaeration of the polarographic solution was presaturated with dimethyl sulfoxide by passing through a bottle filled with 70 vol% dimethyl sulfoxide solution. All polarograms were taken at 30±0.1°C.

Chemicals. *p*-Aminothiophenoxyacetic acid (P-ATPAA) was of research grade, Aldrich Chemical Co., and the solution was freshly prepared for each run.

Dimethyl sulfoxide (DMSO) was of chemical pure reagent (Wako Pure Chemical Industries Co.) and was not further purified.

All the polarograhic solutions contained 0.15M $NaClO_4$ as supporting electrolyte and 0.002% Triton X-100 as maximum suppressor.

Results and Discussion

Uranyl Ion in DMSO in the Absence of p-*ATPAA.* The polarographic behavior of uranyl ion in DMSO was studied in the DMSO concentration range 40—99 vol% over the pH range 2.40—5.25. Beyond this pH range, the waves become less well-defined. Above DMSO concentration 90 vol%, a strong maximum appears and the concentration of Triton X-100 must be increased from 0.002% to 0.03% to suppress the maximum.

Table 1. Wave characteristics of uranyl ion in DMSO (1.0 mM $UO_2(ClO_4)_2$, 0.15M $NaClO_4$, 0.002% Triton X-100)

C_{DMSO} vol %	pH	$-E_{1/2}$ V *vs.* SCE	i_d μA	$E_{1/4}-E_{3/4}$
40	2.40	0.313	1.82	0.058
	3.30	0.312	1.66	0.057
	4.00	0.312	1.71	0.061
	5.00	0.312	1.61	0.062
60	2.50	0.366	1.83	0.055
	3.00	0.378	1.64	0.058
	4.30	0.378	1.44	0.059
	5.25	0.381	1.25	0.061
80	2.60	0.396	1.79	0.060
	3.70	0.420	1.65	0.059
	4.20	0.430	1.51	0.057
	4.78	0.430	1.30	0.061
99[a]	2.95	0.458	2.55	0.067
	3.50	0.474	1.82	4.060
	4.60	0.498	1.17	0.060
	4.95	0.492	1.14	0.066

a) 0.03% Triton X-100

The values of $E_{1/4}-E_{3/4}$ are in the range 0.055—0.067 (Table 1); the temperature coefficients of half-wave potential and diffusion current are −0.3 mV/°C and 1.5%/°C, respectively, in the temperature range 24—36°C. The results indicate that the electrode reductions are one-electron reversible and diffusion-controlled reduction process.

The dependence of the half-wave potential of uranyl ion on pH value in various concentrations of DMSO is shown in Fig. 1. The breaking point on the plots of $-E_{1/2}$ *vs.* pH is a function of the concentration of DMSO. Above 70 vol% DMSO, the breaking points are at pH 4.0; and at pH 3.0 for 50—60 vol% DMSO. However, below 40 vol% DMSO no breaking point appeared indicating that no hydrogen ion is invloved in the electrode reaction for any pH value of solution. The slope of the plots at pH<4.0 is also a function of DMSO concentration. The slope reaches 0.051 at 90 vol% DMSO. It indicates that one hydrogen ion is involved

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1) V. Gutmann, P. Heilmayer, and G. Schoeber, *Monatsh, Chem.*, **92**, 240 (1961).

2) V. Gutmann and G. Schoeber, *Z. Anal. Chem.*, **171**, 339 (1959).

3) G. Gritzner, V. Gutmann, and G. Schoeber, *Monatsch, Chem.*, **96**, 1056 (1965).

4) T. T. Lai and T. Y. Chen, *Rev. Polarogr. Jap.*, **16**, 75 (1969).

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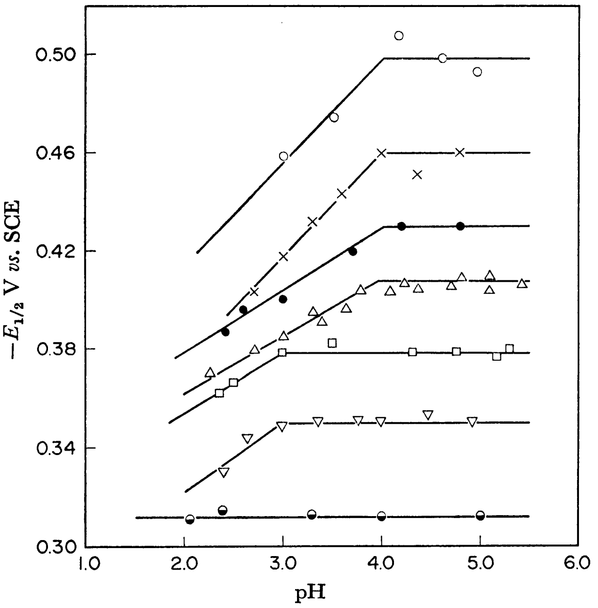

Fig. 1. Effect of pH on the half-wave potential of uranyl ion in DMSO.
1.0 mM $UO_2(ClO_4)_2$, 0.15 M $NaClO_4$, 0.002% Triton X-100 and various concentration of DMSO:
◒40 vol%; ▽50 vol%; □60 vol%; △70 vol%; ●80 vol%; ×90 vol%; ○99 vol%.

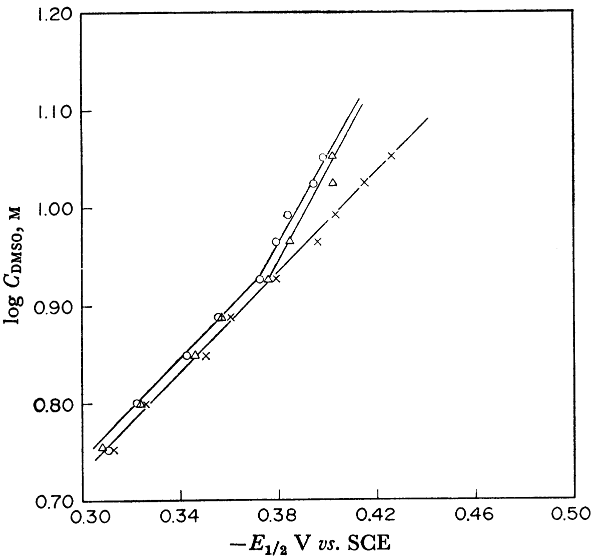

Fig. 2. Plots of log C_{DMSO} vs. $-E_{1/2}$ for uranyl ion in DMSO.
1.0 mM $UO_2(ClO_4)_2$, 0.15 M $NaClO_4$ and 0.002% Triton X-100.
× pH 4.00; △ pH 3.00; ○ pH 2.75.

in the electrode reaction. At $pH>4.0$ no hydrogen ion takes part in the electrode reaction for any concentration of DMSO.

Figure 2 shows the half-wave potential of uranyl ion in DMSO as a function of the lograrithmic concentration of DMSO. At $pH \geq 4.0$ and $[DMSO]<80$ vol%, a straight line with a slope 0.377 was obtained. At $pH<4.0$, breaking points were found; the slopes are 0.377 and 0.230 for 40 vol%$<[DMSO]<$60 vol% and 60 vol%$<[DMSO]<$80 vol%, respectively.

Introducing these values of slopes into the half-wave potential equation

$$(E_{1/2})_c = \text{const.} - (p-q)0.060 \log C_{\text{DMSO}} - 0.060a\,\text{pH} \quad (1)$$

for the electrode reaction

$$UO_2(DMSO)_p^{2+} + aH^+ + e = UO_2(DMSO)_q^+ + a\text{DMSO}\cdot H^+ + (p-q-a)\text{DMSO} \quad (2)$$

the values of (p-q) become equal to 6 at $pH>4.0$ and equal to 6 and 4 at $pH<4.0$.

The coordination between uranyl ion and DMSO has been proved by the donation of a lone pair of electrons on oxygen atom of DMSO of a monodentate ligand.[6]

Thus, it was inferred that the uranyl-DMSO complex species formed is $UO_2(DMSO)_6^{2+}$, proving that the uranyl ion is solvated completely by six molecules of DMSO in the presence of an excess DMSO. However, it is transformed into $UO_2(DMSO)_2^+$ and UO_2^+ after it undergoes the electrode reduction.

Uranyl Ion in DMSO in the Presence of p-*ATPAA*. The polarographic behavior of the uranyl-DMSO-*p*-ATPAA system was studied systematically in the pH range 2.75—6.00 with DMSO concentration 65—99 vol% and *p*-ATPAA concentration 0.01—0.12M.

Typical current-potential curves for the polarographic solution containing 1.0 mM $UO_2(ClO_4)_2$, 0.08M *p*-ATPAA, 90 vol% DMSO, 0.15M $NaClO_4$ and 0.002% Triton X-100 at various pH values are presented in Fig. 3. At pH 4.80, a single well-defined wave was obtained; however, at $pH<4.30$, two-step waves were observed. The electrocapillary curves are shown in Fig. 4. A large decrease in the drop time of the capillary was observed by the addition of *p*-ATPAA proving the existence of adsorption of *p*-ATPAA on the dropping mercury electrode. The formation of two-step waves was attributed to the adsorption of *p*-ATPAA on the dropping mercury

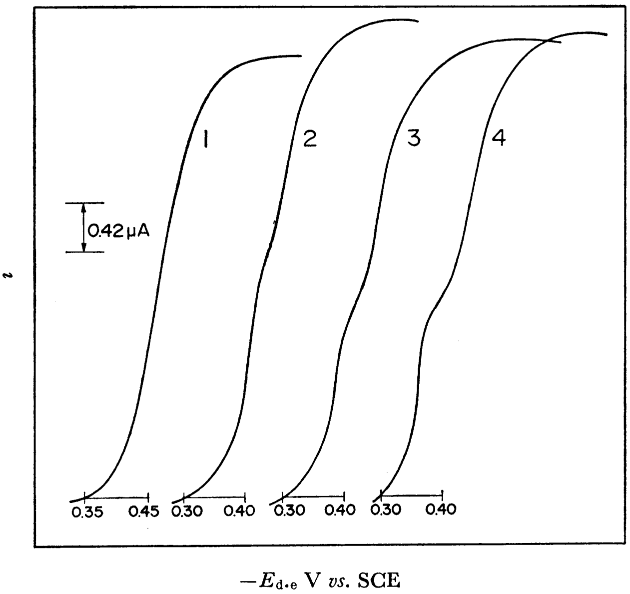

Fig. 3. Typical current-potential curves.
(1.0 mM $UO_2(ClO_4)_2$, 0.08 M *p*-ATPAA, 90 vol% DMSO, 0.15 M $NaClO_4$, 0.002% Triton X-100)
1. pH 4.80; 2. pH 4.30; 3. pH 3.72; 4. pH 3.30.

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[6] V. Krishnan and C. C. Potel, *Indian J. Chem.*, **2**, (10) 416 (1964).

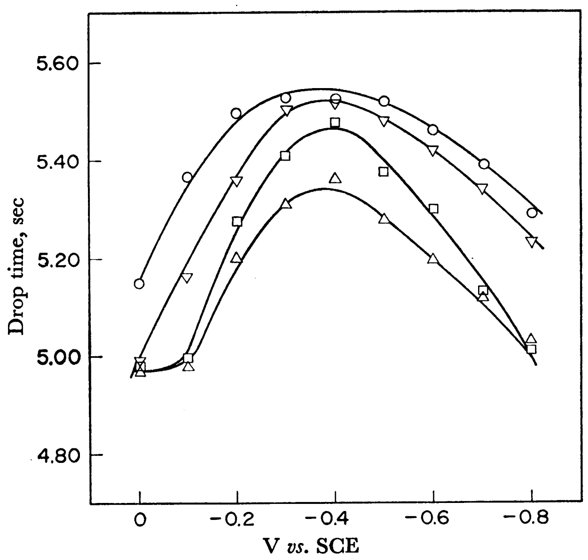

Fig. 4. Electrocapillary curve of mercury.
1 mM $UO_2(ClO_4)_2$, 0.15 M $NaClO_4$, 0.002% Triton X-100, 80 vol% DMSO at pH 4.00 and various concentrations of *p*-ATPAA: ○ 0 M; ▽ 0.02 M; □ 0.04 M; △ 0.08 M.

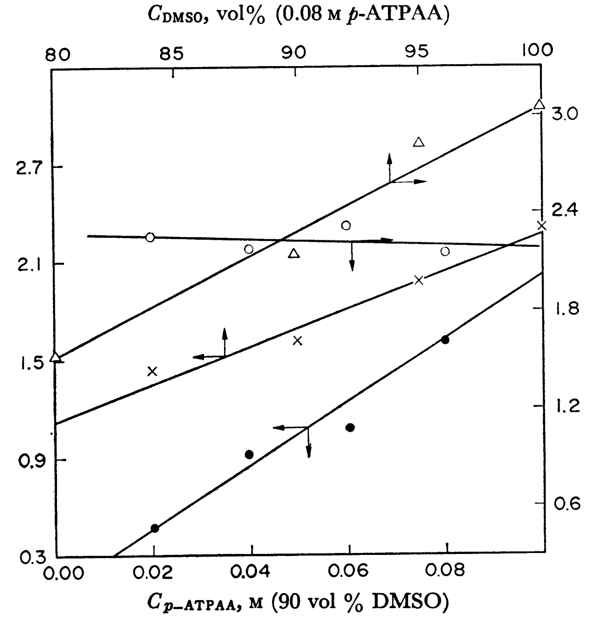

Fig. 5. Effect of concentrations of DMSO and *p*-ATPAA on the limiting currents of the two waves.
(1.0 mM $UO_2(ClO_4)_2$, 0.15 M $NaClO_4$, 0.002% Triton X-100, pH 3.3)

electrode.[7] The lower pH value and higher DMSO concentration favor the formation of two-step waves.

The effect of the concentration of DMSO and *p*-ATPAA on the limiting currents of the two waves is shown in Fig. 5 and the wave parameters of the two-step waves in Table 2. The limiting current of the first wave increases with the concentrations of DMSO and *p*-ATPAA; however, the limiting current of the second wave is independent of the concentration of *p*-ATPAA and increases with the concentration of DMSO.

Table 2. Wave parameters of the two-step waves
(1.0 mM $UO_2(ClO_4)_2$, 0.08 M *p*-ATPAA, 0.15 M $NaClO_4$, 0.002% Triton X-100 at pH 3.30)

C_{DMSO} vol %	$-(E_{1/2})_1$ V *vs.* SCE	$-(E_{1/2})_2$ V *vs.* SCE	$(i_e)_1$ μA	$(i_e)_2$ μA
80	0.370	0.440	4.8	5.1
90	0.360	0.460	5.4	6.8
95	0.355	0.465	6.6	9.6

Nature of the Limiting Current. A preceding chemical reaction takes place between the $UO_2(DMSO)_6^{2+}$ complex and *p*-ATPAA producing a mixed ligand complex and reaches a chemical equilibrium; then an electrode reaction occurs to the mixed ligand complex.

In an attempt to determine both the kinetic parameter of the preceding chemical reaction and the nature of the limiting current of the polarogram of the mixed ligand complex, the following equation[8] was applied

$$\bar{i} = r \cdot 1255 n m^{2/3} \tau^{2/3} C_0 k \left[1 - \mathrm{erf}\left(k\sqrt{\frac{\tau}{D}}\right)\right] \exp\left[\frac{k^2\tau}{D}\right] \quad (3)$$

where k is the rate constant, r the ratio of the average limiting current to the maximum limiting current and a function of τ and $kD^{-1/2}$, and other notations have their usual meaning.

Introducing $m = m_0 H$ and $\tau_0 = \tau H$; Eq. (3) becomes;

$$i = r \cdot 1255 n m_0^{2/3} \tau_0^{2/3} C_0 k \left[1 - \mathrm{erf}\left(k\sqrt{\frac{\tau_0}{HD}}\right)\right] \exp\left[\frac{k^2\tau_0}{HD}\right] \quad (4)$$

and

$$\frac{\bar{i}}{\bar{i}_0} = \frac{r}{r_0} \frac{\left[1 - \mathrm{erf}\left(k\sqrt{\frac{\tau_0}{HD}}\right)\right]}{\left[1 - \mathrm{erf}\left(k\sqrt{\frac{\tau_0}{H_0 D}}\right)\right]} \exp\left[\frac{k^2\tau_0}{HD} - \frac{k^2\tau_0}{H_0 D}\right] \quad (5)$$

The plots of $\bar{i}/\bar{i}_0$ against mercury head H using $kD^{-1/2}$ as parameter are shown in Fig. 6, in which $\bar{i}_0$ is the average limiting current for the polarograms ob-

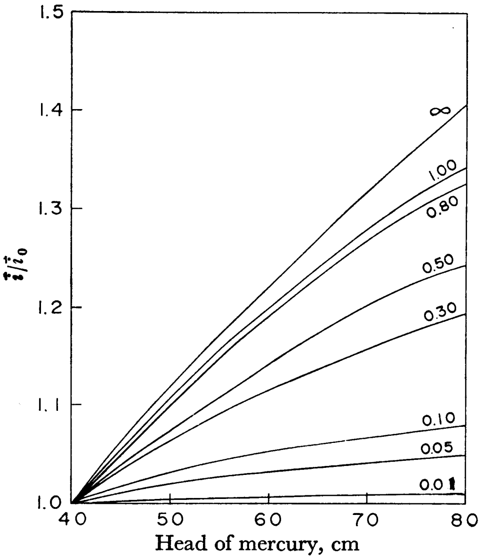

Fig. 6. Plots of the average limiting current ratio *vs.* head of mercury; $kD^{-1/2}$ as paramenser.
($\bar{i}_0$: average limiting current at H=40 cm and τ_0=2700 sec-mm/drop)

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[7] J. Heyrovsky and J. Kuta, "Principles of Polarography," Interscience Publishers, New York, Vol. 1, 96, (1966).

[8] P. Delahay, *J. Amer Chem. Soc.*, **73**, 4944 (1951).

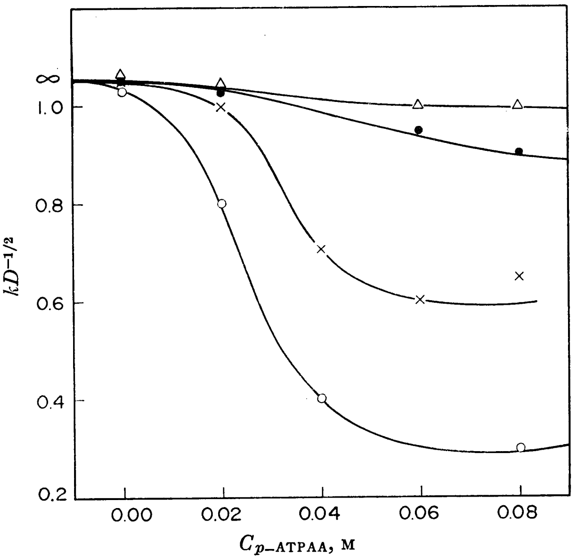

Fig. 7. Variation of $kD^{-1/2}$ value as a function of $C_{p\text{-ATPAA}}$ for different concentrations of DMSO.
(1.0 mM $UO_2(ClO_4)_2$, 0.15 M $NaClO_4$, 0.002% Triton X-100)
△ 70 vol% DMSO at pH 4.90; ● 90 vol% DMSO at pH 4.90; × 70 vol% DMSO at pH 3.30; ○ 90 vol% DMSO at pH 3.30.

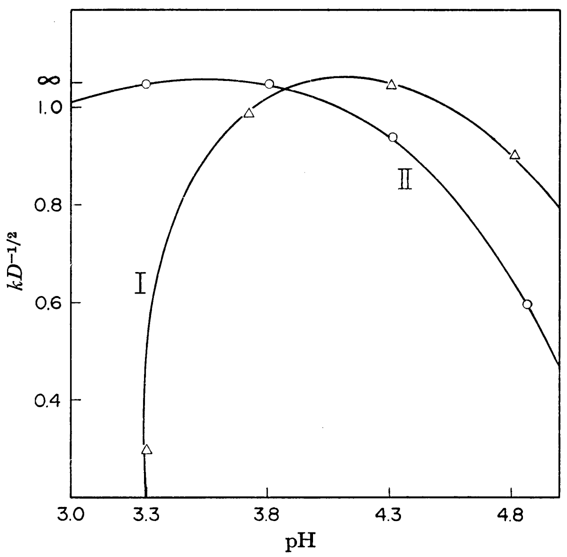

Fig. 8. Variation of $kD^{-1/2}$ values as a function of pH value. (1.0 mM $UO_2(ClO_4)_2$, 90 vol% DMSO, 0.08 M p-ATPAA, 0.15 M $NaClO_4$ and 0.002% Triton X-100)
△ 30°C; ○ 37°C.

tained from a given polarographic solution at $H=$ 40 cm and $\tau_0=2700$ sec-mm/drop. We see that the limiting current is practically diffusion-controlled when $kD^{-1/2}$ is larger than 1.0 $\sec^{-1/2}$. At $k=\infty$, the error function should be expanded into a series and Eq. (3) can be reduced to Ilkovic equation.9) On the contrary, the limiting current is essentially rate-controlled when $kD^{-1/2}$ is smaller than 0.01 $\sec^{-1/2}$. When $kD^{-1/2}$ is between 0.01 and 1.00 $\sec^{-1/2}$, the limiting current is controlled partially by diffusion and partially by the rate of the preceding chemical reaction.

The variations of $kD^{-1/2}$ values as a function of the concentration of p-ATPAA and as a function of pH value are demonstrated in Figs. 7 and 8, respectively. The values of $kD^{-1/2}$ were evaluated by determining the $\bar{i}/\bar{i}_0$ values by varying mercury head and by applying Fig. 6.

It is obvious from Fig. 7 that in the absence of p-ATPAA, irrespective of the concentration of DMSO and the pH value, the value of $kD^{-1/2}$ is infinite, indicating that the electrode reduction of the uranyl-DMSO complexes is completely diffusion-controlled. This result is in accord with that obtained from the temperature coefficient of diffusion current. The $kD^{-1/2}$ value decreases with the increase of the concentration of p-ATPAA and DMSO. This reveals that the higher concentrations of DMSO and p-ATPAA enhance the rate-controlled character of the electrode reduction process of uranyl-DMSO-p-ATPAA complexes.

A complete diffusion-controlled reduction process of uranyl-DMSO-p-ATPAA complex is obtained in the pH range 3.7—4.5 at 30°C (Fig. 8). Polynuclear complexes are formed in the pH range and the increment of viscosity of the polarographic solution rendered the electrode reduction to be diffusion-controlled.10) However, beyond this pH range, a rate-controlled character takes part in the reduction of the complex.

It can be expected that at higher temperature the adsorption is hindered and no rate-controlled phenomenon appeared even at pH<3.7 (curve II, Fig. 8).

Formation of Polynuclear Complexes. The temperature coefficient of the half-wave potential is determined to be 0.6 mV/°C in a polarographic solution containing 1.0 mM $UO_2(ClO_4)_2$, 70 vol% DMSO, 0.08M p-ATPAA, 0.15M $NaClO_4$, and 0.002% Triton X-100 at pH 4.30 in temperature range 18.0—39.5°C. This indicates that the electrode process is reversible. However, as shown in Table 3, in the vicinity of pH 4, the mean $E_{1/4}$—$E_{3/4}$ value is 0.039; the deviation of this value from the

TABLE 3. EVIDENCE FOR THE FORMATION OF BINUCLEAR COMPLEXES
(1.0 mM $UO_2(ClO_4)_2$, 70 vol % DMSO, 0.15M $NaClO_4$, 0.002% Triton X-100 and various concentrations of p-ATPAA)

pH	$\frac{E_{1/2}-E_{7/8}}{E_{1/8}-E_{1/2}}$	$E_{1/4}-E_{3/4}$	a	b
$C_{ATPAA}=0.02$M				
5.50	1.225	0.060	0.80	1.25
4.20	0.770	0.040	2.20	1.10
3.35	1.000	0.060	1.00	1.00
$C_{ATPAA}=0.08$M				
4.90	1.000	0.060	1.00	1.00
4.45	0.920	0.040	1.63	1.30
3.14	1.000	0.060	1.00	1.00
$C_{ATPAA}=0.12$M				
5.60	0.770	0.057	1.60	0.80
4.08	0.900	0.036	1.85	1.40
3.40	0.930	0.051	1.25	1.00

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9) I. M. Kolthoff and J. J. Lingane, "Polarography" Interscience Publisher, New York, Vol. 1, 63 (1952).

10) Michel Boudart, "Kinetics of Chemical Processes" Prentice-Hall, Inc., United Kingdom, 145 (1968).

TABLE 4. RATE CONSTANTS AND DIFFUSION COEFFICIENTS OF URANYL COMPLEXES
(1.0 mM $UO_2(ClO_4)_2$, 0.15M $NaClO_4$, 0.002% Triton X-100)

Complexing agent	pH	$kD^{-1/2}$(sec$^{-1/2}$)	*r*	*k* (cm/sec)	*D* (cm^2/sec)
70 vol% DMSO	3.15	1.00	0.77	2.24×10^{-3}	5.00×10^{-6}
70 vol% DMSO; 0.08M *p*-ATPAA	4.90	1.00	0.77	2.43×10^{-3}	5.90×10^{-6}
90 vol% DMSO; 0.08M *p*-ATPAA	3.30	0.30	0.68	1.99×10^{-3}	4.42×10^{-5}

heoretical value of 0.057 V for one-electron reversible reduction was no doubt due to the asymmetry of the polarogram which arose from the polymerization effect.[11]

The polymerization degree for the polynuclear complexes formed was determined by the same method as described previously.[11] The results are shown in Table 3, in which *a* and *b* denote the polymerization degree of the oxidized and reduced form of the uranium complex, respectively. It is obvious from Table 3 that a binuclear uranyl complex was formed in the vicinity of pH 4.

Rate Constant and Diffusion Coefficient. The rate constant *k* of the preceding chemical reaction and the diffusion coefficient *D* of the uranyl complex can be determined by applying Eq. (4) for $m_0=2.734\times10^{-3}$ mg/sec-mm, $\tau_0=2.7\times10^3$ sec-mm/drop and $n=1$ values. Table 4 lists some data of *k* and *D* of the uranyl complexes. The $kD^{-1/2}=1.00$ and $k\gg D$ for uranyl-DMSO and uranyl-DMSO-*p*-ATPAA (70 vol% DMSO; 0.08M *p*-ATPAA) systems show again that the electrode reaction is diffusion-controlled. However, the data obtained for uranyl-DMSO-*p*-ATPAA (90 vol% DMSO; 0.08M *p*-ATPAA) system indicate a partial kinetic-controlled character. These results support the deduction.

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[11] T. T. Lai and B. C. Wang, *Anal. Chem.*, **36**, 26 (1964).