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Conductance Study of Alkali Metal Chlorides and Ammonium Chloride in 1,2-Dimethoxyethane-Water Mixtures at 25 °C

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Conductance data for alkali metal chlorides and ammonium chloride in 1,2-dimethoxyethane (DME)-water mixtures (14.00<dielectric constant<56.76) at 25 °C are reported in the concentration range 0.0001—0.06 mol·dm^{-3}. The data have been analyzed by Fuoss (1978) conductance-concentration relation. Preferential solvation of cations by water does not show systematic trend depending on the cationic size. Walden product variations indicated the complex dependence of conductance of alkali metal cations on solvent sorting and structural effects. The energy (E_s) values suggest that alkali metal cations and chloride ions in majority exist as contact pairs in these solutions.

A series of investigations[1—6)] on the influence of solvent structure on limiting ionic mobilities of alkali metal cations and halide ions in water-organic solvent mixtures have been carried out in the recent past. Of these the most important contributions are by Kay et al.[1—3)] and also Petrella et al.[4—6)] In their studies the ionic Walden products have been analyzed in terms of the short range ion-solvent interactions. For cations (alkali metal) and anions (halide) they found that the curves for W_p (designated by us), the ratio of the limiting Walden product for the mixture to that of water, show maxima in water-rich regions where the long range order of water is increased by the addition of organic solvent. However, for anions the W_p values are less than unity in solvent mixtures where structure breaking occurs. Also a systematic decrease of W_p value with the increase in cationic or anionic sizes was observed irrespective of the type of change induced by the cosolvent on water structure. With the objective to examine how far these observations could be reproducible for alkali metal chlorides and ammonium chloride in 1,2-dimethoxyethane (DME)-water mixtures analogous conductance studies have been undertaken. DME is a dipolar aprotic solvent and weakly interacts with anions.[7)] The electrolytes in the present study have chloride (Cl^-) as the common anion so that the variations observed in Walden products are considered to be mainly due to the alkali metal cations only. This paper, therefore, deals with the conductance study of LiCl, NaCl, KCl, RbCl, CsCl, and NH_4Cl in 1,2-dimethoxyethane-water mixtures at 25 °C.

Experimental

Conductivity water (κ=0.2—0.5×10^{-6} mho cm^{-1}) was prepared by distillation of double distilled water in the presence of $KMnO_4$ in an all Pyrex glass set.

1,2-Dimethoxyethane (Riedel-De-Haenag) was kept two days over KOH and then refluxed for 24 h. This was distilled over sodium and refluxed again for 24 h. Then the sample was distilled and middle fraction was directly used for measurements.[8)]

Lithium chloride (AR), sodium chloride (AR, BDH), rubidium chloride (E. Merck), cesium chloride (E. Merck), and ammonium chloride (AR, BDH) were recrystallized twice from conductivity water and dried in a vacuum desiccator. Potassium chloride (AR, BDH) was recrystallized as suggested by Hawes and Kay.[9)]

Results and Discussion

The physical properties, density (ρ), viscosity (η) and dielectric constant (D) of DME-water mixtures are given in Table 1. The molar conductance values Λ (S·cm^2·mol^{-1}) as a function of concentration C (mol·dm^{-3}) in six compositions of DME-water mixtures at 25 °C are shown in Table 2. Conductance data in the present investigation are analyzed by the Fuoss conductance-concentration relation.[10)] The use of any other equation or incorporation of slight modification[11)] may introduce small changes in the individual fitting parameters but will not alter the overall conclusions which can be deduced from trends in these parameters. For a set of conductance data (C_j, Λ_j; J=1, N) the three adjustable parameters (Λ_o, K_A, and R) are derived from the following three equations:

$$\Lambda = p[\Lambda_o(1 + \Delta X/X) + \Delta\Lambda_e] \quad (1)$$

$$\gamma = 1 - K_A C \gamma^2 f^2 \quad (2)$$

Table 1. Physical Properties of the Solvent Mixtures (DME-Water) at 25°C

Mole fraction of DME	D	ρ/g cm^{-3}	η/10^{-2}P
0.00	78.54	0.9908	0.8903
0.09	56.75	0.9837	1.9861
0.20	40.01	0.9754	1.9905
0.30	31.05	0.9456	1.5632
0.40	24.00	0.9292	1.2161
0.50	17.53	0.9147	0.9503
0.60	14.00	0.9031	0.7725

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Table 2. Conductance Data in DME–Water Mixtures at 25 °C

$C/10^{-4}$ mol·dm^{-3} (1)	Λ/S cm^2 mol^{-1} (2)	$C/10^{-4}$ mol·dm^{-3} (3)	Λ/S cm^2 mol^{-1} (4)	$C/10^{-4}$ mol·dm^{-3} (5)	Λ/S cm^2 mol^{-1} (6)
1. Lithium chloride					
0.09 mole fraction DME		0.20 mole fraction DME		0.30 mole fraction DME	
601.0	28.01	262.2	29.01	116.5	36.12
500.7	29.78	218.5	30.58	97.0	37.59
429.2	31.35	187.3	31.91	83.2	38.83
375.5	32.73	163.9	33.12	72.8	39.92
300.4	35.17	145.7	34.25	58.2	41.69
250.3	37.22	131.1	35.23	41.6	44.30
187.7	40.58	109.2	36.85	32.3	46.15
150.2	43.26	93.6	38.40	24.2	48.20
125.1	45.47	81.9	39.67	28.8	49.23
107.3	43.35	72.8	40.78	18.2	60.07
83.4	50.40	65.5	41.73	14.5	51.42
62.5	53.84	54.6	43.39	12.1	52.44
0.40 mole fraction DME		0.50 mole fraction DME		0.60 mole fraction DME	
55.0	39.25	14.8	34.10	6.3	46.10
45.8	40.75	12.3	35.85	5.2	48.44
39.3	41.89	10.6	37.37	4.5	50.43
34.4	42.92	9.2	38.79	3.9	51.15
27.5	44.61	7.4	41.81	3.1	55.40
22.9	45.91	6.1	42.82	2.6	57.56
19.6	47.08	5.1	44.72	2.2	59.61
17.2	48.00	4.6	45.79	1.9	61.35
15.2	48.76	3.7	47.98	1.7	62.88
11.4	50.58	3.0	49.73	1.5	64.18
8.6	52.27	2.3	52.38	1.3	66.49
6.8	53.47	2.0	53.40	1.1	68.68
2. Sodium chloride					
0.09 mole fraction DME		0.20 mole fraction DME		0.30 mole fraction DME	
606.8	35.28	206.0	35.16	98.8	34.29
505.7	36.85	171.7	36.79	82.3	35.71
433.4	38.35	147.1	38.20	70.5	36.99
337.1	40.71	128.7	39.45	61.7	38.06
252.8	43.66	114.4	40.41	49.4	39.735
189.6	46.81	85.8	42.91	41.1	41.24
151.7	49.38	75.5	44.02	35.2	42.43
126.4	51.54	64.3	45.30	30.8	43.49
108.3	53.38	51.5	47.21	24.7	45.13
84.2	56.48	42.9	48.58	17.6	47.45
63.2	60.06	32.1	50.80	13.7	49.07
47.4	63.58	25.7	52.38	10.2	50.68
0.40 mole fraction DME		0.50 mole fraction DME		0.60 mole fraction DME	
74.6	27.82	20.2	44.20	10.7	39.73
62.2	29.16	16.8	45.48	9.5	40.85
53.3	30.29	14.4	46.45	8.6	41.86
41.4	32.25	12.6	47.28	7.1	43.72
31.1	34.56	11.2	48.11	6.1	45.26
23.3	36.75	18.1	48.76	5.3	46.67
18.6	38.51	8.4	49.95	4.7	41.91
15.5	39.92	7.2	50.86	4.3	49.04
11.6	42.08	6.3	51.67	3.9	50.06
9.3	43.73	5.0	52.93	3.5	57.02
6.5	46.07	4.2	53.96	2.9	53.18
5.1	47.54			2.6	54.19
3. Potassium chloride					
0.09 mole fraction DME		0.20 mole fraction DME		0.30 mole fraction DME	
604.8	36.77	238.4	40.00	115.1	51.28
549.8	37.91	216.7	40.93	102.2	52.25
465.2	39.78	198.5	41.82	95.9	52.89
432.0	40.62	170.3	43.39	79.9	54.43

Table 2. (Continued)

$C/10^{-4}$ mol·dm^{-3} (1)	Λ/S cm^{2} mol^{-1} (2)	$C/10^{-4}$ mol·dm^{-3} (3)	Λ/S cm^{2} mol^{-1} (4)	$C/10^{-4}$ mol·dm^{-3} (5)	Λ/S cm^{2} mol^{-1} (6)
378.0	42.34	149.0	44.76	68.5	55.62
336.0	43.94	132.4	46.03	59.9	56.70
302.4	45.41	119.2	47.19	53.3	57.65
252.0	47.93	99.3	49.19	47.9	58.43
216.0	50.18	85.2	50.82	39.9	59.89
189.0	52.12	74.5	52.31	36.9	60.57
168.0	53.95	66.2	53.61	34.2	61.20
151.2	55.70	54.1	55.84	31.9	61.65
0.40 mole fraction DME		0.50 mole fraction DME		0.60 mole fraction DME	
48.6	53.81	24.1	49.70	9.3	46.30
44.2	54.60	19.9	51.72	7.7	48.39
37.4	56.28	18.6	52.51	6.6	50.09
32.4	57.70	15.5	54.55	5.4	52.37
28.6	58.93	13.3	56.39	4.9	53.74
25.6	60.03	11.6	51.81	4.2	55.62
22.1	61.38	10.3	59.19	3.5	57.70
18.7	62.89	9.3	68.42	3.1	59.64
16.2	64.03	7.7	62.49	2.7	61.32
12.8	66.11	6.6	64.20	2.4	62.83
11.0	67.20	5.8	65.65	2.1	64.72
8.6	69.01	4.2	69.18	1.9	65.95
4. Rubidium chloride					
0.09 mole fraction DME		0.20 mole fraction DME		0.30 mole fraction DME	
600.6	36.65	208.6	38.54	97.9	41.08
500.5	38.76	173.8	40.55	81.4	42.69
429.0	40.58	149.0	42.26	69.9	44.08
375.4	42.29	130.3	43.77	61.2	45.23
300.4	45.28	115.9	45.12	54.4	46.25
250.2	47.81	86.9	48.42	48.9	47.16
214.5	50.03	74.5	50.20	40.8	48.70
116.8	53.72	65.2	51.74	34.9	49.97
115.1	58.27	57.9	53.05	27.2	51.97
107.2	60.68	52.1	54.24	24.4	52.70
83.4	64.70	43.4	56.27	20.4	54.15
62.5	69.32	37.2	58.01	15.3	56.05
0.40 mole fraction DME		0.50 mole fraction DME		0.60 mole fraction DME	
48.3	34.37	17.3	46.02	10.5	45.51
40.2	36.05	14.4	48.01	8.7	47.58
34.5	37.50	12.3	49.62	7.5	49.39
30.1	38.69	10.8	51.08	6.5	57.05
26.8	39.79	9.6	52.32	5.8	52.53
24.1	40.77	8.6	53.44	5.2	53.90
20.1	42.47	7.2	55.36	4.3	56.22
17.2	43.89	6.1	56.95	3.7	58.09
13.4	46.13	4.8	59.47	3.2	59.95
10.0	48.71	3.6	62.18	2.6	62.73
8.6	50.02	2.4	65.65	2.1	65.14
6.7	52.04	1.8	67.84	1.8	67.18
5. Cesium chloride					
0.09 mole fraction DME		0.20 mole fraction DME		0.30 mole fraction DME	
515.2	63.03	327.3	43.31	305.7	37.14
436.8	63.74	273.2	43.99	252.8	37.92
362.5	64.49	225.1	44.71	201.2	38.78
270.7	65.61	186.3	45.42	150.3	39.85
200.3	66.22	119.7	47.02	104.8	41.31
140.1	67.74	100.9	47.61	80.7	42.37
105.1	68.53	75.7	48.55	64.3	43.26
67.1	69.60	50.4	49.65	52.0	44.07
50.1	70.21	37.2	50.56	35.6	45.41
32.0	71.00	25.3	51.42	21.6	46.99
16.8	71.89	15.8	52.35	11.5	48.58

Table 2. (Continued)

$C/10^{-4}$ mol·dm^{-3} (1)	Λ/S cm^2 mol^{-1} (2)	$C/10^{-4}$ mol·dm^{-3} (3)	Λ/S cm^2 mol^{-1} (4)	$C/10^{-4}$ mol·dm^{-3} (5)	Λ/S cm^2 mol^{-1} (6)
0.40 mole fraction DmE		0.50 mole fraction DME		0.60 mole fraction DME	
98.1	34.59	32.0	25.75	31.9	17.57
82.1	35.71	27.1	26.89	26.4	18.74
68.1	36.88	23.1	28.09	21.2	20.18
57.5	37.91	20.1	29.02	17.8	21.41
49.2	38.85	15.7	30.98	15.2	22.54
42.3	39.74	13.0	32.45	11.5	24.69
34.8	40.87	10.7	34.03	9.4	26.31
27.7	42.12	8.5	35.84	7.7	28.03
22.2	43.29	7.0	37.42	5.8	30.50
18.3	44.26	5.5	39.46	4.5	32.89
13.1	45.82	3.8	42.21	3.4	35.54
9.6	47.11	2.3	45.70	2.2	39.60
6. Ammonium chloride					
0.09 mole fraction DME		0.20 mole fraction DME		0.30 mole fraction DME	
583.7	41.11	208.4	40.65	98.8	34.43
486.4	43.08	173.7	42.43	82.3	35.15
416.9	44.82	148.9	43.88	70.5	35.80
364.8	46.40	130.2	45.20	54.9	36.75
291.8	49.16	115.8	46.49	49.4	37.11
243.2	51.51	104.2	47.49	41.1	37.75
208.4	53.48	86.8	49.32	35.2	38.32
162.1	57.07	74.4	50.79	30.8	38.74
121.6	61.23	65.1	52.06	27.4	39.05
104.2	63.51	57.9	53.11	17.6	40.16
91.2	65.52	52.1	54.06	10.2	41.43
72.9	68.87	43.4	55.72	8.8	41.69
0.40 mole fraction DME		0.50 mole fraction DME		0.60 mole fraction DME	
74.6	28.47	16.8	38.87	12.1	40.49
62.2	29.51	13.3	40.11	10.3	42.22
53.3	30.40	11.4	41.06	8.6	44.05
46.6	31.11	10.2	41.71	7.2	45.98
37.3	32.35	9.2	42.29	6.2	47.61
31.1	33.34	8.5	42.73	4.8	50.28
23.3	34.86	7.2	43.56	3.6	53.28
18.6	35.98	6.3	44.29	3.0	54.88
13.3	37.51	5.6	44.86	2.7	56.20
10.3	38.65	4.5	45.89	2.3	57.53
7.7	39.80	4.2	46.26	1.8	60.06
5.1	41.20	3.5	47.03	1.3	62.56

$$\ln f = -\beta\kappa/2(1 + \kappa R) \qquad (3)$$

Here $\Delta X/X$ and $\Delta\Lambda_e$ are the relaxation and electrophoretic terms respectively and expressions used for these terms are the same as these used by Fuoss.[10] The detailed method of analysis of the data has been described earlier.[12] Various parameters thus derived from the conductance data are assembled in Table 3. Limiting molar conductance values obtained in our present investigation for all the electrolytes, viz., chlorides of Li, Na, K, Rb, Cs, and NH_4 in water at 25 °C are in agreement with the reported values.[13–17] Also the Λ_o values for CsCl in DME–water mixtures obtained in present work are in good agreement with the already reported values.[18] These facts substantiate the accuracy of our experimental results and the computational procedures.

The limiting molar conductance variations as well as the viscosity variation with the mole fraction of DME are depicted in the Fig. 1. DME has been characterized as a structure promoter in water rich mixtures through viscosity studies.[19] On structural characteristics of DME–water mixtures no further information is available in the literature. A decrease in limiting molar conductance for each electrolyte with a corresponding increase in viscosity of the solvent mixtures has been observed both in the water rich and DME rich mixtures. The maximum viscosity and the minimum in the limiting molar conductance ($\Lambda_{o_{min}}$) of any electrolyte does not occur at the same mole fraction of DME and also $\Lambda_{o_{min}}$ is shifted towards the DME rich region. This is because of the pre-

Table 3. Derived Conductance Parameters

Mole fraction of DME (1)	$\Lambda_0 \pm \Delta\Lambda_0$ S·cm² mol⁻¹ (2)	K_A (3)	K_R (4)	K_S (5)	R Å (6)	σ% (7)	$\Lambda_0 \cdot \eta$ Ω⁻¹ cm·mol⁻¹P (8)	E_s/kT J⁻¹ (9)
1. Lithium chloride								
0.00	115.12±0.01	0.79	0.71	0.11	5.12	0.023	1.024	+2.20
0.09	79.31±0.02	120.60	3.16	37.10	6.50	0.009	1.575	−3.61
0.20	65.06±0.10	158.39	6.43	23.61	7.04	0.056	1.294	−3.16
0.30	61.69±0.01	152.93	11.81	11.94	7.51	0.01	0.964	−2.47
0.40	62.53±0.03	282.30	38.60	6.31	14.53	0.044	0.760	−1.84
0.50	69.78±0.07	1988.21	73.28	26.13	7.69	0.052	0.663	−3.26
0.60	91.00±0.04	4172.51	146.37	27.50	9.49	0.021	0.703	−3.31
2. Sodium chloride								
0.00	126.53±0.01	0.81	0.79	0.02	5.56	0.018	1.126	+3.91
0.09	90.36±0.06	185.83	31.24	4.94	19.55	0.036	1.794	−1.59
0.20	64.04±0.08	107.04	7.45	13.36	8.01	0.080	1.274	−2.59
0.30	60.07±0.04	218.38	25.12	7.69	14.00	0.051	0.938	−2.03
0.40	57.86±0.03	467.28	28.90	15.16	5.56	0.045	0.703	−2.71
0.50	64.56±0.06	703.35	272.17	1.58	4.53	0.045	0.613	−0.45
0.60	83.88±0.05	5008.83	890.83	4.62	5.06	0.015	0.648	−1.53
3. Potassium chloride								
0.00	149.90±0.01	0.56	0.45	0.24	4.65	0.012	1.334	+1.42
0.09	117.87±0.47	283.57	20.67	10.53	16.52	0.044	2.341	−2.35
0.20	83.10±0.06	211.68	34.51	5.13	18.61	0.024	1.653	−1.63
0.30	77.69±0.12	148.17	51.19	1.89	2.53	0.072	1.214	−0.63
0.40	81.82±0.08	240.92	24.41	8.86	8.80	0.063	0.994	−2.18
0.50	90.75±0.10	1203.74	195.13	5.16	4.95	0.047	0.862	−1.64
0.60	104.64±0.16	8296.77	1592.20	4.21	4.54	0.036	0.808	−1.43
4. Rubidium chloride								
0.00	153.64±0.01	0.26	0.19	0.36	3.35	0.011	1.367	+1.02
0.09	108.14±0.11	177.75	14.08	11.62	14.03	0.028	2.147	−2.45
0.20	80.20±0.05	168.87	11.05	14.28	10.48	0.025	1.596	−2.65
0.30	67.62±0.04	155.55	11.81	12.16	7.51	0.040	1.057	−2.49
0.40	66.55±0.04	532.58	24.28	20.92	7.02	0.035	0.809	−3.04
0.50	79.67±0.01	1052.82	61.31	16.17	10.54	0.015	0.757	−2.78
0.60	79.67±0.15	4440.91	593.66	6.48	5.53	0.050	0.743	−1.86
5. Cesium chloride								
0.00	153.04±0.02	0.62	0.58	0.06	3.62	0.015	1.362	+2.81
0.09	74.36±0.01	11.18	6.80	0.64	10.02	0.008	1.477	+0.44
0.20	55.65±0.02	13.71	5.85	1.34	3.54	0.056	1.107	−0.29
0.30	52.84±0.02	39.41	18.54	1.12	3.52	0.061	0.826	−0.11
0.40	54.74±0.01	201.79	46.88	3.30	16.55	0.010	0.665	−1.93
0.50	57.98±0.07	1417.99	75.40	17.80	7.51	0.069	0.551	−2.87
0.60	64.64±0.13	5357.60	142.52	36.58	19.04	0.051	0.498	−3.59
6. Ammonium chloride								
0.00	149.75±0.01	0.35	0.29	0.20	4.12	0.018	1.333	+1.60
0.09	108.20±0.01	187.18	27.31	5.85	18.52	0.026	2.148	−1.76
0.20	72.73±0.09	96.76	5.19	17.61	5.03	0.058	1.447	−2.86
0.30	45.22±0.03	76.24	26.76	1.84	14.52	0.092	0.707	−0.60
0.40	46.77±0.02	224.91	29.27	6.68	11.52	0.041	0.568	−1.89
0.50	55.35±0.03	563.46	471.01	2.29	5.15	0.041	0.526	−0.82
0.60	77.61±0.03	2302.65	145.84	14.78	19.52	0.023	0.599	−2.69

ferential solvation of cations (Cl^- common anion) by water as DME is less polar than water. The shift in $\Lambda_{0_{min}}$ towards the DME rich region may be due to gradual replacement of water molecules by DME molecules in the cationic shells as a result of breakdown of the water polymeric structure at higher concentrations of DME.

The Walden product ($\Lambda_0 \cdot \eta$) maximum is observed around 0.1 mole fraction of DME (Fig. 2) for all the alkali metal cations and ammonium ion (Cl^- being the common anion). This behavior of alkali metal cations is similar to that observed by Kay et al., for the

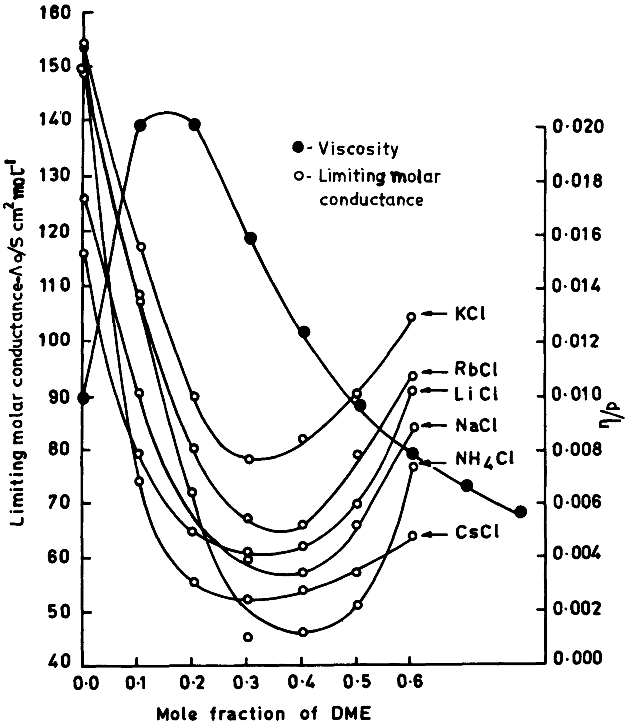

Fig. 1. Variation of viscosity (η) and limiting molar conductances (Λ_0) of alkali metal chlorides and ammonium chloride with mole fraction of DME in water.

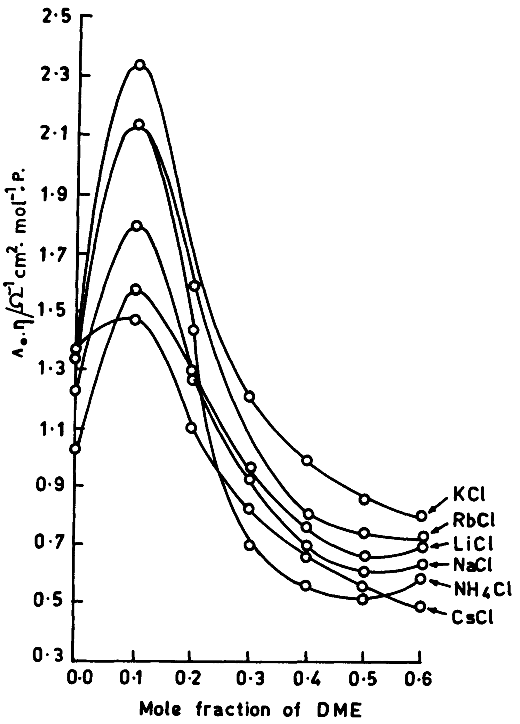

Fig. 2. Variation of Walden products ($\Lambda_0 \cdot \eta$) of alkali metal chlorides and ammonium chloride with respect to mole fraction of DME in water.

same ions in other aqueous binary mixtures of the solvents dioxane,[1] ethanol,[2] and *t*-butyl alcohol.[3] Petrella et al. have also observed similar Walden product maxima for alkali metal cations and halide ions in sulfolane–water,[4] acetonitrile–water,[5] and dimethyl sulfoxide–water[6] mixtures. They have explained the existence of maximum on the basis of Kay's "solvent sorting model".[2] Several other significant reasons[20–22] were also suggested for this variation, and their mathematical treatments[23–30] also have been given by different workers from time to time. The most recent model proposed by Nakahara et al.[30] demonstrates the superiority of residual friction coefficient ($\Delta\zeta$) over the Walden product to explain long range interactions in the case of smaller ions. However, due to the lack of experimental data on intermediate frequency dielectric constants (ε_c) and infinite frequency dielectric constants (ε_∞) for these electrolyte solutions of DME–water mixtures it would not be possible to follow the method of Nakahara. Alternatively, the Walden product maximum observed in the present study has been explained by Kay's model.

In water–DME mixtures the ion water interactions are stronger than ion DME interactions, and therefore in the ionic cosphere there is a higher percentage of water than in the bulk mixture. Due to preferential solvation of these ions by water in this region of the solvent mixtures, viscosity of the solvent in the vicinity of these ions is lower than that of the bulk solvent. Since the bulk viscosity value is used in the calculation of Walden product, the calculated values of $\Lambda_0 \cdot \eta$ are too high up to the point corresponding to the viscosity maximum after which they are low, and therefore a maximum in Walden product occurs. The bulk viscosity of DME - water mixtures also goes through a maximum and since the alkali metal cations as well as ammonium ion have water-rich solvation shells in dilute DME - water mixtures, the observed behavior of these ions is consistent with Kay's model.

However, the height of the Walden product maximum relative to that in pure water (designated as W_p), does not show systematic dependence on the cationic size in the present results (Fig. 2). This is in contrast to the earlier observations.[1–6] The observed order of variation of W_p value, i.e.

$$W_p(\mathrm{Cs}^+) < W_p(\mathrm{Li}^+) < W_p(\mathrm{Na}^+) < W_p(\mathrm{Rb}^+) \approx W_p(\mathrm{NH_4}^+) < W_p(\mathrm{K}^+),$$

cannot be explained on the basis of sorting mechanism alone. Petrella et al.[3–6] have shown that alkali metal cations are sensitive to sorting effect and halide ions are influenced by structural effects. Parker et al.[31] have however concluded through their analogous conductance studies that the behavior of ions (cations and anions) is quite complex and may be influenced by a combination of such factors as solvent sorting and structural changes due to the solvent mixing. Therefore, a plausible explanation may be given as follows for the observed order of variation of W_p value. Let us first consider the Li^+ and Cs^+ ions. As the sorting effect will be more accentuated in the case of smaller ions the order $W_p(Li^+)>W_p(Cs^+)$ is consistent with the sorting model. However, in the case of Na^+ and K^+ ions the order $W_p(K^+)>W_p(Na^+)$ is not in agreement with this model. Na^+ and K^+ ions behave as structure breakers in water. As DME–water mixtures are more structured than water, Na^+ and K^+ may behave as better structure breakers in the mixtures than in water. The largest ion will show the greatest increase and hence the order observed for Na^+ and K^+ ions. In the case of NH_4^+ and Rb^+ the magnitudes of heights of Walden product maxima are equal, which suggests that the contribution of structure breaking effect of these two ions of equal size is the same in these solutions. These results indicate that alkali metal cations are not only sensitive to sorting effect but also influenced by structural effects.

Association constant values (K_A) for all the electrolytes given in Table 3 are greater than 10 indicating significant association in DME–water mixtures. This pairing constant (K_A) is the product of two terms,[10] one (K_R) of which depends explicitly on dielectric constant of the solvent. While the other (K_S) is system-specific depending on short-range ion–ion and ion–solvent interactions. The relationship is represented as,

$$K_A = K_R(1 + K_S). \tag{4}$$

Where

$$K_R = \frac{4\pi N \cdot R^3}{3000} \exp(e^2/RDkT), \tag{5}$$

and

$$K_S = \frac{\alpha}{1-\alpha} = \exp(-E_s/k \cdot T) = \exp(-\varepsilon). \tag{6}$$

N is Avogadro's number, e is electronic charge, k is Boltzmann's constant, D is dielectric constant, R is cosphere (Gurney) diameter, and T is absolute temperature. The plot of $\log K_R$ vs. $1/D$ is therefore expected to show linear variation (Fig. 3) in the present study. But the variation of E_s/kT vs. $1/D$ will not be linear (Fig. 4) as K_S depends on specific ion–solvent interactions.[32] If α is the time average fraction of diffusion pairs (for which $a \leqslant r \leqslant R$) which are in contact, the equilibrium between solvent separated pairs and contact pairs is described[32] by Eq. 6, where E_s is the difference in free energy between states defined as $r=R$ and $r=a$. The magnitude of E_s may give an insight into the mechanism of process of ionic association in these solutions. The values of K_R, K_S, and E_s are shown in Table 3 for all the electrolytes in DME–water mixtures. A remarkable decrease in E_s values from pure water to those of mixtures for all the electrolytes is observed (Fig. 4). Also there is no systematic decrease in these values with the increase in content of DME in the mixtures. This pattern of behavior of E_s becoming less positive as polarizability of the solvent decreases was observed in other systems[32] also. This suggests the predominance of

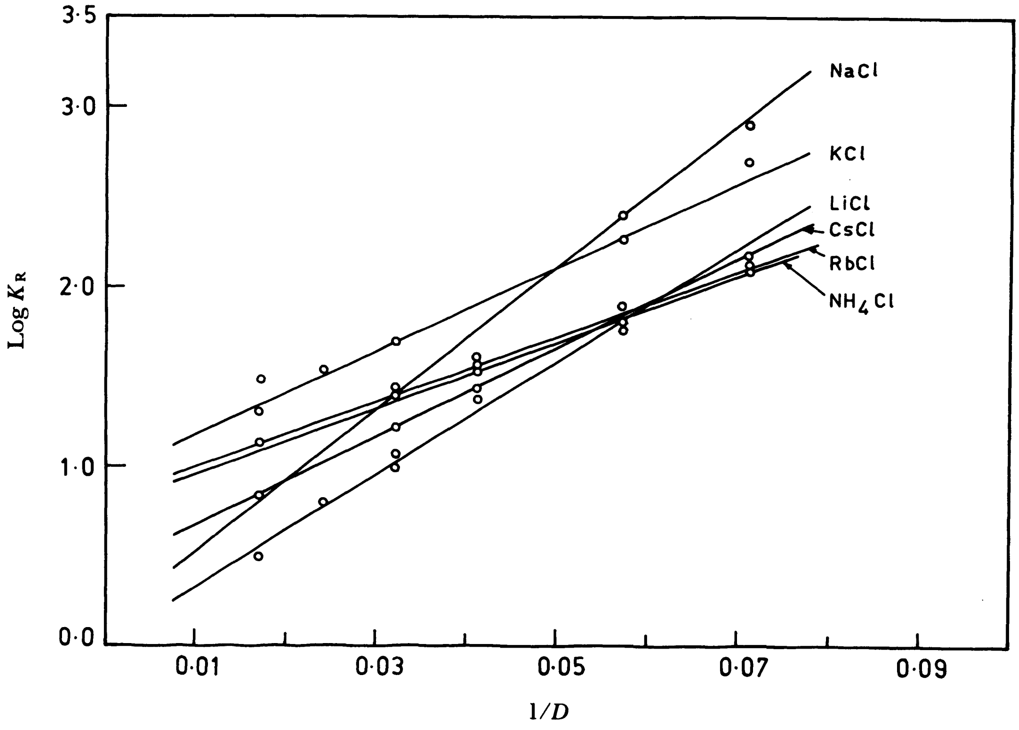

Fig. 3. Plot of $\log K_R$ vs. $1/D$.

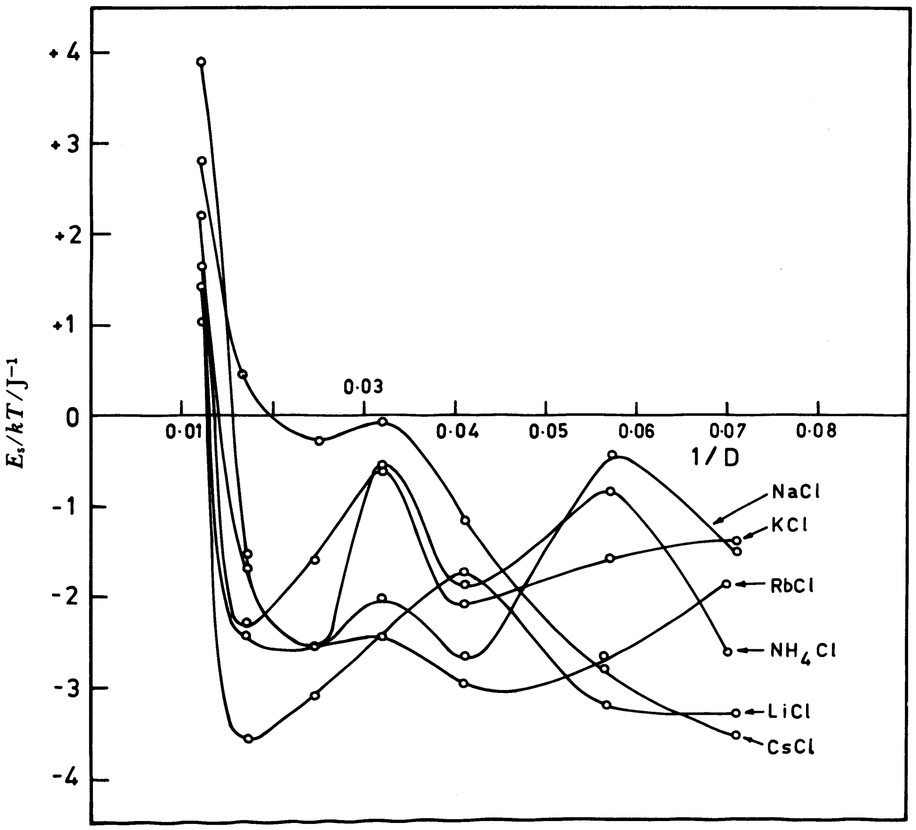

Fig. 4. Variation of E_s/kT with the reciprocal of dielectric constant ($1/D$).

electrostatic effect in the E_s and indicate formation of more contact ion pairs. Even though there is every possibility for the formation of solvent separated ion pairs through the donor-acceptor type of interaction[33-37] in these electrolyte solutions, as there are two bonding oxygen sites available in DME, the trend of the variation in E_s values suggests that alkali metal cations and chloride ions in majority exist as contact pairs. This may be due to the less polarizability of DME which allows the interionic attraction to become greater in these solutions. However, the variations of E_s/kT vs. $1/D$ are not systematic (Fig. 4) because of the competition between the donor-acceptor interactions and electrostatic interactions.

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