Intermolecular Interactions and the Conductance of some Tetra alkyl ammonium Salts in Ethylene Glycol - Ethanol Mixtures at 30°C

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Intermolecular interactions in ethylene glycol-ethanol mixtures at 30°C were studied using density, viscosity and dielectric constant data in the calculation of the excess volume ΔV^{E}_{M12}, deviation in the molar viscosity $\Delta\eta_{M12}$, Gibbs free energy for flow (G^{*E}) and deviation in the dielectric constant ΔD. The presence of a pronounced minimum in ΔV^{E}_{M12} values, a maximum in $\Delta\eta_{M12}$ values and a large variation in the value of both G^{*E} and ΔD at $x_{EG} = 0.5$ gave an indication of a probable existence of the molecular complex (EG : EtOH = 1 : 1).

The conductance of Et_4NBr,Et_4NI, Pr_4NI, Bu_4NI, Hex_4NI and Et_4NClO_4 were reported in the two simple solvents at 30°C, while the conductance of the iodide salts were reported in ethylene glycol-ethanol mixtures at the same temperature. The data were analyzed by Fuoss equation (1980) and all the salts were found to be associated. The variation of Walden proudct with the solvent composition for each salt was used to prove the importance of ionic solvation in the interpretation of the data and to calculate the single ion conductances in the protic - protic (EG-EtOH) mixtures at 30°C applying Sadek and Hafez method.

The intermolecular interactions were studied from density, viscosity and/or dielctric constant measurements by calculating the excess volume (ΔV^{E}_{M12}) or deviation in the molar viscosity ($\Delta\eta_{M12}$) and/or deviation in the dielectric constant (ΔD). This was widely used for protic - protic systems (e.g. aqueous glycol [1], aqueous alcohol [2]), protic - diplar aprotic mixtures (e.g. H_2O-DMSO and H_2O-Me_2CO [2]) dipolar aprotic - dipolar aprotic mixtures (e.g. $PhNO_2$-sulpholane [3]) and polar - nonpolar systems (e.g. H_2O-dioxan [4]). Existence of molecular complexes were suggested in all cases.

The electrical conductance of various tetraalkylammonium salts were reported in simple protic solvents as water [5] and monohydric alcohols [4,6-8]. Similar results were also reported in binary mixtures where at least one is protic e.g. H_2O-dioxan [9], EtOH-Me_2CO [10] and n-PrOH-Me_2CO[11]. A few studies were carried out in the amphiprotic solvent - ethylene glycol [12, 13] which is a difunctional alcohol with relatively high density (1.1095 $g.ml^{-1}$) and high viscosity (0.1619 p) at 25°C.

This work is a part of systematic study of intramolecular interactions in binary liquid mixtures and transport properties of the symmetrical (1:1) electrolytes in their dilute solutions. In the present case, density (d) and viscosity (η) are measured for different composition of EG-EtOH mixture at 30° C; the dielectric constant (D) data are taken from literature [14]. From these ΔV^{E}_{M12}, $\Delta\eta_{M12}$, G^{*E} and ΔD are calculated.

The electric conductance of two series of tetra alkylammonium salts - one series

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with common anion (R_4NI where R=Et, Pr, Bu and Hex) and the other with common cation (Et_4NX where X=Br, I and ClO_4) are measured in the two individual solvents at 30°C. The electric conductance of the first series are reported in EG-EtOH mixtures at the same temperature. The data are analyzed by Fuoss equation (1980) [15] to obtain the characteristic parameters: the equivalent conductance at infinite dilution (Λ_o), the association distance R and the association constant (K_A).

Variation of R and K_A in simple solvents are discussed with reference to the variation of cationic and anionic size of the solutes while their variation in mixed solvents are discussed with the variation in the composition of the solvent.

Finally, the Walden product ($\Lambda\eta$) is calculated for each salt at different solvent compositions; they are used for applying Sadek and Hafez [16] method to obtain and $\lambda^{\cdot}_o$ in EG-EtOH mixtues at 30° C.

Table 1

Purification and drying of salts

Salt	Recrystalized from	Drying condition
Et_4NBr	EtOH [a]	12 hr in a vacuum oven at 160° C
Et_4NI	Me_2CO + H_2O [b]	Some hr in a vacuum oven in presence of P_2O_5 at 80° C
Pr_4NI	MeOH + Ether [c]	Over $CaSO_4$ / P_2O_5 at 70° C in dark vacuum desiccator
Bu_4NI	Me_2CO+ Ether [c]	Over $CaSO_4$ / P_2O_5 at 56° C in dark vacuum desiccator
Hex_4NI	Me_2CO + Ether [c]	Some hrs in a vacuum oven in presence of P_2O_5 at 90°C

(a) L. Bahadur and M.V. Ramanamurthi, *J. Chem. Soc. Faraday I.* **76** (1980) 1409.
(b) D.S. Gill and M.B. Sekhri, *Z.Phys. Chem. (N.F.)*, **137** (1983) 221.
(c) D.F. Evans, C. Zawoyski and R.L. Kay, *J.Phys. Chem.*, **69** (1965) 3878.
(d) L. Rodehuser and H. Schneider, *J.Solution Chem.*, **9** (1980) 683.

EXPERIMENTAL

Solvents

Absolute ethanol(BDH) was purified using the method published earlier [17]. Its specific conductance $(x_o)_{30}$ was equal to $(1\text{-}2)\times10^{-8}$ Ω^{-1} cm^{-1}.

Ethylene glycol (A.R., Flucka) was purified by fractional distillation under vacuum [18]; the middle portion was left in contact with anhydrous sodium sulphate for 24 hr, then decanted by a stream of CO_2 and mositure - free nitrogen. The required volume was fractionaly distilled under vacuum freshly before use. Its $(x_o)_{30}$ was $(2\text{-}3)\times10^{-8}$ Ω^{-1} cm^{-1}.

Conductivity water was obtained by passing distilled water through 500 Deem-A flow deionizer and the collected water was guarded with soda lime tube to prevent contamination with CO_2; $(x_o)_{30}$ was found to be $(3\text{-}6)\times10^{-7}$ Ω^{-1} cm^{-1}.

Salts

Et_4NClO_4, Et_4NBr, Et_4NI, Pr_4NI, Bu_4NI and Hex_4NI (Flucka) were double crystallized from the suitable solvent and dried in a vacuum oven at condition specified in Table 1.

Salts were powdered after preliminary dryness, dried again till constant weight and kept in brown bottles over $CaSO_4$ or P_2O_5 in vacuum desiccator.

Properties of Solvent Mixtures

Density (d) of the individual solvents and of their mixtures were measured in 25 ml pycknometer; viscosity (η) was measured using modified Ubelhode suspended level viscometer. More than one viscometer was used but they were calibrated to each other at 30±0.02°C. The results are reported in Table 2.

Conductance Measurements

An Erlenmeyer type conductance cell with bright platinum electrodes was used. The temperature was maintained using an Ultra-thermostat of the type Mgw Lauda Cs -20. The cell constant was determined from measurements with several KCl solutions at 25, 18 and 10°C and applying Barthel, Feuerlein, Neueder and Wachker equations [19]. $(\delta x/\delta T)_p$ was determined The cell constant at 30 ± 0.02 was found to be 0.04611 cm^{-1}.

Preparation of solutions, the conductivity bridge and accuracy of measurements were already described elsewhere [20]. In all cases, the salt was weighed by difference using Mettler EA 240 balance with accuracy of ± 0.01 mg.

Table 2

Properties of EG - EtOH mixtures at 30° C (Measured / Derived)

X_1	d_{12} g.ml^{-1}	η_{12} CP	ΔV^E_{M12}	ΔV_1	ΔV_2	$\Delta\eta_{M12}$	G^{*E}
0.0000	0.78119	0.9895	0.0000	0.0000	0.0000	0.0000	0.0000
0.0522	0.79922	1.1305	-0.1350	-2.5868	-0.1741	+1.8200	-12.3438
0.1107	0.81908	1.3149	-0.2476	-2.2374	-0.2785	+3.7700	-20.4051
0.2046	0.85076	1.6867	-0.3856	-1.8847	-0.4847	+6.6257	-15.1149
0.3051	0.88479	2.2298	-0.5096	-1.6712	-0.7335	+9.1331	+23.1761
0.3234	0.89050	2.3153	-0.4976	-1.5392	-0.7355	+9.6526	-1.2596
0.4182	0.92191	2.9785	-0.5403	-1.2910	-0.9274	+11.4673	+9.3208
0.5131	0.95328	3.8422	-0.5580	-1.0880	-1.1459	+12.5291	+27.2067
0.6928	1.01078	6.0920	-0.4362	-0.6145	-1.3845	+12.2491	+14.3591
0.7588	1.03192	6.9705	-0.3818	-0.5033	-1.5813	+11.9563	-76.8338
0.8021	1.04508	8.0576	-0.3048	0.3802	-1.5385	+9.8223	+7.2274
0.9039	1.07694	10.4880	-0.1675	-1.1855	-1.7388	+5.2664	+9.2727
1.0000	1.10643	13.3813	0.0000	0.0000	0.0000	0.0000	0.0000

RESULTS

Intermolecular Interaction in Mixed Solvent at 30° C

The excess volume (ΔV^{E}_{M12}) and the partial molal volume ($\bar{V}$) of each component at different composition of EG-EtOH mixtures were computed from the following relations [1]:

$$V_{M12} = \Sigma xM/d_{12}$$

$$\Delta V^{E}_{M12} = V_{M12} - \left(\frac{x_1M_1}{d_1} + \frac{x_2M_2}{d_2}\right)$$

$$M_1\bar{V}_1 = \frac{(V_{M12} - x_1M_1\bar{V}^{\circ}_1)}{x_2} \quad \ldots (1)$$

$$M_2\bar{V}_2 = \frac{(V_{M12} - x_2M_2\bar{V}^{\circ}_2)}{x_1}$$

where, V_{M12} is the molal volume of the mixture, $\bar{V}$ is the partial molal volume of the components in the mixture and $\bar{V}^{\circ}$ is the molal volume of the pure component. The results of ΔV^{E}_{M12} together with the differences are included in Table 2.

Inspection of Table 2 shows that ΔV^{E}_{M12}, ΔV_1 and ΔV_2 have negative values which mean that contraction in volume does not occur only in the mixture but also in each component.

$\Delta\eta_{M12}$ was calculated from the following relationship [21]:

$$\Delta\eta_{M12} = \eta_{calc} - \eta_{expt}$$

$$= X_1\eta_{M1}V^{1/3}_{M1} + X_2\eta_{M2}V^{1/3}_{M2} - \eta_{M12}V^{1/3}_{M12} \ldots (2)$$

where X_1 and X_2 are the mole fraction of EG and EtOH respectively and η_{M12} is the molar viscosity representing the force which acts via the linear velocity gradient on a stationary plane of area $V_M^{2/3}$ at a distance $V_M^{1/3}$ (V_M is the molar volume). It is independent of the state of matter and the type of the molecules and is given by

$$\eta_M = \eta V_M^{1/3} \quad \ldots (3)$$

The results are reported in Table 2. As can be seen, the values of $\Delta\eta_{M12}$ have positive values at all compositions with a maximum at $X_1 \approx 0.6$, indicating inner lubrication.

The Gibbs energy of activation (G^{*E}) for flow was calculated from viscosty data using the following equation [22]

$$G^{*E} = RT\,[\ln\eta_{12}V_M - (X_1\ln\eta^{\circ}_1V^{\circ}_1 + X_2\ln\eta^{\circ}_2V^{\circ}_2)] \ldots (4)$$

and the results are reported in the last column of Table 2. As can be seen, G^{*E} has no trend; but it records maximum positive value at $X_1 \approx 0.5$.

Dielectric constant presented in Table 3, were obtained by interpolation from a large scale plot of the data reported elsewhere [14]. The deviation in the dielectric constant (ΔD) calculated by equation 5 [23] is also included in the Table.

$$\Delta D = D_{obs} - D_{calc} = D_{12} - (X_1D_1 + X_2D_2) \quad \ldots (5)$$

Table 3

Values of Dielectric constants (D_{12}-ΔD) Computed for EG-EtOH mixtures at 30° C

X_1	D_{12}	ΔD
0.0000	25.57	0.0000
0.0996	24.60	-0.2777
0.2268	25.70	-0.8479
0.3062	27.00	-0.5904
0.4042	28.27	-0.6071
0.5036	29.36	-0.8222
0.6181	31.91	+0.2243
0.7021	33.59	+0.8014
0.8008	35.15	0.0000

A graphical representation of this data shows a large variation in ΔD value at $X_1 \sim 0.5$. This and also the presence of a pronounced minimum in ΔV^E_{M12}, a maximum in the variation of $\Delta\eta_{M12}$ and the large variation of G'^E indicate probable existnce of a molecular complex (1EG:1EtOH). This suggestion indicates that EG molecules prefer the gaush conformation.

Conductance of Some Tetra-alkylammonium Salts in EG-EtOH Mixtures

Solvent properties of the specific EG-EtOH mixtures used in the conductance measurements were obtained by interpolation and presented in Table 4.

Molar conductance (Λ in Ω^{-1} mol^{-1} cm^2) at different concentration of Et_4NI, Pr_4NI, Bu_4NI, HeX_4NI, Et_4NBr and Et_4NClO_4 in the two solvents and of the iodide salts in the mixed solvents at 30°C are recorded in Tables 5-7.

The data were analyzed by solving the three parts of Fuoss equation (1980), [15].

$$\Lambda = \Lambda_o (1 - \Delta x/x) - \Delta Ve \qquad (6a)$$

$$v = 1 - k_\Lambda Cv^2F^2 \qquad (6b)$$

$$F = -\beta H/2(1+HR) \qquad (6c)$$

where, R is the association distance and other terms have the meaning as defiend in the original paper.

The NEW-SCAN and the AA programs which are two parts of the PARACOND provided by Prof. Fuoss were used in the calculations to obtain Λ_o and K_Λ corresponding to the value of R which gives the minimum standard deviation. The derived constants are contained in Tables 8 and 9.

Table 4.

Solvent properties of experimental mixed solvents used in conductance measurements.

EG wt%	0.0	25.0	25.6	49.7	76.3	100.0
d $g.ml^{-1}$	0.78119	0.84918	0.85090	0.92410	1.01450	1.10643
η (CP)	0.9895	1.6550	1.6800	3.0150	6.0300	13.3813
D	23.57	25.40	25.44	28.33	33.33	36.70
$x_o \times 10^6$	(3-6)	(5-6)	(3-6)	(7-9)	(2-3)	(2-3)

Table 5

Conductance of some tetraalkylammonium salts in ethanol at 30° C

Et_4NI		Pr_4NI		Bu_4NI		Hex_4NI		Et_4NBr		Et_4NClO_4	
10^4C	Λ	10^4C	Λ	10^4C	Λ	10^4C	Λ	10^4C	Λ	10^4C	Λ
18.775	49.8	19.935	44.03	21.000	39.82	18.876	36.86	22.532	44.94	20.055	48.31
15.235	51.36	17.342	44.81	18.402	40.30	15.449	38.07	17.548	46.25	16.364	49.89
13.596	52.03	14.456	45.71	16.480	41.04	13.248	38.75	14.663	47.10	13.856	51.17
12.488	52.59	11.699	46.81	13.685	41.84	10.820	39.69	11.972	48.18	11.507	52.43
10.797	53.30	9.4857	47.95	11.699	42.59	8.3884	40.61	9.9970	49.09	9.1851	54.19
9.0950	53.97	7.8242	48.74	9.6242	43.33	7.1005	41.15	8.1443	49.98	7.4379	55.42
7.0732	55.07	6.3092	49.73	7.3892	44.69	5.8556	41.87	6.5767	50.71	5.9223	56.69
5.6330	56.09	4.8496	50.63	6.0821	45.24	4.1965	42.68	5.5438	51.50	4.1933	58.46
4.6367	56.86	4.0708	51.20	4.8569	45.96						

Table 6.

Conductance of some Tetra-alkylammonium salts in ethylene glycol at 30°C

Et_4NI		Pr_4NI		Bu_4NI		Hex_4NI		Et_4NBr		Et_4NClO_4	
10^4C	Λ	10^4C	Λ	10^4C	Λ	10^4C	Λ	10^4C	Λ	10^4C	Λ
39.140	7.671	39.192	7.225	35.580	6.930	29.440	6.527	31.266	8.266	28.906	7.431
31.428	7.755	31.934	7.295	27.898	7.044	24.086	6.609	21.944	8.948	21.557	7.511
26.742	7.800	25.781	7.340	21.582	7.121	18.468	6.715	16.596	9.374	17.647	7.565
22.241	7.861	20.508	7.400	17.442	7.183	16.107	6.747	13.051	9.715	14.277	7.625
18.395	7.911	16.644	7.458	13.470	7.261	13.362	6.765	10.564	9.952	10.604	7.666
15.191	7.964	9.6225	7.549	10.345	7.326	10.860	6.856	8.0357	10.314	7.4686	7.723
12.168	8.027	6.9506	7.591	6.7847	7.398	8.7660	6.912	6.1285	10.549	3.7486	7.814
9.4184	8.073	4.9818	7.633	4.7829	7.440	7.0990	6.982	4.2890	10.808	2.5822	7.844
7.4562	8.116			3.7847	7.471	4.8255	7.024				
5.5378	8.152					3.6212	7.066				

Table 7

Conductance of some tetraalkylammonium iodides in EG-EtOH mixtures at 30°C

Et_4NI						Pr_4NI					
D=25.40		D=28.33		D=33.33		D=25.40		D=28.33		D=33.33	
10^4C	Λ	10^4C	Λ	10^4C	Λ	10^4C	Λ	10^4C	Λ	10^4C	Λ
20.631	37.72	17.519	34.70	20.857	17.09	24.283	35.47	18.970	27.87	18.785	14.20
13.255	39.29	14.855	35.10	17.620	18.31	20.192	36.22	17.248	28.35	16.652	14.48
9.7250	40.03	13.286	35.28	15.552	18.54	17.857	36.60	15.087	28.69	14.395	14.78
8.4171	40.60	11.501	35.53	14.364	18.68	15.058	37.18	13.200	28.84	12.206	15.12
7.0046	41.24	9.6947	35.88	12.667	18.94	12.762	37.66	11.156	29.26	10.385	15.44
5.8074	41.68	7.9510	36.20	10.485	19.17	10.608	38.21	9.4586	29.53	8.5741	15.74
4.8782	42.08	6.5776	36.60	8.3754	19.56	8.8621	38.62	7.7200	29.88	6.5386	16.22
3.9088	42.53	5.1588	36.82	7.0584	19.82	7.1448	39.13	5.7234	30.31	4.3087	16.65
3.1972	42.96	3.8085	37.26			5.6038	39.65				
2.4082	43.37					4.3934	40.00				

Table 8

Derived constants in the simple solvents

Salt	Λ_o	R (A)	K_R	K_S	K_A	$10^3\sigma_A$	-Gs
Et_4NI in EtOH	63.03	14.8	39.71	4.16	205.0	130.827	5.323
in EG	8.46	16.5	28.16	0.74	49.0	6.342	3.892
Pr_4NI in EtOH	57.02	23.7	90.08	2.46	311.3	72.461	5.741
in EG	7.88	18.4	35.55	0.44	51.1	8.382	3.93
Bu_4NI in EtOH	51.76	26.4	112.56	1.98	335.1	125.533	5.815
in EG	7.73	14.9	22.87	1.08	47.5	11.996	3.681
Hex_4NI in EtOH	47.72	14.1	37.14	4.72	212.3	127.987	5.358
in EG	7.33	22.6	56.60	0.77	100.3	16.727	4.609
Et_4NBr in EtOH	58.30	30.9	158.65	1.48	393.1	63.712	5.974
in EG	11.93	10.5	12.26	16.38	213.0	42.203	5.361
Et_4NClO_4 in EtOH	66.58	18.6	57.07	5.26	357.5	75.858	6.879
in EG	8.04	18.9	37.70	0.49	56.2	8.929	4.030

Table 9

Derived constants of the iodide salts in EG-EtOH mixtures at 30°C

EG wt%	Λ_o	R(A°)	K_R	K_S	K_A	$10^3\sigma_A$	-Gs
				Et_4NI			
0.0	63.03	14.8	39.71	4.16	205.0	130.827	5.323
25.0	46.16	34.5	194.32	0.98	383.9	82.302	5.950
49.7	39.18	26.6	98.67	0.89	186.7	45.916	5.229
76.3	22.4	11.4	15.89	9.59	168.2	267.681	5.125
100.0	8.46	16.5	28.16	0.74	49.0	6.342	3.892
				Pr_4NI			
0.0	57.02	23.7	90.08	2.46	311.3	72.461	5.741
25.0	43.27	15.5	38.10	2.67	139.8	54.623	4.940
49.7	32.76	12.4	23.10	3.80	110.8	90.458	4.708
76.3	18.39	6.1	8.61	22.80	205.0	34.293	5.323
100.0	7.88	18.4	35.55	0.44	51.1	8.382	3.933
				Bu_4NI			
0.0	51.76	26.4	112.56	1.98	335.1	125.533	5.815
25.6	39.89	14.3	33.56	3.44	149.1	49.081	5.005
49.7	30.04	12.0	22.17	3.75	105.2	159.174	4.656
76.3	17.12	7.0	9.19	24.99	238.8	32.471	5.476
100.0	7.73	14.9	22.87	1.08	47.5	11.996	3.861
				Hex_4NI			
0.0	47.72	14.1	37.14	4.72	212.3	127.987	5.358
25.6	37.55	31.6	31.21	3.79	149.4	47.148	5.007
49.7	26.96	11.1	19.91	6.21	143.4	58.385	4.966
76.3	15.63	6.2	8.66	36.79	327.2	48.570	5.791
100.0	7.33	22.6	56.60	0.77	100.3	16.727	4.609

DISCUSSION

A comparison of Λ_o values of the salts in ethanol with the published data at 25°C shows the expected behavior: The present set of values (30°C) are higher than the values published at 25° C [12, 13].

Inspection of Table 8 indicates that Λ_o values of iodides decrease in the order: tetra-ethyl > tetra-propyl > tetra-butyl > tetra-hexyl. This can be attributed to the decrease of the ionic mobility with the increase of cationic size.

For the tetra-ethylammonium salts (with common cation), Λ_o is in the order: perchlorate > iodide > bromide in ethanol. This is in the order of anion size and opposite to anionc solvation in protic solvents. On the other hand in case of ethylene glycol, Λ_o values follow the trend: bromide > iodide > perchlorate. This trend is opposite to that of the crystallographic radius and parallel to that of solvation and is in good agreement with the observed trend for Et_4NX (X=Cl, Br and I) in EG at 40°C [13].

The values of K_A indicate that all salts exhibit association. R in Table 8 represents the cosphere diameter which contains nonconducting pairs (Fuoss [15]). The increase of R and K_A for iodide salts with increase in the size of the unsolvated cation [24,25] from Et_4NI to Bu_4NI indicates solvophobic solvation for large cations. Accordingly, the dipole moment of the formed ion-pair increases causing the increase of (ion-pair)-solvent interaction which helps in the stabilization of the formed ion-pair. The increase of both R and K_A for salts with solvophobic solvated cations may also be due to solvent-solvent interactions between solvent molecules in the solvent-separated-ion-pair through hydrogen bond formation [26]. On the other hand, lower value of R and K_A for Hex_4NI than those of Bu_4NI may be attributed to the increase in solvophobic solvation of cations, resulting in decrease of electrostatic attraction between the two oppositely charged ions.

Table 8 also shows that the trend of R and K_A for a series of salts of common cation is in the order bromide > perchlorate > iodide. This does not follow the crystallographic radius or the solvation trend of anions. The position of the bromide salts indicates the effect of charge density in forming ion-pair; but the value for perchlorate is higher than those of iodide probably because of the role of the solvent in stabilizing the ion-pair formed with higher dipole moment through (ion-pair)-solvent interaction.

Values of R and K_A in ethylene glycol is opposite to what was previously deduced [12 13]. With the exception of Bu_4NI, R and K_A of iodide salts increase with increase in cation size denoting existence of solute-solvent interaction and the role of the solvent in stablizing the ion-pairs formed.

The above picture indicates the possiblity of application of the solvent-separated-ion-pair (SSIP) model to the used electrolytes in ethanol as well as in ethylene glycol.

Ethylene Glycol-Ethanol Mixtures

It is clear from Table 9 that for the tetra-alkylammonium iodides in different solvent mixtures decrease with the increase of both D and η indicating the variation of solvation of ions and the strength of electrolyte - solvent interaction with solvent composition.

Values of log K_A in different solvent mixtures were plotted *vs* 100/ D for the four Iodide salts (Fig. 1). In all cases the resultant curves can not satisfy the straight line relationship [27]:

$$\ln K_A = \ln \frac{4\pi Na}{3000} + \frac{|Z_1 Z_2| e^2}{aDkT} \quad .....(7)$$

which supports the importance of adding the U term suggested by Accascina, D'Aprano and Triolo [28] and is given by

$$\ln K_A = \ln \frac{4\pi Na}{3000} + \frac{|Z_1 Z_2| e^2}{aDkT} + U \quad ..(8)$$

where $U = \Delta S/k - E_s/kT$

Here (-Es/kT) is the Gilkerson term [29] representing ion-dipole interactions and $\Delta S/k$ represents entropy change resulting from the difference in the solvent arrangement near the ion-pair and near the ions.

Table 9 shows that R (the distance of closest approach or Fuoss cosphere diameter) reaches a minimum in solution rich in ethylene glycol (EG wt% = 76.3).

It can also seen from Table 9 that variation of K_A of Et_4NI for solution rich with ethanol differs from those of the other three salts. This behaviour of Et_4NI (with the unsolvated cation) [23-25] may be attributed to obvious difference in solute - solvent interaction and changes in solvent structure around the electrolyte on adding small amount of one of the used solvents to the other. On the other hand, K_A in other three salts increases with decrease in viscosity and increase in the probability of ion-pair formation. The variation of K_A and R with EtOH is in the expected direction; as D decrease, K_A increase. In both cases, the large value of K_A at EG wt% = 76.3 indicates the stability of the formed ion-pair.

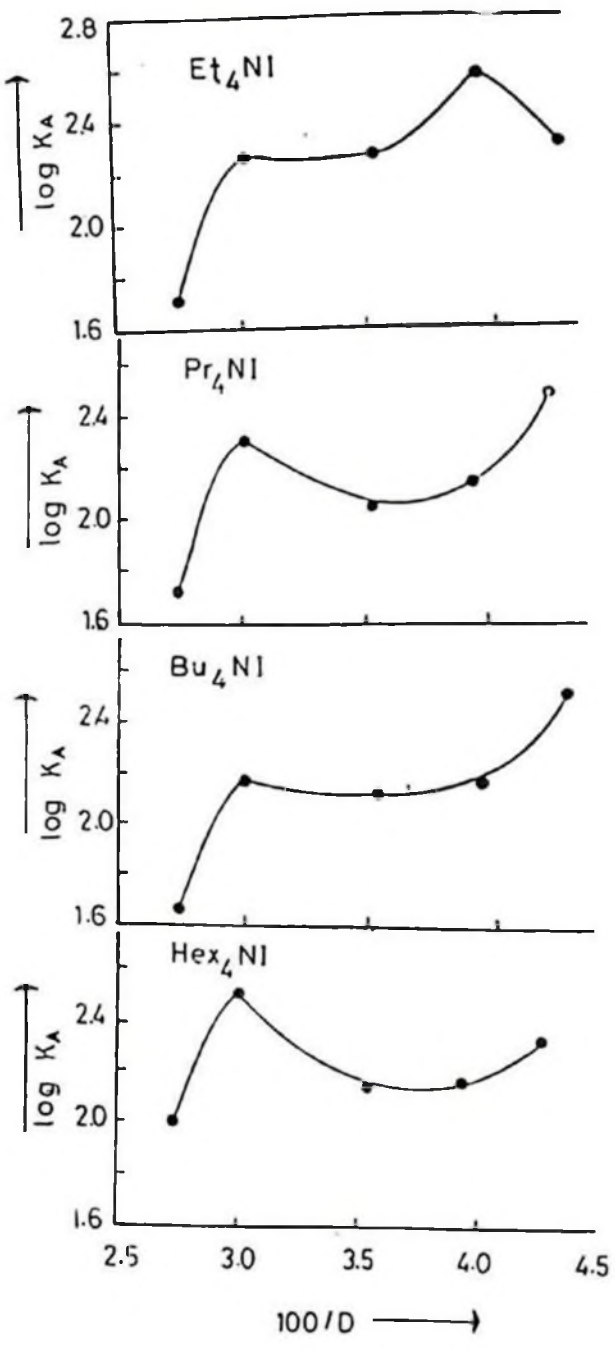


Fig. 1. Variation of log K_A with 100/D for Tetra - alkylammonium Iodides in EG-EtOH Mixtures at 30°C.

The above interpretation is supported by studying the values of the two equilibrium constants K_R, K_S in the equilibria [26]

$$A^+ + B^- \underset{}{\overset{K_R}{\rightleftharpoons}} (A^+....B^-) \overset{K_S}{\rightleftharpoons} A^+ + B^-$$

where K_R describes the formation and separation of solvent separated pairs by diffusion in and out of spheres of diameter R around cations, K_S is the constant describing the short range process by which contact pairs form and dissociate. It is clear from Table 9 that K_R and K_S in case of Et_4NI exhibit maximum variation in the mixture rich with both EG and EtOH; while these constants for the other three salts reach their maximum variation in the mixture rich with EG only. In both cases Gs recorded the more negative value at the same mixtures. Since Gs is used to give an indication to the quantity (H-T ΔS), its high negative value refers to large value of S; i.e., the disorder of the system.

Walden Product and Single Ion Conductance

Fig.2 illustrates variation of the Walden product $\Lambda_o\eta_o$ with EG wt%. The nonconsistency of values support the presence and also the importnace of ion solvation and of electrolyte-solvent interaction in discussing conductance data.

Sadek and Hafez observed (in both simple and mixed solvents) that the plots of $\Lambda_o\eta_o$ *vs* 1/M for a series of salts with common anion give straight lines [22] with intercept equals $\lambda^-_o\eta_o$ from which λ^-_o can be obtained. They suggested the following straight relationship [16]

$$\Lambda_o\eta_o = \lambda^-_o\eta_o + \left(\frac{k^-}{\alpha}\right) e_o F^2 \left(\frac{d_o}{M}\right) \qquad (9)$$

in which k'/α has a constant value; M is the molecular weight of the electrolyte: molecular weight of cation = αM. Application of equatiton 9 to simple protic [17] and simple dipolar aprotic [20,28] solvents prove the agreement of the theoretical slope $[(k'/\alpha)e F^2d_o]$ with the experimental one. Table 10 records the concordance of the theoretical and experimental slopes in the present case.

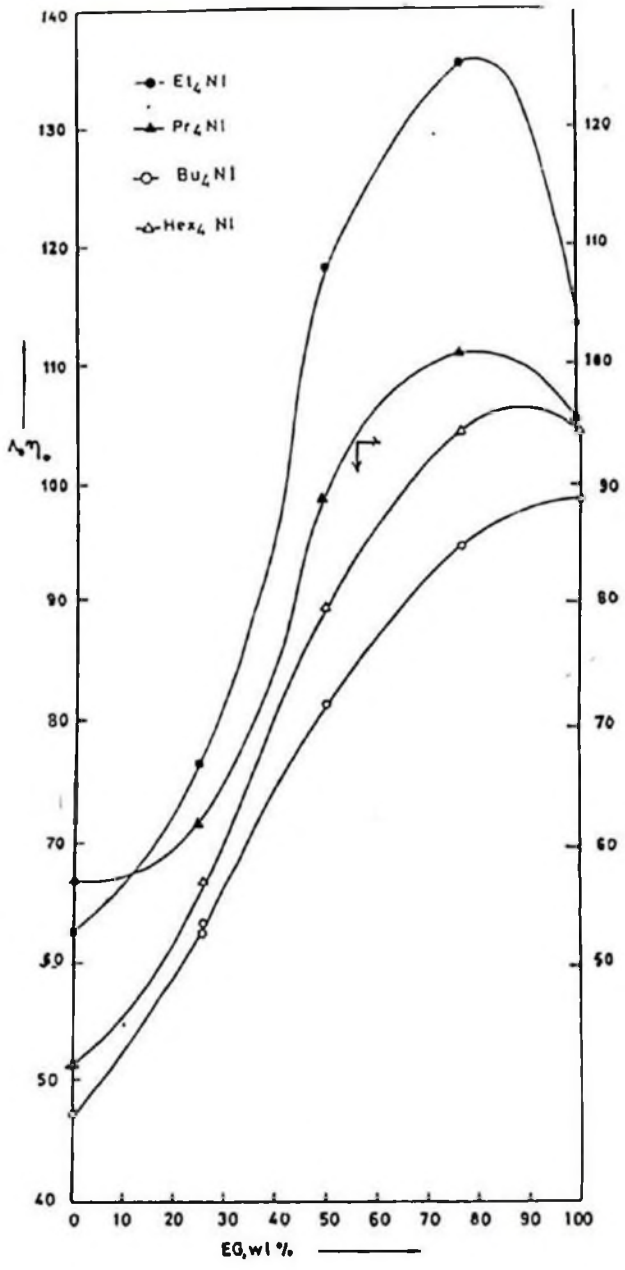


Fig. 2. Variation of with $\Lambda_o\eta_o$EG wt.% for Et_4NI Pr_4NI, Bu_4NI and Hex_4NI at 30°C.

Table 10

Values S_{expti}/S_{theor}

EG wt.%	0.00	10.0	20.0	25.0	30.0	40.0	49.7	60.0	70.0	76.3	80.0	100.0
S_{expti}/S_{theor}	9.99	100.2	97.8	101.9	96.1	100.4	99.7	101.8	94.0	96.9	94.9	100.1

Table 11

Molar conductance at infinite dilution of salts and cations

EG wt.%	Et_4NI		Pr_4NI		Bu_4NI		Hex_4NI	
	Λ_o	λ^+_o	Λ_o	λ^+_o	Λ_o	λ^+_o	Λ_o	λ^+_o
0.0	63.03	33.71	57.02	27.70	51.76	22.44	47.72	18.40
25.0	46.16	20.26	43.27	17.37	-	-	-	-
25.6	-	-	-	-	39.89	14.09	37.55	11.75
49.7	39.18	22.79	32.76	16.37	30.04	13.65	26.96	10.57
76.3	22.44	14.99	18.39	10.94	17.12	9.67	15.63	8.18
100.0	8.46	2.40	7.88	1.82	7.73	1.67	7.33	1.27

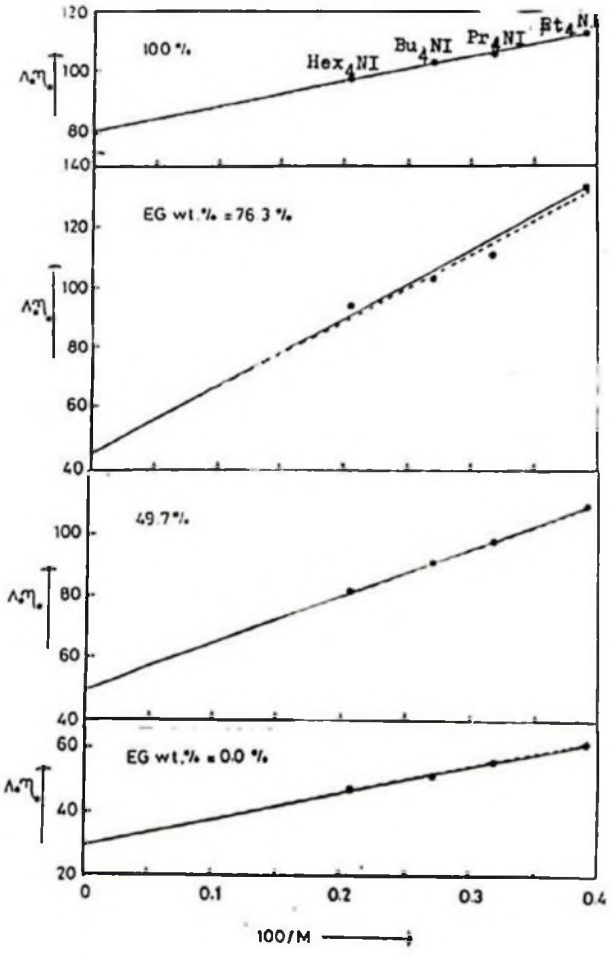


Fig. 3. Plot 100/M for Tetra-alkylammoum Iodides in EG-EtOH Mixtures at 30°C.

Fig.3 illustrates the plots of $\lambda^\circ \pm$ vs 100/M for the iodide salts at different EG wt%. Derived values of the conductance of cations are recorded in Table 11.

Conductance of iodide ion with wt% of ethylene glycol in the solvent mixture is given in Fig.4.

The deduced conductance of the used cations are recorded in Table 11.

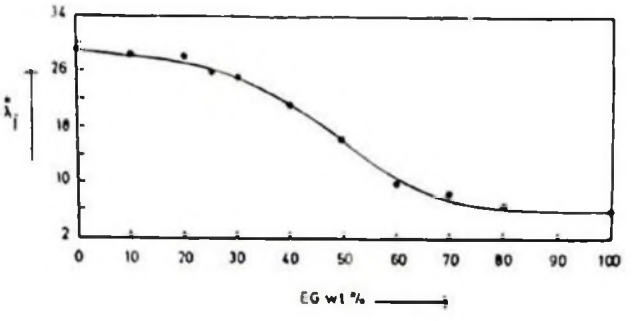


Fig. 4. Variation of single ion conductance Λ°_i of iodide with EG Wt. % EG-EtOH Mixtures at 30 C.

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