J. Electroanal. Chem., 73 (1976) 235—246

ELECTROCHEMICAL STUDIES OF SULFONATES IN NON-AQUEOUS SOLVENTS

PART II. POLAROGRAPHIC REDUCTIONS OF SOME ALKALINE EARTH AND TRANSITION METAL IONS WITH SULFONATE SUPPORTING ELECTROLYTE IN N,N-DIMETHYLFORMAMIDE AND ACETONITRILE

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(Received 29th December 1975)

ABSTRACT

The effect of *p*-toluenesulfonate and trifluoromethanesulfonate supporting electrolytes on the polarographic reduction of some alkaline earth and transition metal ions in N,N-dimethylformamide and acetonitrile has been investigated. Trifluoromethanesulfonate behaved similarly to perchlorate in dimethylformamide, while the half-wave potentials in *p*-toluenesulfonate supporting electrolyte shift to more negative potentials than those in perchlorate. In acetonitrile, the half-wave potentials shift to more negative potentials in trifluoromethanesulfonate than in perchlorate. The effect of the supporting electrolyte on the shift of the half-wave potential can be explained as the ion-pair formation between the divalent cation to be reduced and the supporting electrolyte anion.

INTRODUCTION

In the previous paper [1], we reported on the polarographic behavior of alkali metal ions in N,N-dimethylformamide (DMF) and acetonitrile (AN) using tetraethylammonium salts of *p*-toluenesulfonate (Et_4N-PTS), methanesulfonate (Et_4N-MS) and trifluoromethanesulfonate (Et_4N-TFMS) as the supporting electrolyte. Tetraethylammonium trifluoromethanesulfonate behaved similarly to perchlorate in both solvents. The shift of the half-wave potentials of alkali metal ions in *p*-toluenesulfonate and methanesulfonate supporting electrolytes was explained in terms of ion-pair formation between alkali metal ion and the supporting electrolyte anion.

In the present paper is reported on the polarographic reduction of some alkaline earth and transition metal ions in DMF and AN by using *p*-toluenesulfonate and trifluoromethanesulfonate salts as the supporting electrolyte. The polarographic behavior in these sulfonate supporting electrolytes is compared with that in perchlorate.

EXPERIMENTAL

Reagents

Alkaline earth perchlorates, trifluoromethanesulfonates (M(TFMS)$_2$) and *p*-toluenesulfonates (M(PTS)$_2$) were prepared by neutralizing alkaline earth hydroxide or carbonate with the respective acid. Calcium, strontium and barium perchlorates were recrystallized from water. Magnesium perchlorate of the reagent grade was used without further purification. Magnesium, calcium and strontium trifluoromethanesulfonates were recrystallized first from ethanol + benzene (1 : 10) and second from AN + benzene (1 : 10) mixtures. Barium trifluoromethanesulfonate was recrystallized first from ethanol + n-pentane (1 : 10) and second from AN + n-pentane (1 : 10) mixtures. Alkaline earth *p*-toluenesulfonates were recrystallized from water. All alkaline earth perchlorates, trifluoromethanesulfonates and *p*-toluenesulfonates were dried for 24 h in vacuo on phosphorus pentoxide at 200°C, at 150°C and at 130°C, respectively.

Perchlorates, trifluoromethanesulfonates and *p*-toluenesulfonates of nickel(II), copper(II), zinc(II), lead(II) and manganese(II) were prepared by neutralizing the corresponding metal carbonate with the respective acid. These perchlorates and *p*-toluenesulfonates were recrystallized from water, and trifluoromethanesulfonates first from acetone and second from ethanol. These perchlorates were dried on phosphorus pentoxide, which have the following formula [2] respectively; $Ni(ClO_4)_2 \cdot 6\ H_2O$, $Cu(ClO_4)_2 \cdot 6\ H_2O$, $Zn(ClO_4)_2 \cdot 6\ H_2O$, $Pb(ClO_4)_2 \cdot 3\ H_2O$ and $Mn(ClO_4)_2 \cdot 6\ H_2O$. These trifluoromethanesulfonates and *p*-toluenesulfonates were dried for 24 h in vacuo on phosphorus pentoxide at 150°C and at 130°C, respectively.

Tetra-n-buthylammonium trifluoromethanesulfonate (Bu$_4$N-TFMS) and perchlorate were prepared similarly to the method reported previously with Et$_4$N-TFMS [1]. Tetra-n-buthylammonium trifluoromethanesulfonate was recrystallized from a dichloromethane + n-pentane (1 : 10) mixture, and the perchlorate from ethyl acetate. These salts were dried for 24 h in vacuo on phosphorus pentoxide at 60°C.

The other reagents used were purified following the method in the previous paper [1].

Apparatus

The apparatus used in measurements of polarography and conductivity were the same as those used before [1].

RESULTS

The specific conductivities were measured in DMF and AN by using tetra-n-buthylammonium and sodium salts. The results are summarized in Table 1.

TABLE 1

Specific conductivities for tetra-n-buthylammonium and sodium salts in DMF and AN at 25° C

Electrolyte	Concentration /M	Specific conductivity/Ω^{-1} cm^{-1}	
		DMF $\times 10^{-2}$	AN $\times 10^{-2}$
Bu_4NClO_4	0.6 [a]	1.30	2.70
	0.5 [a]	1.22	2.56
	0.1	0.459	0.928
	0.05	0.259	0.530
Bu_4N-TFMS	1.0 [a]	1.08	2.30
	0.5 [a]	1.12	2.25
	0.2 [a]	0.685	1.30
	0.1 [a]	0.407	0.826
	0.05	0.247	0.525
$NaClO_4$	0.1	0.543	0.973
	0.05	0.301	0.569
Na-TFMS	0.1	0.489	0.755
	0.05	0.270	0.478
Na-PTS	0.1	0.246	—
	0.05	0.159	—

[a] See ref. 3.

The useful potential range for the dropping mercury electrode in 0.05 *M* Bu_4N-TFMS was found to be identical with that in 0.05 *M* Bu_4NClO_4 both in DMF and AN; the potential range in DMF and AN is from —0.08 to —3.43 V and from +0.28 to —3.23 V vs. Ag/0.1 *M* $AgClO_4$, respectively.

Polarographic reduction of alkaline earth and transition metal ions

The polarographic reductions of magnesium, calcium, strontium and barium ions were examined in DMF by using 0.05 *M* Et_4NClO_4, Et_4N-TFMS, Et_4N-PTS, Bu_4NClO_4 and Bu_4N-TFMS as supporting electrolytes. The results are summarized in Table 2. In Et_4N-PTS supporting electrolyte, the half-wave potentials ($E_{1/2}$) of alkaline earth metal ions shift to more negative potentials than those in perchlorate. In Et_4N-TFMS and Bu_4N-TFMS, however, the half-wave potentials agree with those in the corresponding perchlorate.

The reduction behaviors of nickel(II), copper(II), zinc(II), lead(II) and manganese(II) in DMF are similarly summarized in Table 2. In Et_4N-TFMS, the half-wave potentials of these ions are almost the same as those in perchlorate, while those in Et_4N-PTS shift to more negative potentials.

The polarographic reductions of alkaline earth and transition metal ions in AN were similarly examined by using 0.05 *M* Bu_4NClO_4, Bu_4N-TFMS, $NaClO_4$

TABLE 2

Results of d.c. polarographic reduction of some alkaline earth and transition metal ions in DMF at 25° C

Metal ion [a] (1 mM)	Supporting electrolyte (0.05 M)								
	$-E_{1/2}$/V vs. Ag/AgClO$_4$ (0.1 M)			I_d [b]/μA s$^{1/2}$ mg$^{-2/3}$ mM^{-1}			Slope of $-E$ vs. $\log_{10}[i/(i_d - i)]$ plot/mV		
	Et$_4$NClO$_4$			Et$_4$N-TFMS			Et$_4$N-PTS		
Mg^{2+}	2.918	2.15	71	2.942	2.22	70	2.993	1.95	67
Ca^{2+}	2.854	2.53	38	2.857	2.64	36	2.904	2.45	42
Sr^{2+}	2.719	2.71	38	2.722	2.68	35	2.756	2.56	37
Ba^{2+}	2.520	2.76	34	2.521	2.64	31	2.552	2.59	35
	Bu$_4$NClO$_4$			Bu$_4$N-TFMS					
Mg^{2+}	(2.69) [c]	2.38	max	(2.69)	2.56	max			
Ca^{2+}	2.776	2.63	35	(2.78)	2.72	max			
Sr^{2+}	2.660	2.71	36	(2.66)	2.74	max			
Ba^{2+}	(2.48)	2.76	max	(2.47)	2.77	max			
	Et$_4$NClO$_4$			Et$_4$N-TFMS			Et$_4$N-PTS		
Ni^{2+}	1.389	2.78	62	1.389	2.64	69	1.411	2.32	72
Cu^{2+} [d]	0.456	2.08	37	0.451	2.28	36	—	1.94	max
Zn^{2+}	1.447	2.48	30	1.447	2.47	28	1.471	2.51	31
Pb^{2+}	0.897	3.19	30	0.902	3.09	37	0.941	2.91	33
Mn^{2+}	2.023	2.65	49	2.020	2.60	33	2.055	2.58	36
	NaClO$_4$			Na-TFMS			Na-PTS		
Ni^{2+}	(1.34)	2.69	max	(1.34)	2.66	max	1.358	2.48	52
Cu^{2+} [d]	0.454	1.84	35	0.455	1.82	38	—	1.89	max
Mn^{2+}	(2.00)	2.52	max	(2.00)	2.47	max	2.033	2.47	32

[a] Any salt is trifluoromethanesulfonate.

[b] I_d = diffusion current constant.

[c] Values in parentheses are only approximate.

[d] Values for the first wave. The second wave is small and ill-defined.

and Na-TFMS as supporting electrolytes. The results are presented in Table 3.

As shown in Table 3, the half-wave potentials of alkaline earth metal ions in Bu$_4$N-TFMS shift to more negative potentials than those in perchlorate. A similar negative shift of the half-wave potential is observed with zinc(II), lead(II) and manganese(II) in Bu$_4$N-TFMS and Na-TFMS, as well.

The reduction behavior of nickel(II) in AN is shown in Fig. 1. Itabashi et al. [4] reported that nickel(II) gave a single irreversible wave in LiClO$_4$, NaClO$_4$ and Me$_4$NClO$_4$ electrolyte solutions and double waves in the other quaternary ammonium perchlorate solutions. Nickel(II) gave double waves in 0.05 M

TABLE 3

Results of d.c. polarographic reduction of some alkaline earth and transition metal ions in AN at 25° C

Metal ion [a] (1 mM)	Supporting electrolyte (0.05 M)					
	$-E_{1/2}$/V vs. Ag/AgClO$_4$ (0.1 M)	I_d [b]/μA s$^{1/2}$ mg$^{-2/3}$ mM^{-1}	Slope of $-E$ vs. $\log_{10}[i/(i_d - i)]$ plot/mV	$-E_{1/2}$/V vs. Ag/AgClO$_4$ (0.1 M)	I_d [b]/μA s$^{1/2}$ mg$^{-2/3}$ mM^{-1}	Slope of $-E$ vs. $\log_{10}[i/(i_d - i)]$ plot/mV
	Bu$_4$NClO$_4$			Bu$_4$N-TFMS		
Mg^{2+}	2.000	3.31	[c]	2.095	3.22	[c]
Ca^{2+}	2.190	4.86	49	2.235	4.83	50
Sr^{2+}	2.115	4.89	max	2.147	4.85	40
Ba^{2+}	1.975	4.51	29	1.995	4.47	29
Ni^{2+} [d]	0.751	0.79	50	0.768	2.06	50
[e]	1.249	3.80	87	1.250	2.71	68
Cu^{2+} [f]	0.695	2.89	68	0.700	2.89	75
Zn^{2+}	1.015	4.72	43	1.035	4.53	43
Pb^{2+}	(0.39) [g]	5.46	max	0.417	4.99	30
Mn^{2+}	1.480	4.85	29	1.510	4.55	30
	NaClO$_4$			Na-TFMS		
Ni^{2+}	0.820	4.67	160	(0.82)	4.52	max
Zn^{2+}	0.972	4.92	30	0.985	4.84	31
Pb^{2+}	(0.39)	5.36	max	(0.42)	5.55	max
Mn^{2+}	1.463	5.07	34	1.485	4.97	32

[a] Any salt is trifluoromethanesulfonate.

[b] I_d = diffusion current constant.

[c] The magnesium ion is reduced very irreversibly. The slope is ca. 100 mV in the first half and ca. 230 mV in the second half of the polarogram measured.

[d] Values for the first wave.

[e] Values for the second wave.

[f] Values for the second wave (Cu$^+$ + e = Cu^0).

[g] Values in parentheses are only approximate.

Bu$_4$NClO$_4$, Et$_4$NClO$_4$, Bu$_4$N-TFMS and Et$_4$N-TFMS, and a single wave in 0.05 M NaClO$_4$, Na-TFMS and Et$_4$N-PTS.

Calculation of ion association constant

Ion association constants of 1-1 electrolytes were calculated from the conductivity data according to the Shedlovsky equation as described previousky [1]. The calculation for 2-1 electrolytes was performed according to the Fuoss and Edelson equation [5] on a FACOM 230-75 computer.

The Fuoss and Edelson equation is expressed for 2-1 electrolyte, MX$_2$, as

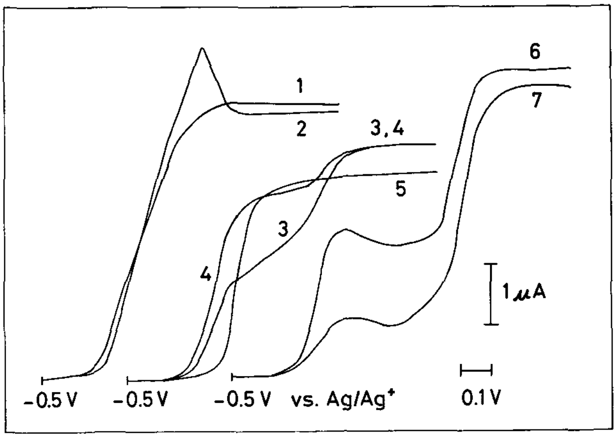
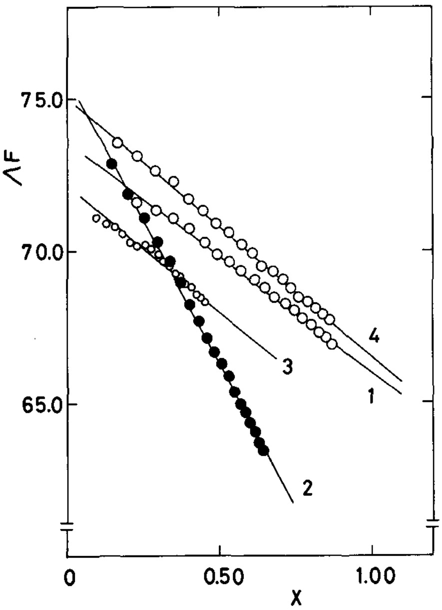


Fig. 1. D.c. polarographic reduction of nickel(II) in AN at 25° C. Supporting electrolyte (0.05 *M*); (1) $NaClO_4$, (2) Na-TFMS, (3) Et_4NClO_4, (4) Et_4N-TFMS, (5) Et_4N-PTS, (6) Bu_4N-TFMS, (7) Bu_4NClO_4. Concentration of $Ni(TFMS)_2$; 0.91 m*M* in (1) and (2), 0.78 m*M* in (3), (4) and (5), 0.99 m*M* in (6) and (7).



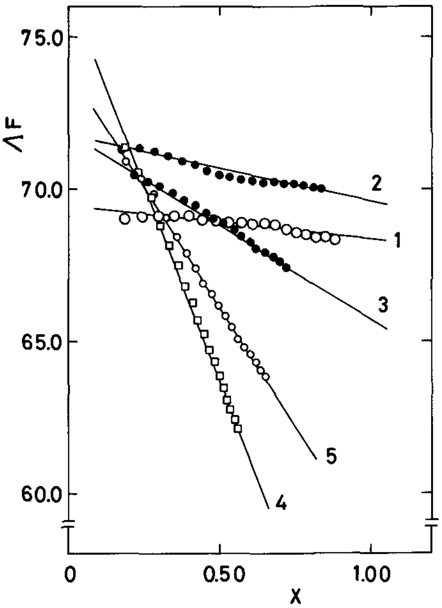


Fig. 2. Fuoss and Edelson plots for alkaline earth *p*-toluenesulfonates in DMF at 25° C. (1) $Mg(PTS)_2$, (2) $Ca(PTS)_2$, (3) $Sr(PTS)_2$, (4) $Ba(PTS)_2$.

Fig. 3. Fuoss and Edelson plots for transition metal *p*-toluenesulfonates in DMF at 25° C. (1) $Ni(PTS)_2$, (2) $Cu(PTS)_2$ (3) $Zn(PTS)_2$, (4) $Pb(PTS)_2$, (5) $Mn(PTS)_2$.

follows,

$$\Lambda F = \Lambda_0 - [cf\Lambda F(\Lambda F - \Lambda_0/2)]K_1/\Lambda_0 = \Lambda_0 - XK_1/\Lambda_0 \tag{1}$$

where

F = the Fuoss and Edelson function
c = the concentration of the anion, X^-
f = the activity coefficient of the divalent cation, M^{2+}
K_1 = the ion association constant of the equilibrium: $M^{2+} + X^- = MX^+$.

In the derivation of eqn. (1), it is assumed that the following ion association, $MX^+ + X^- = MX_2$, is negligible and that the limiting equivalent conductivity of the ion-pair, MX^+, is equal to one half of that of M^{2+}.

The typical results of the calculation were shown as the plots of ΛF vs. X in Figs. 2—5. The calculated values of K_1 were presented in Table 4.

In DMF, the ion association constants K_1 of perchlorates and trifluoromethanesulfonates of alkaline earth and transition metals studied were obtained as negative values in these calculations. From these values, which have not been included in Table 4, it was concluded that these salts are completely dissociated. On the other hand, *p*-toluenesulfonate anion is found to be asso-

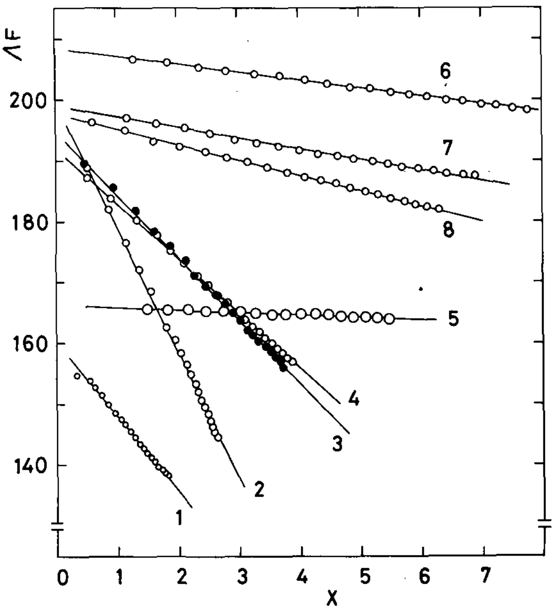


Fig. 4. Fuoss and Edelson plots for alkaline earth trifluoromethanesulfonates and perchlorates in AN at 25° C. (1) $Mg(TFMS)_2$, (2) $Ca(TFMS)_2$, (3) $Sr(TFMS)_2$, (4) $Ba(TFMS)_2$, (5) $Mg(ClO_4)_2$, (6) $Ca(ClO_4)_2$, (7) $Sr(ClO_4)_2$, (8) $Ba(ClO_4)_2$.

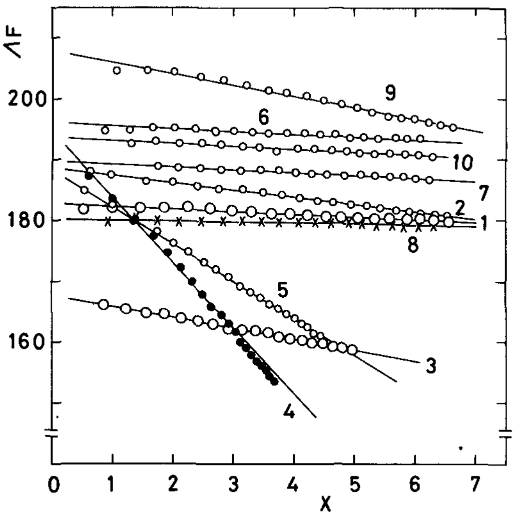


Fig. 5. Fuoss and Edelson plots for transition metal trifluoromethanesulfonates and perchlorates in AN at 25° C. (1) $Ni(TFMS)_2$, (2) $Cu(TFMS)_2$, (3) $Zn(TFMS)_2$, (4) $Pb(TFMS)_2$, (5) $Mn(TFMS)_2$, (6) $Ni(ClO_4)_2$, (7) $Cu(ClO_4)_2$, (8) $Zn(ClO_4)_2$, (9) $Pb(ClO_4)_2$, (10) $Mn(ClO_4)_2$.

TABLE 4 (a)

Limiting equivalent conductivities (Λ_0) and ion association constants (K_1) of 2-1 electrolytes in DMF and AN at 25° C [a]

Solvent	Cation	Trifluoromethanesulfonate		Perchlorate	*p*-Toluene-sulfonate
		Λ_0/cm^2 Ω^{-1} mol^{-1}	$10^{-2} K_1/M^{-1}$	$10^{-2} K_1/M^{-1}$	$10^{-2} K_1/M^{-1}$
DMF	Mg^{2+}	79.5 ± 0.1	*	*	5.48 ± 0.20
	Ca^{2+}	81.4 ± 0.7	*	*	14.5 ± 0.4
	Sr^{2+}	86.0 ± 0.1	*	*	5.57 ± 0.46
	Ba^{2+}	82.6 ± 0.1	*	*	6.44 ± 0.12
	Ni^{2+}	75.6 ± 0.2	*	*	0.81 ± 0.17
	Cu^{2+}	82.7 ± 0.1	*	*	1.53 ± 0.23
	Zn^{2+}	78.3 ± 0.3	*	*	4.36 ± 0.19
	Pb^{2+}	84.2 ± 0.2	*	*	19.3 ± 0.6
	Mn^{2+}	79.8 ± 0.2	*	*	11.7 ± 0.3
AN	Mg^{2+}	160.2 ± 0.5	19.0 ± 0.6	0.17 ± 0.17	—
	Ca^{2+}	201.4 ± 1.0	42.5 ± 0.9	2.72 ± 0.05	—
	Sr^{2+}	195.8 ± 0.3	20.5 ± 0.2	3.19 ± 0.17	—
	Ba^{2+}	192.7 ± 0.3	17.7 ± 0.2	4.82 ± 0.10	—
	Ni^{2+}	182.7 ± 0.3	0.68 ± 0.15	0.85 ± 0.20	180 ± 80
	Cu^{2+}	188.4 ± 0.2	2.44 ± 0.09	0.97 ± 0.10	—
	Zn^{2+}	167.5 ± 0.1	3.17 ± 0.06	0.44 ± 0.13	—
	Pb^{2+}	195.8 ± 1.1	22.8 ± 0.8	4.02 ± 0.31	—
	Mn^{2+}	188.3 ± 0.2	11.9 ± 0.1	1.03 ± 0.12	—

[a] Values obtained by the Fuoss and Edelson method.

* Completely dissociated.

TABLE 4 (b)

Limiting equivalent conductivities (Λ_0) and ion association constants (K_A) of 1-1 electrolytes in DMF and AN at 25° C [a]

Solvent	Cation	Trifluoromethanesulfonate		Perchlorate	p-Toluene-sulfonate
		$\Lambda_0/\mathrm{cm}^2\ \Omega^{-1}$ mol^{-1}	K_A/M^{-1}	K_A/M^{-1}	K_A/M^{-1}
DMF	Na^+ [b]	73.7	*	*	39.2
	Et_4N^+ [b]	78.7	*	*	8.7
	Bu_4N^+	71.9 ± 0.1	2.1 ± 2.2	0.4 ± 4.1	—
AN	Na^+ [b]	171.9 ± 0.2	28.0 ± 3.3	6.8 ± 3.5	7.7×10^2
	Et_4N^+ [b]	181.4 ± 0.2	1.0 ± 3.0	7.3 ± 1.6	10.6 ± 3.1
	Bu_4N^+	158.3 ± 0.1	4.4 ± 2.1	3.0 ± 2.5	—

[a] Values obtained by the Shedlovsky method.

[b] See ref. 1.

* Completely dissociated.

TABLE 5

Limiting equivalent conductivities (λ_0), crystallographic radii (r_c) and Stokes radii (r_s) of ions in DMF and AN at 25° C

Ion	$\lambda_0^a/\mathrm{cm}^2\ \Omega^{-1}\ \mathrm{mol}^{-1}$		r_c/Å	r_s/Å	
	DMF	AN		DMF	AN
Mg^{2+}	35.9	63.9	0.65	5.74	7.52
Ca^{2+}	37.8	105.1	0.99	5.45	4.57
Sr^{2+}	42.4	99.5	1.13	4.85	4.83
Ba^{2+}	39.0	96.4	1.35	5.28	4.99
Ni^{2+}	32.0	86.4	0.70	6.44	5.56
Cu^{2+}	39.1	92.1	0.82	5.27	5.22
Zn^{2+}	34.7	71.2	0.74	5.93	6.75
Pb^{2+}	40.6	99.5	1.32	5.07	4.83
Mn^{2+}	36.2	92.0	0.80	5.69	5.22
Bu_4N^+	28.3	62.0	4.94	3.64	3.88
Et_4N^+ [b]	35.1	85.1	4.00	2.93	2.82
Na^+ [b]	29.9	76.6	0.95	3.44	3.14
ClO_4^- [b]	52.4	103.8	2.40	1.97	2.32
TFMS$^-$ [b]	43.6	96.3	—	2.36	2.50
PTS$^-$ [b]	35.6	74.1	—	2.89	3.24

[a] The λ_0 values of divalent cations were calculated from the Λ_0 values of trifluoromethanesulfonates.

[b] See ref. 1.

ciated with these metals, as can be seen from the K_1 values shown in Table 4. In AN, both perchlorates and trifluoromethanesulfonates seem to be associated to some extent, as the K_1 values of trifluoromethanesulfonates are apparently larger than those of perchlorates.

The limiting equivalent conductivities of ions are presented in Table 5 together with the crystallographic and Stokes radii.

DISCUSSION

Tables 2 and 3 show the half-wave potentials of some alkaline earth and transition metal ions, which are obviously dependent upon the supporting electrolyte used. In DMF, the half-wave potentials in trifluoromethanesulfonate as the supporting electrolyte are almost the same as those in perchlorate, while those in *p*-toluenesulfonate as the supporting electrolyte shift to more negative potentials. In AN, the half-wave potentials in trifluoromethanesulfonate as the supporting electrolyte shift to more negative potentials than those in perchlorate.

These shifts of the half-wave potentials were successfully explained by taking into consideration the ion-pair formation between the divalent cation to be reduced and the supporting electrolyte anion. According to the Schaap equation [6], the reversible half-wave potential of a divalent cation, M^{2+}, in a uni-univalent supporting electrolyte, SX, is given by the following equation, supposing that only MX^+ exists as possible ion-pair.

$$(E_{1/2})_{MX^+} = E_a^{0'} - (0.059/2)\log_{10}(f_a I_{MX^+}/I_a) - (0.059/2)\log_{10}[1/f_{M^{2+}} + K_{1(MX^+)}(1-\alpha_{SX})c_{SX}\,f_{X^-}/f_{MX^+}] \qquad (2)$$

Here,

$(E_{1/2})_{MX^+}$ = the half-wave potential of M^{2+} in the solution containing the ion-pair, MX^+
$E_a^{0'}$ = the standard potential of the metal amalgam electrode vs. the reference electrode used
I_{MX^+} = the over-all measurable diffusion current constant
I_a = the same constant for the metal in the amalgam
c_{SX} = the concentration of the 1-1 supporting electrolyte, SX
α_{SX} = the degree of association of SX
$K_{1(MX^+)}$ = the ion association constant of the ion-pair, MX^+
f_i = the activity coefficient of each species, i.

The difference of the half-wave potential, $\Delta E_{1/2}$, is defined here as eqn. (3), assuming that the activity coefficient of the ion-pair, f_{MX^+}, is equal to that of the anion, f_{X^-}, in eqn. (2).

$$\Delta E_{1/2} \equiv (E_{1/2})_{MClO_4^+} - (E_{1/2})_{MX^+} = \frac{0.059}{2}\log_{10}\frac{I_{MX^+}}{I_{MClO_4^+}}\,\frac{f_{M^{2+}}^{-1} + K_{1(MX^+)}(1-\alpha_{SX})c_{SX}}{f_{M^{2+}}^{-1} + K_{1(MClO_4^+)}(1-\alpha_{SClO_4})c_{SClO_4}} \qquad (3)$$

TABLE 6

Effect of ion association on half-wave potential in DMF and AN at 25° C

Solvent	Supporting electrolyte	Cation	$(\Delta E_{1/2})_{\mathrm{obs.}}$ [a] /mV	$(\Delta E_{1/2})_{\mathrm{calc.}}$ [b] /mV
DMF	Et_4N-PTS	Ba^{2+}	32	20
		Zn^{2+}	24	18
		Pb^{2+}	44	32
		Mn^{2+}	32	28
	Na-PTS	Mn^{2+}	33	24
AN	Bu_4N-TFMS	Ba^{2+}	20	15
		Pb^{2+}	27	18
		Mn^{2+}	30	22
	Na-TFMS	Zn^{2+}	13	11
		Mn^{2+}	22	21

[a] Values obtained polarographically.

[b] Values calculated by eqn. (3) using the conductivity data.

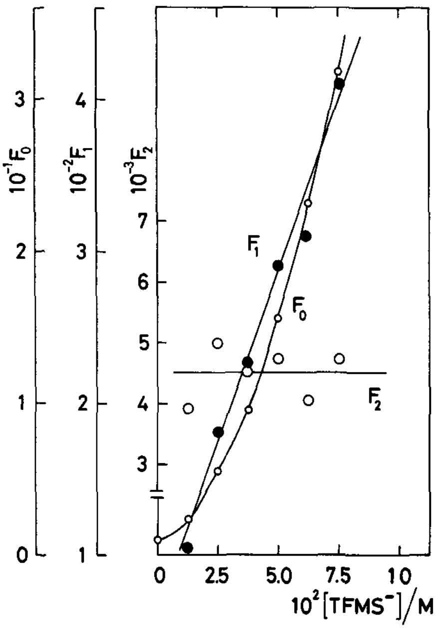


Fig. 6. DeFord and Hume function for Mn^{2+}-$TFMS^-$ system in AN at 25° C. Concentration of Mn^{2+}, 1 mM; ionic strength, $[Bu_4NClO_4]$ + $[Bu_4N\text{-}TFMS]$ = 0.15 M.

The calculated values of the difference of the half-wave potential, $(\Delta E_{1/2})_{\text{calc.}}$, are presented in Table 6 together with those observed polarographically, $(\Delta E_{1/2})_{\text{obs.}}$. The activity coefficient, $f_{M^{2+}}$, was estimated by the Debye-Hückel theory, assuming that the distance of closest approach was almost the same as the sum of the Stokes radii of cation and anion. The values of $(\Delta E_{1/2})_{\text{obs.}}$ agreed well with those of $(\Delta E_{1/2})_{\text{calc.}}$ both in DMF and AN. This fact shows that the ion association of the divalent cation in question with the supporting electrolyte anion is a dominant factor on the shift of the half-wave potential.

The stability constants between manganese(II) cation and trifluoromethanesulfonate anion were obtained in AN by the DeFord and Hume method [7]. The results are shown in Fig. 6. It can be seen that two species of ion-pair exist, i.e., Mn(TFMS)^+ and Mn(TFMS)_2, and no further complexes exist. The K_1 and K_2 values, which were obtained in terms of concentration at the ionic strength of 0.15 M, were 5.6×10 and 4.5×10^3, respectively.

In conclusion, the degrees of the negative shift of the half-wave potential of the divalent cation due to the change of supporting electrolyte are related to the ion association constant between the cation and the supporting electrolyte anion.

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