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The Polarographic Behavior of Tl(I) and Na(I) Ions and Bis(*o*-phenylenediamine)nickel(II) in *N,N*-Dimethylformamide–Dimethyl Sulfoxide Mixtures

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The polarographic behavior of Tl(I) and Na(I) ions and the bis(*o*-phenylenediamine)nickel(II) [Ni(opd)$_2$] complex were studied using *N,N*-dimethylformamide (DMF)–dimethyl sulfoxide (DMSO) mixed solvents of various compositions. The diffusion currents of the Tl(I) and Na(I) ions and [Ni(opd)$_2$] complex decreased linearly with an increase in the concentration of the supporting electrolyte in DMF–DMSO solvent mixtures. The ratio of the slope to the intercept is related to the D coefficient in the revised Jones-Dole equation of viscosity. Ion-solvent interaction was considered from the Stokes radius, calculated from the diffusion current at an infinite dilution of the supporting electrolyte. The half-wave potentials of both the Tl(I) ion and the [Ni(opd)$_2$] complex shifted to a negative direction with an increase in the concentration of the supporting electrolyte. Although the half-wave potential of the [Ni(opd)$_2$] complex shifted to a slightly positive potential, that of the Tl(I) ion shifted to a negative potential with an increase in the content of DMSO.

It has been reported that, in water-organic mixed solvent systems, the observed diffusion current (i_d) becomes lower than that calculated from the solution viscosity (η) by means of this equation: $i_d = i_{d\,aq}\,\eta_{aq}^{1/2}/\eta^{1/2}$ (aq=aqueous solution) with an increase in the organic solvent contents for metal ions and ionic organic compounds, but the reverse tendency is found for neutral organic compounds.[1] In such systems, the phenomena may be due to the characteristics of water as a solvent, that is, its strong capacities of hydrogen-bonding and dissociation. DMF–DMSO mixed solvents in which both components have similar dielectric constants and dipole moments, but different viscosities, were chosen in order to clarify the above points. The present paper aims to examine the change in polarographic behavior between ionic and neutral depolarizers with the change in the composition of DMF–DMSO mixed solvents by using the Tl(I) ion and the [Ni(opd)$_2$] complex.

Experimental

DMF and DMSO were used as the solvents. The solvents were purified by distillation under reduced pressure, adding Wako 5A molecular sieves. The water contents, as determined by the Karl-Fischer method, were less than 0.01%. The mixed solvents were represented in volume %. The $TlClO_4$ was recrystallized once from distilled water. The tetraethylammonium perchlorate (TEAP), after having been prepared in the usual manner, was recrystallized at least eight times from distilled water.[2] The tetrapropylammonium perchlorate (TPAP) was prepared in the usual manner and recrystallized from distilled water. The tetrabutylammonium perchlorate (TBAP) was prepared by ion-exchange methods[3] and purified by recrystallization from acetone–water and ethanol–water. These crystals were dried under reduced pressure at 60 °C. The [Ni(opd)$_2$] was prepared by air-oxidizing, for over 24 h, nickel(II) chloride hexahydrate and *o*-phenylenediamine; it was purified by using Soxlet's extractor with acetone.[4]

The polarographic diffusion current was measured by means of a Yanagimoto Type P-8 polarograph. An aqueous saturated calomel electrode was used as the reference electrode. The characteristics of the dropping mercury electrode used were m=1.710 mg s^{-1} and t=4.1 s at h=50 cm. The counter electrode was 0.5 mm ϕ platinum wire. The electrolytic cell was an H-shaped cell separated by a diaphragm; contact between the electrolytic cell and the reference electrode was made by means of an agar bridge containing saturated NaCl and a 1500-cps methylcellulose bridge containing 1 M (1 M=1 mol dm^{-3}) $NaClO_4$ in the same solvent composition as the test solution.[5] These bridge were renewed for each experiment. The viscosity and density were measured with, respectively, an Ostwald viscometer and a Weld-type picnometer at 25 °C.

Results and Discussion

The wave heights of the Tl(I) ion at various concentrations of TBAP were measured in DMF–DMSO mixed solvents. The results are shown in Fig. 1. Since the concentration (c) of the supporting electrolyte is

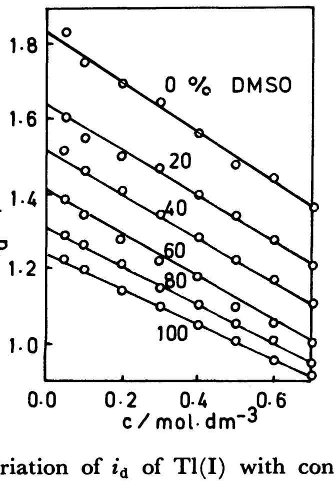

Fig. 1. Variation of i_d of Tl(I) with concentration of TBAP in DMF–DMSO.

sufficiently higher relative to the depolarizer, there was no influence of the migration current. The diffusion current of the Tl(I) ion varies little with the c of the supporting electrolyte in an aqueous solution, but it varies significantly in DMF–DMSO mixed solvents. According to the tracer-diffusion theory, the diffusion coefficient, *D*, decreases linearly with the $c^{1/2}$ of the supporting electrolyte; also, the diffusion current must decrease linearly with the $c^{1/2}$ of the supporting electrolyte. In the present work, however, the diffusion current decreased linearly with the c of the supporting electrolyte at higher concentrations of the supporting electrolyte. This might be attributed to a depreciation of solvent activity due to the solvation of the ion. The measurements were also carried out by exchanging the supporting electrolyte with NaClO$_4$, TEAP, and TPAP. Furthermore, the measurements were also carried out on the Na(I) ion and [Ni(opd)$_2$], depolarizers other than the Tl(I) ion. In order to facilitate the comparison of the slope of the plot of i_d *vs.* the c of the supporting electrolyte, the following equation was used:

$$i_{d.r} = i_d/i_{d.0} = 1 - \alpha c \qquad (1)$$

where i_d is the diffusion current at the c of the supporting electrolyte; $i_{d.0}$, that at an infinite dilution of the supporting electrolyte, and α, the slope. Table 1 represents the α values for Tl(I) and Na(I) ions and for [Ni(opd)$_2$] in DMF–DMSO mixed solvents containing each supporting electrolyte. It may be seen from Table 1 that the α values become larger in this order: TEAP, NaClO$_4$, and TBAP. However, since the effect of the c of the supporting electrolyte on the viscosity of the solution is contained in the magnitude of the value of α, the concentration dependence of the viscosity must also be examined.

The viscosity of the solution at various concentra-

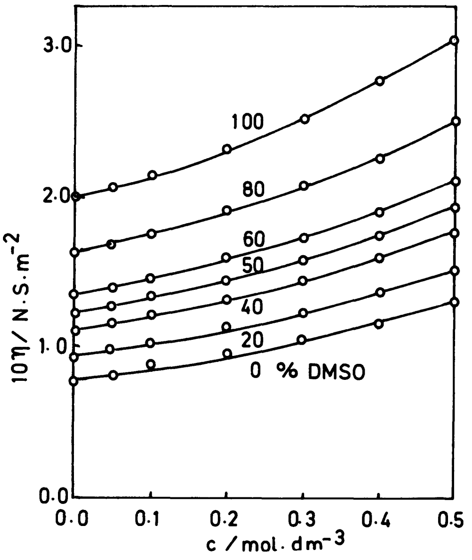

Fig. 2. Plots of η *vs.* concentration of TBAP in DMF–DMSO.

Table 1. α values in DMF–DMSO mixed solvents for NaClO$_4$, TEAP, and TBAP as supporting electrolytes

DMSO%	α/l·mol^{-1}						
	Tl(I)			Na(I)		[Ni(opd)$_2$]	
	NaClO$_4$	TEAP	TBAP	TEAP	TBAP	TEAP	TBAP
0	0.32	0.19	0.37	0.12	0.39	0.15	0.31
20	0.31	0.16	0.35	0.17	0.36	0.24	0.32
40	0.30	0.20	0.40	0.17	0.34	0.15	0.36
50	0.30	0.20	0.41	0.20	0.33	—	—
60	0.25	0.23	0.41	0.26	0.33	0.29	0.38
80	0.22	0.22	0.39	0.20	0.33	0.27	0.42
100	0.32	0.30	0.38	0.27	0.34	0.23	0.38

Table 2. A, B, and D coefficients of the Jones-Dole equation for NaClO$_4$, TEAP, TPAP, and TBAP

DMSO%	A/l$^{1/2}$·mol$^{-1/2}$				B/l·mol^{-1}				D/l^2·mol^{-2}			
	NaClO$_4$	TEAP	TPAP	TBAP	NaClO$_4$	TEAP	TPAP	TBAP	NaClO$_4$	TEAP	TPAP	TBAP
0	−0.088	0.021	0.042	0.022	0.70	0.61	0.60	0.75	1.10	0.24	0.71	0.84
20	0.009	0.010	−0.023	0.011	0.35	0.60	0.59	0.70	0.66	0.26	0.62	0.94
40	0.038	0.039	−0.003	0.067	0.56	0.46	0.66	0.58	0.52	0.30	0.42	0.98
50	0.070	0.104	—	0.068	0.46	0.49	—	0.56	0.69	0.34	—	1.05
60	0.054	0.054	0.021	0.021	0.56	0.52	0.62	0.68	0.36	0.28	0.45	0.81
80	−0.008	0.030	−0.009	0.017	0.71	0.49	0.58	0.68	0.47	0.29	0.52	0.87
100	−0.046	0.010	−0.026	0.018	0.79	0.47	0.50	0.58	0.47	0.29	0.67	0.87

Table 3. K values in DMF-DMSO mixed solvents for $NaClO_4$, TEAP, and TBAP as supporting electrolytes

DMSO%	K/l·mol^{-1}						
	Tl(I)			Na(I)		[Ni(opd)$_2$]	
	$NaClO_4$	TEAP	TBAP	TEAP	TBAP	TEAP	TBAP
0	0.163	0.133	0.069	0.214	0.028	0.141	0.136
20	0.057	0.162	0.078	0.148	0.083	0.058	0.128
40	0.049	0.107	0.009	0.151	0.086	0.160	0.073
50	0.062	0.072	−0.002	0.076	0.117	—	—
60	0.096	0.063	−0.017	0.024	0.117	−0.019	0.060
80	0.175	0.049	−0.005	0.077	0.105	−0.016	−0.012
100	0.125	−0.072	0.004	−0.012	0.079	−0.005	0.055

tions of TBAP were measured in DMF-DMSO mixed solvents. Fig. 2 shows the results. The viscosity of the solution increased quadratically with the concentration of the electrolyte, and the relative viscosity obeyed the following revised Jones-Dole equation[6]:

$$\eta_r = \eta/\eta_0 = 1 + Ac^{1/2} + Bc + Dc^2 \qquad (2)$$

where η is the viscosity at the c of the electrolyte, where η_0 is that at zero of c, and where A, B, and D are constants. The experiment was carried out by exchanging the electrolyte with $NaClO_4$, TEAP, and TBAP. The values of the constants were evaluated by the least-squares method. Table 2 shows the results. It may be seen from Table 2 that the magnitudes of both A and B for the four electrolytes are nearly equal, but that of D becomes larger in this order: TEAP, $NaClO_4$, and TBAP, as in the case of the α values. Hence, the D coefficient and the α values may have the same cause.

If the cause of the i_d depression with the increase in the concentration of the supporting electrolyte were only the increase in the viscosity, then $i_{d.r}\eta_r^{1/2}$ would remain at unity. However, as influences other than the viscosity act on it, $i_{d.r}\eta_r^{1/2}$ varies from unity with the c of the supporting electrolyte as follows:

$$i_{d.r}\eta_r^{1/2} = 1 + Kc \qquad (3)$$

where K is the coefficient representing the deviation from the Stokes equation. The above equation holds within about 0.5 M only. The values of K was evaluated in each case. Table 3 shows the results. In the cases in which the supporting electrolyte is TEAP or TBAP without the Na(I) ion, the value of K gradually decreases with the increase in the DMSO content. In the cases in which the depolarizer is the Tl(I) ion, the value of K for TBAP as the supporting electrolyte is smaller than TEAP. On the other hand, in the cases in which the depolarizer is [Ni(opd)$_2$], there is no difference between the values of K for TEAP and TBAP. The results show that the extent of the solvation of the depolarizer varies with the c of the electrolyte and that tendency differs with the kind of electrolyte and the kind of depolarizer[7].

The interaction between the supporting electrolyte and the solvent or the interaction between the solvents appears in the supporting-electrolyte-concentration-dependence of the polarographic diffusion current, but the interaction between the depolarizer and the solvent appears in the diffusion current at an infinite

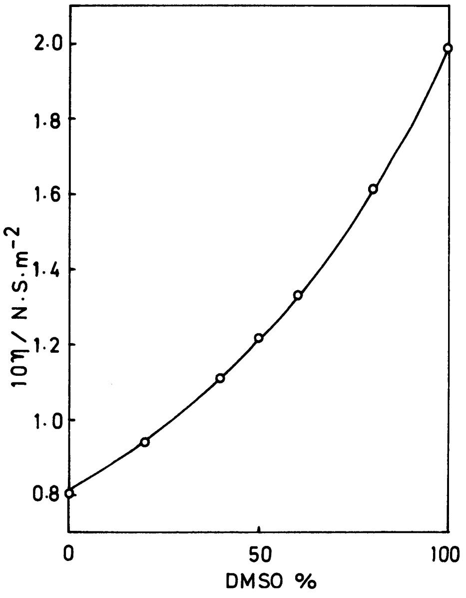

Fig. 3. Plots of η *vs.* DMSO % in DMF-DMSO.

Table 4. Stokes radii in DMF-DMSO

DMSO%	r_s/Å		
	Tl(I)	Na(I)	[Ni(opd)$_2$]
0	2.5	3.2	3.0
20	2.5	3.2	2.9
40	2.3	3.1	2.8
50	2.4	3.1	—
60	2.3	3.1	2.8
80	2.3	3.0	2.7
100	2.0	2.9	2.7

TABLE 5. $E_{1/2}$ OF Tl(I) AND [Ni(opd)$_2$] IN DMF–DMSO MIXED SOLVENTS CONTAINING 0.1 OR 0.7 M TETRAALKYLAMMONIUM PERCHLORATE

Concn.	DMSO%	TEAP			TBAP		
		Tl(I)	[Ni(opd)$_2$]		Tl(I)	[Ni(opd)$_2$]	
			1st	2nd		1st	2nd
0.1 M	0	−0.42	−0.93	−1.63	−0.49	−0.96	−1.65
	20	−0.47	−0.93	−1.62	−0.54	−0.95	−1.63
	40	−0.50	−0.92	−1.62	−0.57	−0.92	−1.62
	60	−0.51	−0.91	−1.60	−0.58	−0.92	−1.60
	80	−0.52	−0.91	−1.59	−0.58	−0.91	−1.60
	100	−0.53	−0.90	−1.56	−0.58	−0.91	−1.59
0.7 M	0	−0.41	−0.91	−1.59	−0.47	−0.91	−1.59
	20	−0.44	−0.90	−1.57	−0.52	−0.90	−1.56
	40	−0.47	−0.90	−1.56	−0.53	−0.90	−1.55
	60	−0.50	−0.89	−1.56	−0.54	−0.89	−1.54
	80	−0.50	−0.88	−1.54	−0.55	−0.89	−1.53
	100	−0.52	−0.88	−1.51	−0.55	−0.88	−1.54

dilution of the supporting electrolyte. The diffusion current extrapolated to the concentration zero of the supporting electrolyte is independent of the kind of supporting electrolyte and is the same if the depolarizer and the solvent are the same. The diffusion coefficient D was evaluated from the diffusion current at an infinite dilution by means of the Ilkovic equation. The viscosity of the solvent in DMF–DMSO mixtures varied, as Fig. 3 shows. The Stokes radius was calculated by means of the following Stokes–Einstein equation:

$$r_s = kT/(6\pi\eta_0 D) \qquad (4)$$

where k is the Boltzmann constant and η_0, the viscosity of the solvent. Table 4 shows the results. It may be seen that the Stokes radius becomes smaller with an increase in the DMSO content. Since DMSO is easier to solvate than DMF, the size of the diffusing particle in DMSO should become larger. However, the greater the DMSO content, the smaller the size of the observed Stokes radius. This might be ascribed to the presence of the association of DMSO.[8]

Table 5 shows the half-wave potentials of the Tl(I) ion and the [Ni(opd)$_2$] complex in DMF–DMSO mixed solvents containing 0.1 or 0.7 M TPAP and TBAP. The half-wave potentials of the Tl(I) ion and the [Ni(opd)$_2$] complex shifted to positive potentials with an increase in the concentrations of TPAP and TBAP in every solvent composition. This is attributable to the shift to the positive potential of the liquid-junction potential with an increase in the concentration of the supporting electrolyte. The half-wave potentials shifted to slightly negative potentials with an increase in the numbers of carbon atoms in the alkyl group of the tetraalkylammonium ion. While the half-wave potential of [Ni (opd)$_2$] shifted by about 0.03 V to a positive potential with an increase in the content of DMSO, the half-wave potential of the Tl(I) ion shifted by about 0.10 V to a negative potential. This is attributable to the stronger solvation of the Tl(I) ion by DMSO than by DMF, while [Ni(opd)$_2$], having a large size and a zero charge, is solvated only weakly in both solvents.

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