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Conductance of Electrolytes in Dipolar Aprotic Solvent Mixtures. II. Conductance of Lithium Perchlorate in Mixtures of Ethyl Methyl Ketone and Acetone with *N,N*-Dimethylformamide at 25 °C

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The electrolytic conductance of $LiClO_4$ has been determined in *N,N*-dimethylformamide (DMF) and its binary mixtures with acetone (Ac) and ethyl methyl ketone (MEK) at 25 °C. Ion association constants (K_A) and limiting molar conductance (Λ_0) were calculated from these data using Fuoss equation with modifications. The K_A values of $LiClO_4$ in these binary mixtures are interpreted in terms of solvent separated ion pairs while in pure Ac and MEK almost contact ion pairs are expected. A comparison is made for Λ_0 and K_A values of this salt in Ac and Ac-DMF mixtures with those obtained by Gill et al. Further, a comparison is made between these results and spectroscopically derived results by others in analogous media. $LiClO_4$ has been found more associated in Ac-DMF solvent system than in the MEK-DMF mixed solvent system.

A large number of conductometric and spectroscopic studies of concentrated solutions of $LiClO_4$ have been carried out in an aprotic solvent systems in various laboratories.[1–4,14] But very few number of precise conductance measurements on dilute solution of this salt in acetone (Ac), *N,N*-dimethylformamide (DMF), and Ac-DMF mixed solvent system are available in literature.[5–7] No literature data have been found about conductance of $LiClO_4$ in ethyl methyl ketone (MEK) and its binary mixtures with DMF at 25 °C.

As a continuation of conductance measurements of electrolytes in dipolar aprotic solvent mixtures,[8] present paper reports conductance of $LiClO_4$ in Ac, MEK, DMF, Ac-DMF, and MEK-DMF binary mixtures in a concentration range 10^{-4}—10^{-2} mol dm^{-3} at 25 °C. The limiting molar conductance (Λ_0) and ion association constant (K_A) were evaluated from the conductance data using the Fuoss equation[10] with modifications. The Bjerrum ion association theory as modified by Fernandez-Prini and Pure[11,12] was also used for derivation of K_A (as $K_A{}^{BFPP}$) and ion pair distance parameter *a*. The derived parameters are compared with those obtained by Gill et al. for this salt in Ac-DMF binary mixtures. Further, results of spectroscopic studies of $LiClO_4$ in pure solvents (in Ac and DMF) which are available from literatures[4b,5,13] are discussed for comparison purpose with the present results.

Experimental

Chemicals. Acetone, DMF, and MEK were products of Merck (for synthesis). The procedure for purification of these solvents together with densities ρ, viscosities η, and dielectric constants ε are given in detail in previous papers.[8,9] All solution preparation was carried out in the presence of dry nitrogen gas. The purified solvents contained no more than 0.01% (w/w) water. The mixtures were prepared by weight and are given in Table 1. $LiClO_4$ and KCl were of analytical grade (pure p. a Fluka). They were twice recrystallized from conductivity water, dried in an oven at 170 °C for several days and then dried in vaccum at 70 °C over P_2O_5 and were kept in a desiccator over P_2O_5.

Conductance Measurements. Conductance measurements were carried out using ORION Research Conductivity Meter, Model 101 at 1 kHz. Two 1 dm^3 Kraus-type conductance cells were used, whose cell constants were 1.1538 and 0.1932 cm^{-1} calibrated with aqueous KCl solutions at 25±0.005 °C. The platinized Pt electrodes were used. Further procedure was the same as described earlier.[8] Measurements were carried out in a water bath at 25±0.005 °C and the reproducibility of the conductance measurement was better than ±0.01%. The conductance data are listed in Tables 2 and 3 and are presented in Figs. 1 and 2.

Results

The molar conductance of the salt solutions (listed in Tables 2 and 3) were corrected for the solvent conductances. The Fuoss conductance equation,[10] with modifications was used to evaluate the limiting molar conductance (Λ_0) and the conductometric association constant (K_A) from conductance data using his scan

Table 1. Physical Properties of AC-DMF and MEK-DMF Binary Mixtures at 25 °C

S.No.	DMF/wt%	ε	η/cp[a]	ρ/g cm^{-3}
		Ac-DMF mixture		
1	0.00	20.14	0.300	0.7838
2	3.45	20.62	0.310	0.7890
3	11.50	21.85	0.334	0.8000
4	28.00	24.26	0.383	0.8238
5	36.00	25.44	0.405	0.8363
6	45.00	27.16	0.457	0.8503
7	62.00	29.74	0.514	0.8815
8	82.00	33.47	0.649	0.9141
9	100.00	36.71	0.796	0.9439
		MEK-DMF mixture		
1′	0.00	18.01	0.379	0.7998
2′	5.00	18.80	0.396	0.8045
3′	11.00	19.78	0.411	0.8128
4′	17.00	20.70	0.430	0.8237
5′	28.00	22.49	0.471	0.8445
6′	54.00	27.29	0.560	0.8748
7′	77.00	31.85	0.669	0.9199
8′	86.00	33.77	0.713	0.9235

a) 1cp=10^{-3} Pa s.

Table 2. Molar Concentrations and Conductances of $LiClO_4$ Solutions in AC-DMF Mixtures at 25 °C

Acetone		3.45% DMF		11.50% DMF		28.00% DMF		36.00% DMF	
$10^4 c$	Λ	$10^4 c$	Λ	$10^4 c$	Λ	$10^4 c$	Λ	$10^4 c$	Λ
mol dm^{-3}	S cm^2 mol^{-1}	mol dm^{-3}	S cm^2 mol^{-1}	mol dm^{-3}	S cm^2 mol^{-1}	mol dm^{-3}	S cm^2 mol^{-1}	mol dm^{-3}	S cm^2 mol^{-1}
1.1822	168.836	2.1862	170.354	1.8623	158.888	1.2243	149.666	1.3785	134.908
2.3248	152.629	4.2994	165.122	3.6624	154.585	2.4076	146.624	3.6943	132.133
3.4299	142.372	6.3430	161.283	5.4033	151.485	3.554	144.886	5.4503	130.042
4.4990	134.587	8.3205	158.075	7.0875	148.777	4.6595	142.258	7.1495	128.321
5.5345	128.613	10.3250	155.221	8.7187	146.678	5.7316	140.642	8.7945	126.870
6.5345	123.656	12.0895	153.128	10.2985	144.702	6.7702	139.021	10.3881	125.591
7.5092	119.473	13.8868	150.111	11.8295	143.021	7.7702	138.859	11.9324	124.454
8.4515	115.905	15.6295	149.428	13.3140	141.598	8.7525	136.503	13.4298	123.442
9.3656	112.706	17.3200	147.888	14.7541	140.228	9.6992	135.425	14.8824	122.504
10.2528	110.081	18.9607	146.445	16.1517	139.025	10.6179	134.501	16.2921	121.666
11.2528	107.390	20.5536	145.227	17.5086	137.887	11.6179	133.522	17.9213	120.753
11.9909	105.393	22.1009	143.933	18.8267	136.854	12.3765	132.649	18.9905	120.176
12.7639	103.636	23.6046	142.708	20.1076	135.892	13.2186	132.000	20.2824	119.503
13.5544	101.759	25.0663	141.758	21.3528	135.128	14.0371	131.205	21.5385	118.882
14.3231	100.137	27.8709	140.855	22.5637	134.354	14.8332	130.642	22.7598	118.222
15.0709	98.648	29.2171	139.999	23.7419	133.588	15.6077	130.001	23.9484	117.735
16.5075	96.006	30.5276	139.125	24.8886	132.001	16.3676	129.432	25.1050	117.224
17.1977	95.628	31.8041	138.656	26.3526	131.628	17.0955	128.844		

45% DMF		62% DMF		Pure DMF		82% DMF	
$10^4 c$	Λ	$10^4 c$	Λ	$10^4 c$	Λ	$10^4 c$	Λ
mol dm^{-3}	S cm^2 mol^{-1}	mol dm^{-3}	S cm^2 mol^{-1}	mol dm^{-3}	S cm^2 mol^{-1}	mol dm^{-3}	S cm^2 mol^{-1}
1.7127	129.032	0.9717	107.638	1.9044	75.004	1.5158	86.655
3.3625	126.499	1.9108	106.808	3.7454	73.898	2.9809	85.400
4.9527	124.488	2.8191	104.888	5.5255	73.053	4.5778	84.528
6.4865	122.955	3.6980	104.003	7.2481	72.246	5.7688	83.787
7.9668	121.563	4.5489	103.344	8.9158	71.722	8.3821	82.613
9.3964	120.446	5.3731	102.846	10.5313	71.156	9.6282	82.006
10.7778	119.404	6.1719	102.272	12.0970	70.721	10.8365	81.642
12.1195	118.465	6.9464	101.844	13.6150	70.266	12.0086	81.058
13.4057	117.642	7.6978	101.415	15.0877	69.788	13.1461	80.522
14.6567	116.801	8.4269	101.002	16.5168	69.342	14.2505	80.012
15.8678	116.200	9.1349	100.623	17.9045	69.001	15.3233	79.488
17.0666	115.535	9.8226	99.988	19.2524	68.653	16.3658	78.900
		10.4909	99.333	20.5622	68.349	17.3793	78.384
		11.1405	98.489	21.8355	68.001	18.3649	77.867
		11.6129	97.788	23.0739	67.752	19.3231	77.244
		12.3871	97.212	24.2787	67.482	20.2572	76.849

program[10a)] in which R (Gurney cosphere distance) was varied from 3 to 30 Å with increment of 0.2 Å.

K_A for ion pair formation of the type $M^+ + X^- = M^+X^-$ is given by

$$K_A = (1-\gamma)/C\gamma^2 f_{\pm}^{2}\ , \tag{1}$$

where $f_{\pm}$ was given by $\exp[-\tau/(1+kR)]$ with $\tau=\beta k/2$ where k^{-1} is the Debye distance, $\beta=e^2/\varepsilon RT$, and other symbols have their usual meanings. The scan program also evaluated σ (standard deviation expressed as a percentage of Λ_0). Plots of σ vs. R showed minima for each solvent mixtures and the derived values of Λ_0 and K_A along with σ and R are given in Tables 4 and 5.

The association constant K^{BFPP} from the Bjerrum ion association theory[11)] as modified by Fernandez-Prini and Prue[12)] was also evaluated from the following expression

$$K_A^{\mathrm{BFPP}} = 4\pi NA \int_{r=a}^{q} \exp[-U(r)/K_B T]\, r^2\, dr, \tag{2}$$

and

$$U(r) = \int_{\infty}^{r} e^2 \cdot dr/\varepsilon' r^2 = e^2 \int_{\infty}^{r_1} dr/\varepsilon r^2 + e^2 \int_{r_1}^{r} dr/\varepsilon' r^2, \tag{3}$$

where q is Bjerrum distance parameter.

In this modification, the association is corrected by introduction of a distance dependent dielectric coefficient ε' replacing the static dielectric constant (ε) of the medium. Booth[23)] derived the following expression for the variation of ε' with intensity of electric field

$$\varepsilon' = (3/y)(\varepsilon - n^2)L(y) + n^2, \tag{4}$$

where $y=\beta' Ze/\varepsilon' r^2$, $L(y)$ is the Langevin function, $L(y)$ $=\mathrm{Cot}\, h(y) - 1/y$, and $Ze/\varepsilon' r^2$ is the intensity of electric

Table 3. Molar Concentrations and Conductances of $LiClO_4$ Solutions in MEK-DMF Mixtures at 25°C

Pure MEK		5% DMF		11% DMF		17% DMF	
$10^4 c$	Λ	$10^4 c$	Λ	$10^4 c$	Λ	$10^4 c$	Λ
$mol\,dm^{-3}$	$S\,cm^2\,mol^{-1}$	$mol\,dm^{-3}$	$S\,cm^2\,mol^{-1}$	$mol\,dm^{-3}$	$S\,cm^2\,mol^{-1}$	$mol\,dm^{-3}$	$S\,cm^2\,mol^{-1}$
0.9878	165.078	1.9608	150.136	1.9608	139.312	1.9608	129.022
1.9427	158.053	3.8461	144.062	3.8461	134.754	3.3461	125.441
2.8661	152.736	5.6604	139.582	5.6604	131.342	5.6604	122.694
3.7596	148.422	7.4074	136.030	7.4074	128.600	7.4074	120.457
4.6247	144.804	9.0909	133.075	9.0909	126.301	9.0909	118.668
5.4627	141.688	10.7143	130.568	10.7143	124.316	10.7143	116.987
6.2748	139.001	12.2807	128.477	12.2807	122.602	12.2807	115.502
7.0622	136.564	13.7931	126.456	13.7931	121.043	13.7931	114.232
7.8261	134.408	15.2542	124.753	15.2542	119.882	15.2542	113.0178
8.5674	132.460	16.6666	123.220	16.6666	118.430	16.6666	112.043
9.2872	130.587	18.0328	121.905	18.0328	117.300	18.0328	111.098
9.9863	129.081	19.3548	120.588	19.3548	116.270	19.3548	110.220
10.6658	127.600	20.6349	119.425	20.6348	115.321	20.6349	109.410
11.3262	126.232	21.3750	118.781	21.3750	114.445	21.3750	108.676
11.9686	125.000	23.0769	117.457	23.0769	113.610	23.0769	107.999
12.5935	123.886	24.2424	116.482	24.2424	112.903	24.2424	107.345
13.2018	122.700	25.3731	115.555	25.3731	112.128	25.3731	106.745
		26.2706	114.849	26.2706	111.506	26.2706	106.193
		27.5314	113.222	27.5314	110.905	27.5314	105.657

28% DMF		54% DMF		77% DMF		86% DMF	
$10^4 c$	Λ	$10^4 c$	Λ	$10^4 c$	Λ	$10^4 c$	Λ
$mol\,dm^{-3}$	$S\,cm^2\,mol^{-1}$	$mol\,dm^{-3}$	$S\,cm^2\,mol^{-1}$	$mol\,dm^{-3}$	$S\,cm^2\,mol^{-1}$	$mol\,dm^{-3}$	$S\,cm^2\,mol^{-1}$
1.9608	123.854	1.9608	118.8521	1.9608	96.859	1.9608	85.500
3.8461	120.137	3.8461	114.2111	3.8461	93.284	3.8461	82.715
5.6604	117.586	5.6604	111.568	5.6604	91.036	5.6604	80.585
7.4074	115.241	7.4074	109.555	7.4074	89.285	7.4074	79.238
9.0909	113.006	9.0909	107.121	9.0909	88.176	9.0909	77.956
10.7143	111.586	10.7143	106.103	10.7143	87.034	10.7143	76.834
12.2807	110.132	12.2807	104.889	12.2807	86.003	12.2807	75.723
13.7931	109.211	13.7931	103.522	13.7842	85.135	13.7842	74.688
15.2592	107.867	15.2542	102.285	15.2542	84.276	15.2542	73.601
16.6666	106.999	16.6666	101.200	16.6666	83.358	16.6666	72.702
18.0328	105.878	18.0328	100.285	18.0328	82.488	18.0328	71.811
19.3548	105.003	19.3548	99.376	19.3548	81.693	19.3548	70.928
20.6349	104.355	20.6349	98.433	20.6349	80.888	20.6349	70.037
21.8769	103.853	21.8769	97.621	21.8750	80.001	21.8750	69.254
23.0760	103.021	23.0760	96.831	23.0769	79.205	23.0769	68.600
24.2424	102.285	24.2424	96.100	24.2424	78.531	24.2424	68.000
25.3731	101.573	25.3731	95.452	25.3731	77.866	25.3731	67.418
26.5362	101.003	26.4706	94.833	26.4704	77.214	26.4704	66.805
27.5362	99.582	27.5362	94.304	27.5314	76.666	27.5314	66.233

field in the region r from the charge (Ze). The β' is given by the expression

$$\beta' = (n^2+2)\mu/2K_BT, \qquad (5)$$

where n, μ are the refractive index and dipole moment of the medium respectively. The values of n and μ for pure solvents were taken from the literature[24] and for mixture it was supposed that $n_{mix.}=x_1n_1+x_2n_2$ and $\mu_{mix.}=(x_1\mu_1+x_2\mu_2)$ as found in case of other physical properties of these solvent mixtures.[9] Integrals Eqs. 2 and 3 were solved numerically and derived parameters are listed in Tables 6 and 7. In Eq. 2, a is the contact ion-pair distance. All the symbols in Eqs. 2 and 3 are described in detail in original papers.[12a] The values of K_A^{BFPP} were found almost the same as K_A. The values of $U(r)/K_BT$ and a derived from Eqs. 2 and 3 are given in Tables 6 and 7.

The thermodynamic ion pair association constant K_a for the reaction $M^+ + X^- \rightleftarrows M^+X^-$ was calculated from the K_A values using a relationship

$$K_a = (1000\,\rho/M)K_A, \qquad (6)$$

where $M/1000\rho$ ($dm^3\,mol^{-1}$) is the molecular volume of the solvent and M is its molecular weight.[10] The free energy of ion pair formation is related with K_a through a relationship

$$\Delta G = -RT \ln K_a. \qquad (7)$$

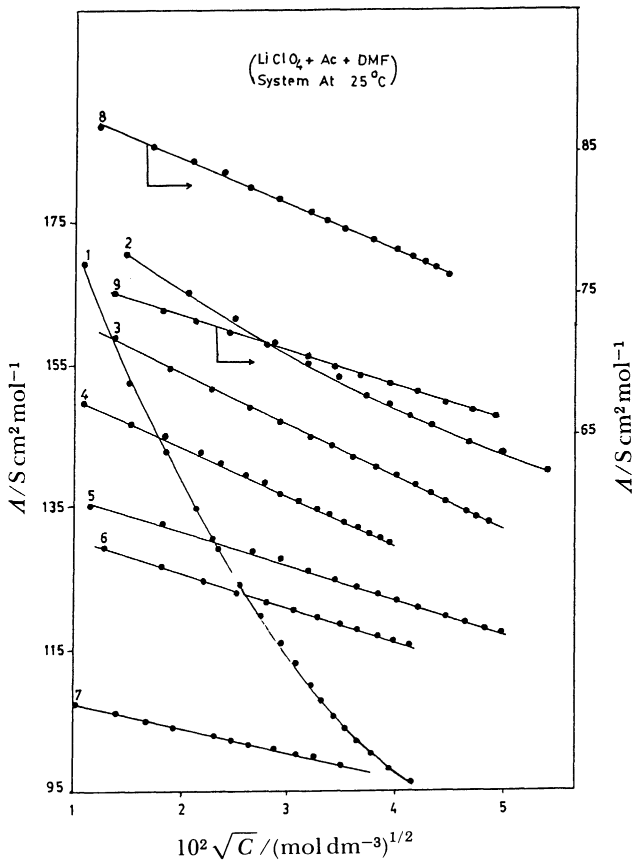

Fig. 1. Dependence of molar conductances of $LiClO_4$ on square root of its concentration in Ac-DMF binary mixtures at 25 °C.

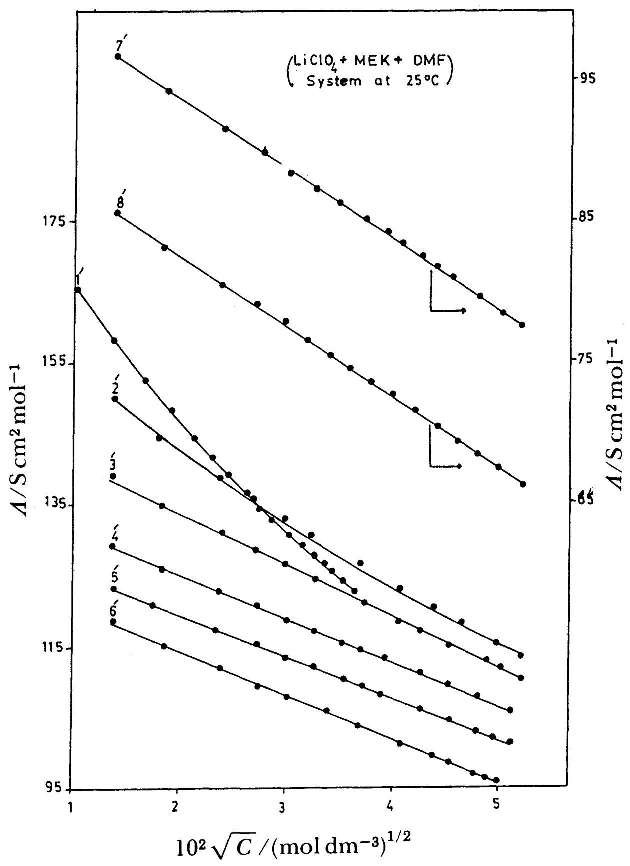

Fig. 2. Dependence of molar conductances of $LiClO_4$ on square root of its concentration in MEK-DMF binary mixtures at 25 °C.

Table 4. Conductance Parameters for $LiClO_4$ in Ac-DMF Binary Mixtures at 25°C

DMF wt%	Λ_0 S cm^2 mol^{-1}	K_A	σ %	10^8R cm
0.00	197.24 ±2.42	1550±255	0.032	15—18
3.45	182.36 ±0.14	540±20	0.021	10—12
11.50	168.32 ±0.16	198±9	0.060	8.6
28.00	155.81 ±0.12	93±4	0.103	8.2
36.00	143.23 ±0.03	55±3	0.033	7.8
45.00	134.00 ±0.04	41±7	0.012	7.4
62.00	110.79 ±0.03	26±4	0.011	6.8
82.00	90.40 ±0.02	17±3	0.005	6.6
100.00	77.24 ±0.18	9±2	0.003	6.00

Table 5. Conductance Parameters for $LiClO_4$ in MEK-DMF Binary Mixture at 25°C

DMF wt%	Λ_0 S cm^2 mol^{-1}	K_A	σ %	10^8R cm
0.00	178.86±0.63	785±25	0.037	13—15
5.00	163.45±0.55	231±8	0.014	10.8
11.00	155.92±0.13	126±6	0.011	9.4
17.00	149.38±0.39	89±3	0.005	8.6
28.00	137.3 ±0.28	63±5	0.033	7.8
54.00	125.75±0.06	28±4	0.027	7.6
77.00	96.85±0.03	18±3	0.041	6.8
86.00	86.63±0.02	12±2	0.007	6.6

The values of $-\Delta G/RT$ for $Li^+ClO_4^-$-ion-pair formation in the Ac, MEK, DMF, Ac-DMF, and MEK-DMF solvent systems are included in Tables 6 and 7.

Discussion

Limiting Molar Conductances. The Λ_0 ($LiClO_4$) values found for pure Ac, DMF, and MEK in the present work are 197.24, 77.24, and 178.86 S·cm^2·mol^{-1}, respectively, in agreement with values reported in literature.[5—7] No values of Λ_0 for $LiClO_4$ in MEK were available in literature. Comparing with the values of Λ_0 for $LiClO_4$ in Ac and LiBr and LiI in MEK (154 and 147 S·cm^2·mol^{-1}) respectively,[12b] the present value seems to be reasonable. This can be confirmed further by comparing viscosities of Ac and MEK which are 0.300 and 0.379 cp respectively. Addition of DMF either to Ac or to MEK decreased the values of Λ_0 for $LiClO_4$ in the Ac-DMF and MEK-DMF mixed solvent systems (Tables 4 and 5) due to the corresponding increase of viscosities of the mixtures.

The Association Constants. The association constants K_A and K_A^{BFPP} for $LiClO_4$ in Ac-DMF as well as in MEK-DMF showed no significant difference and consequently, only K_A are reported in Tables 4 and 5. These values for $LiClO_4$ in pure Ac, MEK, and DMF derived from conductance data in present work are

Table 6. Parameters Derived for $LiClO_4$ Using Eqs. 2 and 3 and Values of Free Energy Change of Ion-Pair Formation in Ac-DMF Binary Mixtures at 25°C

DMF wt%	K_A^{BFPP}	ε	ε'	$10^8 q$ cm	$10^8 a$ cm	$-U^{(r)}/K_BT$	$-\Delta G/RT$
0.00	1650	20.14	7.42	13.91	3.00	11.26	9.91
3.45	580	20.64	9.69	13.57	3.25	9.68	8.89
11.50	212	21.80	15.38	12.85	3.73	7.35	7.88
28.00	99	24.12	19.77	11.61	4.11	5.86	7.13
36.00	62	25.28	23.21	11.08	4.92	4.58	6.59
45.00	48	26.77	24.83	10.46	5.03	4.21	6.29
62.00	31	29.58	27.55	9.47	5.03	3.81	5.81
82.00	21	33.23	30.35	8.43	4.69	3.65	5.40
100.00	9	36.71	34.87	7.63	5.33	2.90	4.63

Table 7. Parameters Derived for $LiClO_4$ Using Eqs. 2 and 3 and Values of Free Energy Change of Ion-Pair Formation in MEK-DMF Mixture at 25°C

DMF wt%	K_A^{BFPP}	ε	ε'	$10^8 q$ cm	$10^8 a$ cm	$-U/K_BT$	$-\Delta G/RT$
0.00	790	18.01	10.03	15.56	3.66	9.51	9.04
5.00	235	18.95	16.17	14.78	4.72	6.46	7.82
11.00	128	20.07	18.77	13.96	5.66	4.99	7.23
17.00	92	21.19	20.04	13.22	6.04	4.42	6.89
28.00	68	23.25	22.04	12.05	5.76	4.22	6.58
54.00	31	28.11	26.66	9.97	5.54	3.64	5.80
77.00	18	32.41	31.28	8.65	5.93	2.94	5.41
86.00	14	34.00	33.37	8.22	6.12	2.48	5.01

1.5×10^3, 7.9×10^2, and 9 mol^{-1} dm^3, respectively, in agreement with the literature.[5,7,18] But literature survey shows that $LiClO_4$ is almost dissociated in pure DMF. These results have been derived both from spectroscopic as well as conductimetric studies of $LiClO_4$ in DMF. Gill et al. have recently reported the value of K_A for $LiClO_4$ in Ac and DMF, but not reported K_A values in Ac-DMF binary mixtures.[7] Justice[18] has reported the K_A value of 8 mol^{-1} dm^3 for $LiClO_4$ in pure DMF, which is in good agreement with the value 9±2 $mol^{-1}dm^3$ derived in the present work. Tables 4 and 5 show that, as the proportion of DMF increased, the corresponding association constant decreased in both Ac-DMF and MEK-DMF binary solvent systems. This is mainly due to the increase in dielectric constant of the medium with addition of DMF to Ac or MEK.

Comparing the K_A values for $LiClO_4$ in the Ac-DMF and MEK-DMF binary solvent system, it is observed that, despite higher dielectric constant values of the Ac-DMF binary mixtures, $LiClO_4$ is more associated in these mixtures than in the MEK-DMF binary mixtures. Thus, the isodielectric rule is again not valid in the present case. The present results also do not agree with the K_A values of $LiClO_4$ in MEK reported by Milaev.[15] Similar results were found in a previous study on LiCl in these mixed solvent systems.[8] Though MEK has lower dielectric constant, it has a greater polarizability volume than Ac. As pointed out by others[19] the solute-solvent interaction is specific. Both solute and solvent nature (shape, size, polarizability, dipole moment, and refractive index, etc.) are determinative factors for evaluation of the extent of association constant of electrolytes.

Further, the values of the contact ion-pair distance a for $Li^+ClO_4^-$ in pure Ac and DMF have been found to be 3±0.2 and 5.33±0.15 Å, respectively, which are in good agreement with values cited in literature.[5-7] The values of K_A and a in pure Ac, indicate that $LiClO_4$ exists as contact ion pairs; in MEK partial solvent-separated and in DMF almost solvent-separated ion pairs are expected (Tables 6 and 7). But small values of K_A and large values of a of $LiClO_4$ in the Ac-DMF binary solvent system clearly indicate that $LiClO_4$ is almost dissociated in these solvent systems. The value of K_a of $LiClO_4$ in MEK-DMF are smaller than those found in the Ac-DMF solvent system. Also, the values of a of $LiClO_4$ are larger in the MEK-DMF system than those found in the Ac-DMF solvent system. It shows that, the nature of the solvent is an important factor for determining an extent of ionic association. The order of preferential solvation of the Li^+ ion by these solvents is found to be DMF>MEK>Ac. Comparing the present results with those observed by others spectroscopically, in pure Ac[4b] and DMF,[13] an agreement with Popov's results of complete dissociation of $LiClO_4$ in DMF and disagreement with James et al.'s results—postulating no association of $LiClO_4$ in Ac upto 1 mol dm^{-3} concentration were found.

Free Energy Changes of Ion-Pair Formation and Potential Energy Function of Interionic Interaction. The values of ΔG, calculated from $\Delta G^\circ = -RT \ln K_a$

for ($Li^+ClO_4^-$) ion pair formation, become less negative as ε increases or the contents of DMF increase in Ac-DMF and MEK-DMF binary mixtures (Tables 6 and 7). This is because the enthalpic term ΔH in ΔG contains the work done in constituting a contact pair from free ions. The ΔH also contains a positive term due to replacement of nearest neighbor solvent molecule by the partner ion and hence causing a decrease in entropy. Tables 6 and 7 show that for $LiClO_4$—$|\Delta G(\mathrm{MEK})|<|\Delta G(\mathrm{Ac})|$, which is mainly due to larger polarizability volume of MEK than that of Ac and consequently major role of entropy term and decrease of ΔG value of ion-pair formation.

Tables 6 and 7 include the value of ε' —a parameter from dielectric saturation modification, and potential energy function ($U(r)/K_BT$) of interionic interactions. It is observed that the effect of dielectric saturation plays effective role in pure Ac, MEK and in mixtures of Ac-DMF; MEK-DMF, rich in Ac or MEK contents, respectively, for evaluation of K_A and a parameters for $LiClO_4$ in these solvent systems. As the contents of DMF increase in these two mixed solvent systems, the difference of ($\varepsilon-\varepsilon'$) became less. The same trend is found for potential energy function (P.E.F) of Li^+ ion and ClO_4^- ion interactions. Both, ε' and P.E.F. are interionic distance dependent. Therefore, it can be postulated that Li^+ and ClO_4^- ions are separated by solvent molecules in Ac-DMF and MEK-DMF mixtures.

Gilkerson et al.[20] have recently studied conductimetrically some lithium salts in MEK and 2-proponal respectively. They have discussed their results in terms of the square-mound potential model[21] modification of Bjerrum's theory for ion association. Similarly, Salomon et al.[17] have also studied some lithium salts in dimethylsulfite (DMSI). They have discussed their results on the basis of Barthel's model[22] modification of the Bjerrum theory for ion association. In both above models, non-coulombic interaction term in P.E.F has been introduced. It has been found that in present case of Ac-$LiClO_4$-DMF and MEK-$LiClO_4$-DMF systems, all the three modifications of Bjerrum ion association theory, (i.e. those by Fernandez-Prini and Prue, Justice and Justice's squaremound potential model, and that of Barthel), give almost the same result which indicates that $LiClO_4$ ion pair is solvent-separated. Since it has been found previously a preferential solvation of Li^+ ion by DMF molecules,[7,8] it can be concluded that solvation of Li^+ ion by these solvents is of the order DMF > MEK > Ac.

Finally, it can be concluded that though Ac-DMF and MEK-DMF constitute almost ideal systems,[9,16] the binary mixtures do not act as a single solvent towards an electrolyte. The previous[8] as well as the present studies show that the ion association process depends upon both solvent and solute.

A comparison of above mentioned modifications of the Bjerrum ion association theory, for the systems Ac-LiCl-DMF, MEK-LiCl-DMF, Ac-$LiClO_4$-DMF, and MEK-$LiClO_4$-DMF will be published later on in a near future.

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