CONDUCTANCE AND VISCOSITY MEASUREMENTS OF SOME ELECTROLYTES IN BINARY SOLVENT MIXTURES OF DIMETHYLSULPHOXIDE AND DIOXANE AT 25°C

Vijay K. SYAL*, Pushpa BISHT and Prakash C. RANOWT

Department of Chemistry, Himachal Pradesh University, Summer Hill, Shimla - 171 005, India

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The conductance and viscosity measurements of Bu_4NBPh_4, Bu_4NI, $NaBPh_4$, Pr_4NI, Et_4NI, Me_4NI, Bu_4NNO_3, KI, $KClO_4$, $NaClO_4$, KNO_3, $AgNO_3$, $LiNO_3$ and NaBr have been carried out in the concentration range of $(0-100) \cdot 10^{-4}$ mol dm^{-3} for conductance and $(0-250) \cdot 10^{-4}$ mol dm^{-3} for viscosity in dimethylsulphoxide (DMSO) and DMSO + dioxane mixtures at 25°C. The conductance and viscosity data have been analysed by the Shedlovsky and Jones–Dole equations, respectively. The limiting ionic conductance (λ_i^0), solvated radii (r_i) and the ionic viscosity coefficient ($B_\pm$) values have been evaluated. The variation of r_i and $B_\pm$ value as a function of solvent composition has been interpreted in terms of preferential solvation of ions in these solvent mixtures.

The present study is in continuation of our earlier research in transport properties of binary liquid mixtures[1-4]. Here we report the conductance and viscosity results for some electrolytes in DMSO and DMSO + dioxane mixtures at 25°C.

The properties of DMSO have been the subject of considerable interest because of its versatility as a solvent. It is a highly polar self associated liquid and has ability to participate in hydrogen bonding. In liquid mixtures, the enhancement of its donor ability may result from the breaking of DMSO structure by the second liquid component. 1, 4 dioxane, is an inert aprotic solvent having dielectric constant value of 2·2 at 25°C.

Recently, attention has been focussed on the use of non-aqueous binary solvent mixtures namely DMSO + dioxane[1,2], DMSO + acetonitrile (AN)[3,4], acetone (AC) + dimethylformamide (DMF)[5,6], AN + DMF[7] and AN + benzene[8]. The investigation of conductance and viscosity properties of solutions of various solutes in binary mixtures containing associated DMSO and inert dioxane can be, therefore, quite interesting.

EXPERIMENTAL

The purification of DMSO and dioxane have already been reported[1]. The binary mixtures of

these solvents were prepared by weight. The dielectric constants (D) of solvent mixtures have been calculated using the following equation:

$$D_{\text{solution}} = D_{\text{dioxane}} + w(D_{\text{DMSO}} - D_{\text{dioxane}}) , \qquad (1)$$

where w represents the weight fraction of DMSO in solution. The calculated values of dielectric constant (D), Bjerrum critical distance (q), and experimentally determined densities and viscosities of solvent systems are reported in Table I. The electrolytes used were prepared/purified as reported earlier[1,3,9]. Conductances were measured at 1 000 Hz frequency with a digital conductivity meter type NDC-732, manufactured by Naina Electronics, Chandigarh, India. Viscosities at 25 ± ·01°C were measured with an Ubbelohde suspended bulb level viscosimeter calibrated with triply distilled water (η_0 = 0·8903 mPas)[10] and other distilled organic solvents. Densities at 25 ± ·01°C were measured with the help of a sealable type of pycnometer[11] of capacity $2 . 10^{-5}$ m^3. The pycnometer was also calibrated with distilled water (d = 997·0 kg $^{-3}$)[10] and other organic solvents. The overall accuracy of the conductance, viscosity and density measurements are ±0·2%, ±0·1% and ±0·1 kg m^{-3}, respectively.

RESULTS AND DISCUSSION

Conductance Measurements

The conductances of tetrabutylammonium tetraphenylborate (Bu_4NBPh_4); tetrabutylammonium iodide (Bu_4NI) and nitrate (Bu_4NNO_3); sodium and potassium perchlorate ($NaClO_4$) and ($KClO_4$); potassium, lithium and silver nitrate (KNO_3), ($LiNO_3$) and ($AgNO_3$); sodium bromide (NaBr); tetraethylammonium iodide (Et_4NI) and sodium tetraphenylborate ($NaBPh_4$) have been measured in DMSO and DMSO + dioxane mixtures containing 10, 25, 40 and 55 mole % of dioxane in the concentration range of $(0-100) . 10^{-4}$ mol dm^{-3}. The experimental data consisting of molar concentration and corresponding molar conductance values of electrolytes in various solvent systems are given in Table II. The conductance data

Table I

Dielectric constant (D), viscosity (η_0), density (d) and Bjerrum critical distance (q) for DMSO and DMSO + dioxane mixtures at 25°C

Solvent (mole % DMSO)	D	η_0, mPa s	d, kg m^{-3}	q, nm
100	46·6	2·004	1 094·6	0·6013
90	42·4	1·861	1 086·2	0·6608
75	36·0	1·752	1 076·0	0·7783
60	29·5	1·577	1 065·4	0·9948
45	22·9	1·468	1 055·4	1·2238

TABLE II

Molar concentration C (mol dm^{-3}) and corresponding molar conductance Λ (S cm^2 mol^{-1}) values for some electrolytes in DMSO and DMSO + dioxane mixtures at 25°C

Electrolyte	Solvent (mole % DMSO)									
	100		90		75		60		45	
	$C \cdot 10^4$	Λ	$C \cdot 10^4$	Λ	$C \cdot 10^4$	Λ	$C \cdot 10^4$	Λ	$C \cdot 10^4$	Λ
	05·55	20·0	01·41	23·20	01·41	23·50	01·41	24·40	02·82	22·80
	08·23	19·60	02·81	22·70	02·82	22·90	02·82	23·80	04·19	22·30
	10·83	19·20	04·19	22·30	04·19	22·40	04·19	23·30	05·55	21·90
Bu_4NBPh_4	13·37	18·90	05·55	22·00	05·55	22·10	05·55	22·90	08·23	21·10
	19·45	18·20	08·22	21·40	08·23	20·90	08·23	22·30	10·83	20·50
	30·57	17·28	10·83	20·90	10·83	20·50	10·83	21·70	13·37	20·20
	53·49	15·82	13·37	20·61	13·37	19·50	13·37	21·20	19·45	19·90
			19·45	19·70	19·45	18·10	19·45	20·30	30·56	17·30
			30·56	18·56	30·56	16·20	30·56	18·70	40·48	16·10
							40·48	17·60	53·49	14·70
	01·50	24·20	00·75	25·20	00·75	26·20	01·50	28·00	01·50	27·34
	02·98	23·80	02·98	24·40	01·50	25·70	02·98	27·30	02·98	26·49
	05·89	23·40	05·89	23·60	02·98	25·20	04·45	26·80	04·45	26·01
	08·73	22·90	08·73	23·10	05·89	24·30	05·89	26·40	05·89	25·59
$NaBPh_4$	14·19	22·30	14·19	22·20	08·73	23·60	08·73	25·70	08·73	24·90
	20·64	21·70	20·64	21·40	14·19	22·70	11·49	25·20	11·49	24·40
	32·96	20·87	32·44	20·20	20·64	21·69	14·19	24·81	14·19	23·81
	42·96	20·06	42·96	19·30	32·44	20·31	20·64	23·84	20·64	22·81
	56·78	19·40			42·96	19·28	32·44	22·26	32·44	21·70
							42·96	21·27	42·96	20·24
	05·63	31·6	2·85	34·1	1·43	37·3	1·07	38·5	1·07	37·1
	10·97	30·1	5·63	32·9	2·85	36·3	2·13	37·4	2·13	35·9
	16·05	28·9	10·97	31·4	4·25	35·5	3·18	36·5	3·18	34·9
	20·89	27·9	16·05	30·07	5·63	34·8	4·22	35·9	4·22	34·4
Bu_4NI	25·50	27·3	20·89	29·11	8·33	33·7	6·25	34·8	6·25	33·0
	29·90	26·5	25·50	28·4	10·97	32·9	8·23	33·8	8·23	32·1
	38·11	25·32	34·10	27·1	13·55	32·08	10·16	33·0	10·16	31·2
	45·64	24·51	41·96	25·99	19·70	30·6	14·78	31·54	14·78	29·4
	50·03	24·1	45·64	25·61	30·97	28·1	23·22	28·99	23·22	26·9
			61·94	24·06	41·01	26·4	30·76	27·1	30·76	24·79
	03·07	38·55	01·03	40·41	1·03	42·91	2·13	42·86	1·03	46·63
	4·57	38·33	2·04	39·78	2·04	42·25	4·19	41·69	2·02	45·4
	6·06	37·93	3·05	39·33	3·05	41·7	5·51	41·0	2·99	44·12
	8·97	37·01	5·98	38·37	5·98	40·64	6·80	40·55	4·86	41·81
Et_4NI	14·59	35·86	9·72	37·35	9·72	39·52	9·90	39·46	7·07	39·88
	21·22	34·41	14·14	36·36	14·14	38·38	15·56	38·0	11·11	37·59
	33·35	32·79	22·23	35·1	22·23	37·0	20·61	36·78	14·72	25·88
	44·16	31·58	29·44	34·22	29·44	35·77	27·23	35·67	19·45	34·23
	58·36	30·38	38·91	32·97	38·91	34·46				

TABLE II
(*Continued*)

Electrolyte	Solvent (mole % DMSO)									
	100		90		75		60		45	
	$C \cdot 10^4$	Λ	$C \cdot 10^4$	Λ	$C \cdot 10^4$	Λ	$C \cdot 10^4$	Λ	$C \cdot 10^4$	Λ
	10·05	36·55	7·19	38·50	3·67	40·95	5·40	42·05	5·06	40·34
	13·15	36·45	10·55	38·21	7·19	40·35	7·19	41·75	7·56	39·74
	16·14	36·10	13·77	37·75	10·55	39·95	10·08	41·3	10·56	39·15
Bu_4NNO_3	19·03	35·85	16·86	37·50	13·77	39·65	13·77	40·9	13·60	38·60
	21·81	35·70	20·55	37·23	16·86	39·40	16·86	40·6	16·60	38·18
	27·09	35·43	24·06	36·88	19·83	39·20	21·16	40·23	20·25	37·70
	29·60	35·20			25·42	38·85				
	4·08	39·2	3·61	41·25	3·49	42·25	2·64	43·2	2·40	39·25
	7·1	38·2	6·28	40·35	8·63	40·25	4·59	41·8	3·41	38·05
KNO_3	10·09	37·5	8·92	39·2	11·98	39·15	6·52	40·3	4·74	36·75
	14·02	36·75	12·39	38·9	16·11	38·2	9·06	39·2	6·37	35·55
	18·84	35·95	16·65	38·0	20·96	37·0	12·78	38·0	8·29	34·0
	24·51	35·0	21·66	37·2			15·84	36·8		
	1·86	41·6	5·44	41·1	2·66	42·95	2·33	45·0	1·69	42·8
	3·42	40·95	7·72	40·15	6·57	40·15	4·06	43·55	6·81	40·75
	4·61	40·55	9·23	39·75	9·13	39·2	5·76	42·0	8·55	40·25
$AgNO_3$	6·40	40·0	14·42	38·1	12·27	37·8	8·01	40·55	13·48	38·95
	8·61	39·45	18·76	37·2	15·96	36·5	10·76	39·0	19·01	37·8
	11·20	38·8					14·0	37·2	28·43	36·3
	2·65	38·22	1·33	40·47	0·67	42·32	5·24	39·63	1·33	39·61
	3·96	37·51	2·66	39·32	2·65	40·78	7·77	39·10	2·65	38·48
	5·24	37·05	3·96	38·53	5·24	39·43	12·62	36·82	5·24	37·0
	7·77	36·24	7·77	37·16	7·77	38·44	18·36	35·21	7·77	35·92
$KClO_4$	10·22	35·63	10·23	36·44	10·22	37·57	28·86	32·99	12·62	34·17
	12·62	35·02	12·62	35·78	12·62	36·92	38·22	30·90	18·36	32·58
	18·36	33·84	18·36	34·54	18·36	35·42	50·50	29·13	28·86	30·31
	28·86	32·06	28·86	32·57	28·86	33·21			38·22	28·42
	38·22	30·87	38·22	31·08	38·22	31·65				
	50·50	29·36	50·50	29·50	50·50	29·89				
	1·86	36·92	3·70	37·91	5·52	38·5	1·86	42·64	3·70	38·28
	3·70	36·02	5·52	37·15	7·31	37·8	3·70	41·65	5·52	37·33
	5·52	35·31	7·31	36·46	9·08	37·3	5·52	41·1	7·31	36·36
	7·31	34·73	10·83	35·64	12·55	36·26	7·31	40·45	10·83	35·44
$NaClO_4$	10·83	33·83	14·26	34·78	15·94	35·46	10·83	39·50	14·26	34·35
	14·26	33·02	17·60	33·82	25·60	33·53	14·26	38·69	17·60	33·5
	17·60	32·4	25·60	32·81	40·24	31·12	17·60	38·0	25·60	31·8
	25·60	31·14	40·24	31·12	53·29	29·39	25·60	36·71	40·24	29·18
	40·24	29·03	53·29	29·1			40·24	34·58	53·29	27·2
							53·29	33·08		

TABLE II
(*Continued*)

Electrolyte	Solvent (mole % DMSO)									
	100		90		75		60		45	
	$C \cdot 10^4$	Λ	$C \cdot 10^4$	Λ	$C \cdot 10^4$	Λ	$C \cdot 10^4$	Λ	$C \cdot 10^4$	Λ
	16·48	36·2	32·77	36·95	32·77	38·8	29·49	40·2	29·49	37·8
	32·77	35·55	48·88	36·3	48·88	38·1	43·99	39·5	43·99	37·15
$LiNO_3$	48·88	35·10	64·82	35·8	64·81	37·55	58·33	38·95	58·33	36·6
	64·81	34·7	80·6	35·35	80·57	36·65	72·51	38·45	72·51	36·1
	80·57	34·35	96·15	34·95	96·15	36·20	100·40	37·6		
	11·03	36·35	11·03	37·55	11·03	38·4	9·29	38·9	9·29	34·75
	16·50	36·15	16·50	37·2	16·50	37·95	14·85	38·15	14·85	33·9
NaBr	27·34	35·65	27·34	36·65	27·34	37·2	34·26	36·3	34·26	31·8
	38·07	35·3	38·07	36·2	38·07	36·6	57·93	34·65	57·93	30·01
	53·93	34·9	53·93	35·7	53·93	35·85	71·81	33·8	71·81	29·1
	79·79	34·35	79·79	35·0						

has been analysed by Shedlovsky method[12,13] using the least square computer program of Salomon[14] by supermicro computer (SM 32) at Himachal Pradesh University, Shimla, India. The results obtained from computer calculations for molar conductance at infinite dilution (Λ_0), association constant (K_A), standard deviation (σ), root mean square deviation (σ_Λ) and correlation coefficient (R) have been presented in Table III.

The standard deviation of Λ_0 and K_A values given in Table III have been found to be less than $\pm 0{\cdot}2\%$ and $\pm 10\%$, respectively. As the root mean square deviation calculated from the standard deviations no where exceeded the experimental uncertainty of the present conductance measurements, i.e., $\pm 0{\cdot}2\%$ this shows a good applicability of Shedlovsky equation to our experimental conductance data.

The precision of our conductance measurements is $\pm 0{\cdot}2\%$, hence the data has not been analysed by any other conductance equation which requires higher precision in conductance measurements and give similar Λ_0 values for an electrolyte but different K_A values which correspondingly produce no change in the r_i values[15]. Also, our aim was only to see the solvation behaviour of ions in terms of their solvated radii (r_i) values which depend only upon the Λ_0 values of the electrolytes.

The observed Λ_0 values of the electrolytes in DMSO are found in good agreement with the literature values (given in parenthesis in Table III) which shows the accuracy of our conductance measurements.

TABLE III

Molar conductance Λ_0 (S cm^2 mol^{-1}), association constant[a] K_A (m^3 mol^{-1}), standard deviation (σ), root mean square deviation (σ_Λ) and correlation coefficient (R) of some electrolytes in DMSO and DMSO + dioxane mixtures at 25°C

Electrolyte	Solvent (mole % DMSO)														
	100					90					75				
	Λ_0	K_A	σ	σ_Λ	R	Λ_0	K_A	σ	σ_Λ	R	Λ_0	K_A	σ	σ_Λ	R
Bu_4NBPh_4	22·03 22·02[b]	·032	0·173	0·134	0·999	24·39	·052	0·154	0·119	0·997	25·24	·067	0·265	0·198	0·998
$NaBPh_4$	25·13 24·6[c]	·018	0·196	0·160	0·992	25·89	·050	0·158	0·126	0·999	27·13	·056	0·196	0·150	0·998
Bu_4NI	34·85 35·0[d]	·087	0·156	0·118	0·999	36·44	·078	0·174	0·129	0·999	37·38	·115	0·227	0·173	0·997
Et_4NI	40·50 40·86[e]	·052	0·207	0·178	0·998	41·25	·043	0·180	0·160	0·997	44·06	·048	0·182	0·153	0·999
$KClO_4$	39·92 39·04[c]	·063	0·131	0·110	0·999	41·58	·075	0·218	0·193	0·998	43·57	·082	0·189	0·142	0·999
$NaClO_4$	38·49 38·34[e]	·053	0·127	0·107	0·999	40·52	·045	0·330	0·258	0·985	42·82	·060	0·254	0·192	0·997
Bu_4NNO_3	38·49 38·34[f]	—	0·165	0·154	0·975	40·52	—	0·167	0·154	0·867	42·35	—	0·198	0·185	0·995
KNO_3	41·12 41·5[d]	·049	0·121	0·110	0·998	43·24	·047	0·121	0·109	0·998	44·97	·075	0·161	0·187	0·999
$AgNO_3$	42·85 43·12[g]	·056	0·544	0·506	0·999	44·41	·082	0·137	0·119	0·997	46·06	·154	0·223	0·196	0·996
$LiNO_3$	38·31 38·0[c]	—	0·408	0·374	0·992	40·65	—	0·612	0·541	0·996	43·00	—	0·823	0·724	0·998
NaBr	38·14	—	0·330	0·303	0·990	39·68	—	0·401	0·363	0·993	41·12	—	0·428	0·383	0·972

TABLE III
(*Continued*)

Electrolyte	Solvent (mole % DMSO)									
	60					45				
	Λ_0	K_A	σ	σ_Λ	R	Λ_0	K_A	σ	σ_Λ	R
Bu_4NBPh_4	26·37	·045	0·327	0·243	0·976	26·10	·080	0·586	0·394	0·956
$NaBPh_4$	29·73	·031	0·310	0·309	0·987	29·5	—	0·528	0·394	0·842
Bu_4NI	40·74	·157	0·281	0·211	0·995	40·31	·179	0·450	0·330	0·988
Et_4NI	45·11	·060	0·223	0·189	0·998	44·00	·270	0·334	0·288	0·997
$KClO_4$	45·30	·104	0·466	0·361	0·993	42·44	·083	0·426	0·311	0·992
$NaClO_4$	45·71	—	0·419	0·327	0·905	43·70	·042	0·618	0·438	0·963
Bu_4NNO_3	44·39	—	0·277	0·256	0·995	43·52	—	0·422	0·375	0·965
KNO_3	46·43	·135	0·281	0·242	0·992	44·37	·343	0·188	0·151	0·997
$AgNO_3$	49·24	·222	0·192	0·153	0·998	45·19	—	0·433	0·364	0·986
$LiNO_3$	45·32	—	1·255	1·089	0·994	43·60	—	1·953	1·698	0·997
NaBr	42·61	—	0·774	0·640	0·934	39·58	—	1·269	0·993	0·929

[a] K_A values $\leq$·010 ($m^3\ mol^{-1}$) have no physical significance[13] and are not reported. Taken from [b] ref.[26]; [c] ref.[3]; [d] ref.[27]; [e] ref.[28]; [f] ref.[29]; [g] ref.[30].

It is clear from Table III that limiting molar conductance for each salt increases with the increase of dioxane content upto 60 mole % and then decreases with further addition of dioxane. The plots of molar conductance (Λ) vs $\sqrt{C}$ for all studied electrolytes have been found to be linear and are given for some salts in Fig. 1.

From Table III, it is clear that $LiNO_3$, Bu_4NNO_3 and NaBr do not show any ion-association in DMSO + dioxane mixtures. The ion association constant (K_A) in general increases with the decrease of dielectric constant for all studied electrolytes. $AgNO_3$ in DMSO and DMSO + dioxane mixtures is highly associated.

Ion Conductance and Walden Product

The single ion contribution of the measured conductance of an electrolyte is an important aspect for understanding the ion–solvent interactions and preferential solvation of ions in solution since cation–solvent and anion–solvent interactions are known to be different.

The molar conductances of the studied electrolytes have been resolved into their ionic contributions using Gill's model[8] involving the following equations:

$$\frac{\lambda_+^0}{\lambda_-^0} = \frac{5{\cdot}35 - (0{\cdot}0103D + r_y)}{5{\cdot}00 - (0{\cdot}0103D + r_y)} \qquad (2)$$

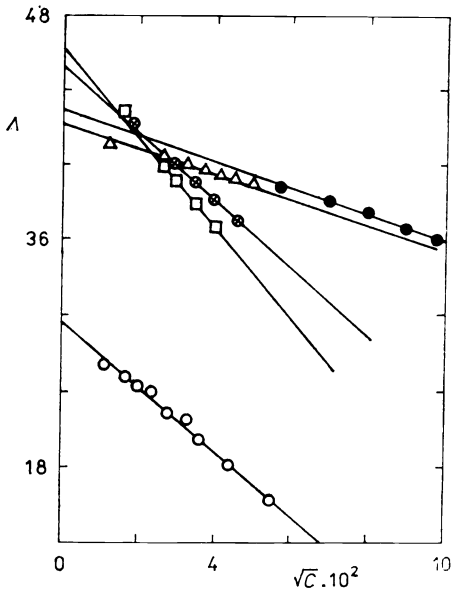

FIG. 1

Plot of molar conductance Λ vs $\sqrt{C}$ for some electrolytes in DMSO containing 25 mole % dioxane at 25°C: ○ Bu_4NBPh_4, △ Bu_4NNO_3, □ $AgNO_3$, ⊗ KNO_3, ● $LiNO_3$

and

$$\lambda_+^0 + \lambda_-^0 = \Lambda_0(Bu_4NBPh_4)\,. \qquad (3)$$

Here r_y is an empirical constant which depends upon the structure of solvent and has been taken equal to 0·113 nm for DMSO as an associated solvent[16-18] and equal to 0·085 nm for dioxane as an unassociated solvent[16]. In DMSO + dioxane mixtures, the r_y values have been obtained by interpolation between the values 0·113 nm and 0·085 nm, respectively.

Using Eqs (2) and (3), the Λ_0 values of Bu_4NBPh_4 have been split up for λ_i^0 values of Bu_4N^+ and Ph_4B^- ions in DMSO and DMSO + dioxane mixtures. λ_i^0 values of I^- ion have been calculated from λ_i^0 values of Bu_4N^+ and Λ_0 values of Bu_4NI. From these values, the λ_i^0 values of other ions have been split up with the help of Kohlrausch's law of independent ionic conductances. These ionic values have been given in Table IV.

The self consistency of the present results can be checked by comparing Λ_0 values of $NaClO_4$ and KNO_3 in Table III with the corresponding Λ_0 values calculated by adding λ_i^0 values of Na^+, K^+, ClO_4^- and NO_3^- ions from Table IV. There is a close agreement between these two sets of Λ_0 values of $NaClO_4$ and KNO_3 in DMSO and DMSO + dioxane mixtures (with in maximum uncertainty of $\pm 0{\cdot}2$ conductance units).

λ_i^0 values for ions in DMSO are in agreement with the values reported in literature and have been given in brackets alongwith the calculated values in Table IV.

Similar to the limiting molar conductances (Λ_0) for electrolytes, limiting ionic conductance (λ_i^0) values do increase with the increase of dioxane content upto 60 mole % and then decrease with the further addition of dioxane in DMSO.

The variation of limiting ionic conductance ($\lambda_\pm^0$) as a function of mole % of dioxane for some ions has been shown in Fig. 2.

The ionic Walden product ($\lambda_i^0\eta_0$) given in Table IV decreases in DMSO + dioxane mixtures as the mole % of dioxane in the mixture increases. A decrease in the Walden product with decreasing dielectric constant has also been observed by Fuoss[19]. Similar behaviour for decrease of ionic Walden product as a function of decrease of dielectric constant of solvent mixtures has also been observed for ions in AN + DMSO mixtures[20]. The decrease of Walden product with decrease of dielectric constant can be attributed to a reduction in the velocity of the moving ion due to interaction with the oriented solvent dipole.

Solvated Radii of Ions and Preferential Solvation

The solvated radii (r_i) of Li^+, Na^+; K^+, Ag^+, Et_4N^+, Bu_4N^+, Br^-, I^-, NO_3^-, Ph_4B^- and ClO_4^- ions in DMSO and DMSO + dioxane mixtures have been cal-

TABLE IV

Limiting ion conductance λ_i^0 (S cm^2 mol^{-1}), Walden product ($\lambda_i^0\eta_0$) and solvated radii r_i (nm) values for some ions in DMSO and DMSO + dioxane mixtures at 25°C

Ion	Solvent (mole % DMSO)														
	100			90			75			60			45		
	λ_i^0	$\lambda_i^0\eta_0$	r_i	λ_i^0	$\lambda_i^0\eta_0$	r_i	λ_i^0	$\lambda_i^0\eta_0$	r_i	λ_i^0	$\lambda_i^0\eta_0$	r_i	λ_i^0	$\lambda_i^0\eta_0$	r_i
Bu_4N^+	11·56 11·67[a]	0·232	0·50	12·78	0·238	0·50	13·21	0·231	0·50	13·78	0·217	0·51	13·62	0·200	0·52
Et_4N^+	16·10 17·10[a]	0·323	0·41	17·47	0·325	0·41	17·55	0·307	0·41	17·59	0·277	0·42	17·45	0·256	0·44
Li^+	11·38 11·0[b]	0·228	0·52	12·91	0·240	0·50	13·87	0·243	0·48	14·76	0·232	0·50	13·70	0·201	0·52
Na^+	13·42 14·0[b]	0·269	0·46	14·92	0·278	0·45	15·69	0·275	0·45	16·44	0·259	0·45	15·63	0·229	0·47
K^+	14·87 14·5[b]	0·298	0·44	15·52	0·288	0·44	16·45	0·288	0·43	16·66	0·263	0·45	14·83	0·218	0·47
Ag^+	15·92 16·15[c]	0·319	0·41	16·67	0·310	0·42	16·92	0·296	0·42	18·68	0·295	0·43	15·29	0·224	0·47
Ph_4B^-	10·47 10·57[c]	0·210	0·54	11·61	0·216	0·53	12·03	0·211	0·52	12·59	0·198	0·54	12·48	0·183	0·55
ClO_4^-	25·05 24·45[c]	0·502	0·32	26·06	0·485	0·32	27·12	0·475	0·32	28·64	0·452	0·32	27·61	0·405	0·32
NO_3^-	26·93 26·97[c]	0·540	0·31	27·74	0·516	0·31	29·14	0·510	0·30	30·56	0·482	0·31	29·90	0·439	0·31
Br^-	24·72 24·1[b]	0·495	0·33	24·76	0·461	0·33	25·43	0·445	0·33	26·17	0·413	0·33	23·95	0·352	0·34
I^-	23·29 24·3[b]	0·467	0·33	23·66	0·440	0·34	26·17	0·458	0·32	26·96	0·425	0·33	26·69	0·392	0·33

Taken from [a] ref.[4]; [b] ref.[3]; [c] ref.[30].

culated using Gill's modification[21] of Stokes law as given by following Eq. (*4*) which predicts these radii within an average uncertainty of ±2% in non-aqueous and mixed solvents.

$$r_i = |Z| F^2/(6\pi N\eta_0\lambda_i^0) + 0{\cdot}0103D + r_y\,, \qquad (4)$$

where D and η_0 are taken from Table I, and r_y is an adjustable parameter of solvent system as explained above. The r_i values, thus, obtained are reported in Table IV.

The plots of solvated radii (r_i) for some ions against mole fraction of dioxane in solvent mixtures are given in Fig. 3.

In binary solvent mixtures if solvated radii (r_i) of an ion shows a linear dependence on the composition of solvent then that ion experiences no preferential solvation. Otherwise, if an ion shows non-linear variation then that ion has preferential solvation.

In the present studies, the r_i values of Li^+, Na^+, K^+ and Ag^+ ions either remain practically constant or these values increase regularly as the dioxane content increases in the DMSO + dioxane solvent system. The results, thus, show that there is no preferential solvation of these ions in DMSO + dioxane mixtures. The non-

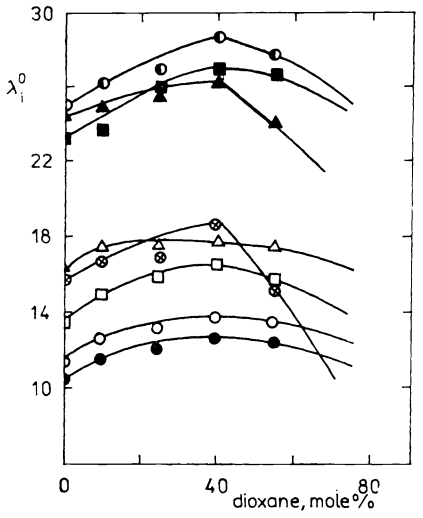

FIG. 2

Plot of limiting ionic conductance λ_i^0 for some ions vs mole % dioxane in DMSO + dioxane mixtures at 25°C: ○ Bu_4N^+, △ Et_4N^+, □ Na^+, ⊗ Ag^+, ● Ph_4B^-, ◐ ClO_4^-, ▲ Br^-, ■ I^-

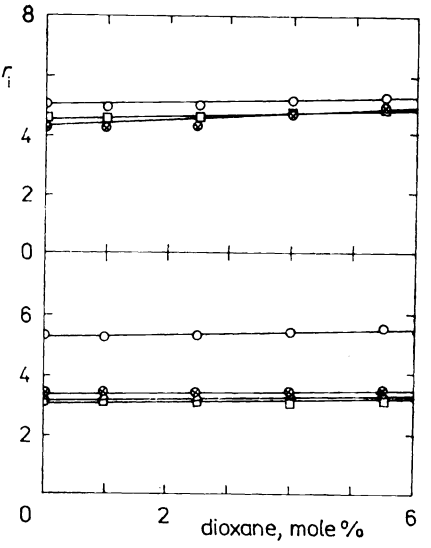

FIG. 3

Plot of solvated radii r_i for some ions vs mole % dioxane in DMSO + dioxane mixtures at 25°C: ○ Bu_4N^+, □ Na^+, ⊗ K^+ (*A*); ⊙ Ph_4B^-, △ ClO_4^-, □ NO_3^-, ⊗ I^- (*B*)

-solvation behaviour of these ions in the present studies may be due to the effect of dioxane in DMSO + dioxane mixtures though these ions are known to be solvated by DMSO.

These results are in contrast to the results reported in the literature. It has been reported that r_i values of Li^+, Na^+ and K^+ ions vary non-linearly with a maximum in the AN-rich region of DMF + AN[7] mixtures, showing preferential solvation of these ions in DMF + AN systems. Li^+ and Na^+ ions show preferential solvation in DMF + AC[5] and in DMSO + AN mixtures[3]. These results also indicate that Li^+, Na^+ and K^+ ions experience stronger electrostatic cation–solvent interactions with DMSO in DMSO + AN mixtures as compared to DMF in DMF + AN mixtures as no maxima for solvated radii (r_i) values for these ions is observed in DMSO + AN mixtures.

The r_i values of anions Br^-, I^-, NO_3^-, ClO_4^- and Ph_4B^- do not change from DMSO to DMSO + dioxane mixtures and almost remain constant. Anions are known to be poorly solvated in dipolar aprotic solvents[22]. It is also clear from Table IV that the solvated radii of Bu_4N^+, Et_4N^+ ions either remain practically constant equal to their crystallographic radii or increase regularly with the increase of dioxane in DMSO + dioxane mixtures. It has also been reported in the literature that tetraalkylammonium ions and anions do not show preferential solvation in DMSO + AN mixtures[3,4]. Hence, conductance measurement in DMSO + dioxane mixtures suggest that all studied cations and anions show no preferential solvation.

Viscosity Measurements

The investigation of the viscosity of electrolytic solutions in non-aqueous binary solvent mixtures is useful for ion–solvent interaction, the structure of electroytic solutions and preferential solvation of ion. In order to obtain additional support for conductance results, the viscosities of similar electrolytes have been measured in same mixtures in the concentration range $(0-250) \cdot 10^{-4}$ mol dm^{-3}.

The molar concentration (C) and the corresponding ψ values are reported in Table V. The ψ value has been defined as follows:

$$\psi = \frac{\eta - \eta_0}{\eta_0 \sqrt{C}}, \tag{5}$$

where η_0 and η are viscosities of pure solvent or solvent mixture and solution, respectively. The η_0 values for each solvent mixture used to calculate ψ is the same as reported in Table I.

The entire viscosity data has been analysed by Jones–Dole equation[23] in the following form:

$$\psi = A + B\sqrt{C}\,. \tag{6}$$

TABLE V

Molar concentration (C) and corresponding ψ values for some electrolytes in DMSO and DMSO + dioxane mixtures at 25°C

Electrolyte	Solvent (mole % DMSO)									
	100		90		75		60		45	
	$C \cdot 10^4$	$\psi \cdot 10^2$	$C \cdot 10^4$	$\psi \cdot 10^2$	$C \cdot 10^4$	$\psi \cdot 10^2$	$C \cdot 10^4$	$\psi \cdot 10^2$	$C \cdot 10^4$	$\psi \cdot 10^2$
	14·75	7·04	14·75	8·60	14·75	7·78	14·75	7·66	13·44	9·84
	28·15	9·21	28·15	10·73	28·15	10·24	28·15	9·81	25·67	12·22
	40·39	10·83	40·39	12·44	40·39	11·78	40·39	11·63	36·83	13·89
Bu_4NBPh_4	51·61	12·05	51·61	13·54	51·61	13·24	51·61	12·85	47·05	15·20
	61·93	13·12	61·93	14·63	61·93	14·22	61·93	13·94	56·47	16·02
	71·46	13·88	71·46	15·45	71·46	15·25	71·46	14·82	65·15	16·21
	33·54	6·62	22·58	6·12	23·27	6·88	22·76	7·63	22·54	9·05
	65·49	8·74	43·11	7·82	44·43	8·65	43·44	9·56	43·03	11·24
Bu_4NI	95·95	10·40	61·86	9·13	63·74	10·05	62·33	11·22	61·74	12·83
	125·03	11·63	79·04	10·02	81·45	11·14	79·64	12·35	78·89	14·15
	152·82	12·75	94·85	10·83	97·74	12·23	95·57	13·44	94·67	15·14
	179·39	13·64	109·44	11·74	112·78	12·78	110·28	14·21	109·23	16·22
	24·35	7·24	17·25	6·91	21·22	8·05	19·25	8·66	21·34	10·21
	46·49	9·63	32·94	8·62	40·51	10·64	36·75	11·27	40·73	13·10
$NaBPh_4$	66·70	11·40	47·26	10·73	55·70	12·33	52·72	13·13	58·44	14·93
	85·23	12·81	60·39	12·05	74·27	13·82	67·37	14·64	74·67	16·44
	102·27	13·82	72·47	13·05	89·12	14·95	80·84	15·81	89·61	18·05
	118·0	15·08	83·61	13·94	102·83	16·04	93·28	16·85	103·39	19·27
	50·27	7·52	44·76	7·52	49·87	8·91	26·36	7·92	26·36	9·24
	80·44	9·11	71·63	9·21	79·80	10·82	51·07	10·21	51·07	12·15
	108·28	10·24	113·80	11·05	120·45	13·04	110·10	14·13	110·00	16·26
Pr_4NI	134·06	11·44	135·51	11·83	145·09	14·13	136·19	15·94	136·19	17·64
	169·35	12·52	155·72	12·81	168·00	15·15	172·03	17·25	172·03	19·45
	201·10	13·63			199·50	16·22				
	32·13	5·53	17·47	4·27	22·0	5·63	22·06	6·51	22·0	8·01
	44·05	6·01	54·18	6·81	42·22	7·33	42·32	8·32	42·22	10·02
Et_4NI	61·05	6·92	72·93	7·83	65·27	8·72	65·44	10·04	65·27	11·73
	82·18	8·04	114·07	9·56	78·06	9·44	78·26	10·78	78·06	12·44
	97·0	8·63	135·45	10·43	94·03	10·25	94·27	11·66	94·03	13·55
					108·88	10·86			108·88	14·21
	22·92	3·92	24·63	5·85	27·30	6·67	16·82	6·78	27·30	8·60
	43·98	5·22	40·62	6·93	35·03	7·34	21·58	7·45	35·03	9·54
Me_4NI	97·97	7·41	54·86	7·60	45·59	8·09	28·08	7·95	45·59	10·42
	113·43	8·05	63·32	8·12	52·02	8·45	32·05	8·34	52·02	10·86
	139·61	8·74	75·43	8·63	58·02	8·83	52·02	9·83	58·02	11·37
	165·79	9·43	145·07	11·19						

TABLE V
(*Continued*)

Electrolyte	Solvent (mole % DMSO)									
	100		90		75		60		45	
	$C \cdot 10^4$	$\psi \cdot 10^2$	$C \cdot 10^4$	$\psi \cdot 10^2$	$C \cdot 10^4$	$\psi \cdot 10^2$	$C \cdot 10^4$	$\psi \cdot 10^2$	$C \cdot 10^4$	$\psi \cdot 10^2$
	24·98	5·22	23·26	5·83	22·28	6·44	32·43	7·55	20·57	8·12
	48·76	6·81	45·42	7·55	43·50	8·36	61·91	10·04	40·16	10·43
	93·09	9·13	86·71	9·84	83·05	10·74	88·84	11·67	76·67	13·45
KI	133·57	10·74	124·40	13·66	119·17	12·55	113·51	13·05	109·99	15·54
	170·67	11·82	158·96	13·08	152·27	13·81	136·22	13·95	140·55	17·24
	240·81	13·01	190·75	14·09	182·72	15·13	157·17	15·02	168·66	18·58
	44·35	6·02	23·8	6·63	25·70	6·44	32·43	7·55	31·80	9·04
	84·67	8·40	63·53	8·44	49·06	8·45	61·91	10·04	60·71	11·65
	121·48	9·99	91·16	9·65	70·39	9·72	88·84	11·67	87·11	13·44
$KClO_4$	155·23	10·85	116·48	10·82	89·95	10·83	113·51	13·05	111·31	14·86
	186·28	12·10	139·78	11·81	107·94	11·04	136·22	13·95	133·57	15·94
	214·94	12·83	161·28	12·54	124·54	12·45	157·17	15·02	154·12	17·24
	34·36	6·92	28·63	5·65	19·82	7·44	20·88	6·09	26·09	6·55
	65·60	8·35	54·09	7·46	37·85	8·89	39·87	7·64	49·82	8·87
	94·12	10·0	77·61	8·83	54·30	10·02	57·21	9·22	71·48	10·40
$NaClO_4$	120·27	11·03	99·16	9·94	69·39	10·91	73·10	10·05	91·34	11·81
	144·32	11·92	119·0	10·66	83·27	11·65	87·72	11·03	109·60	12·84
	166·53	13·41	137·31	11·27	96·08	12·38	101·21	11·74	126·47	13·82
	39·94	6·82	37·98	8·05	33·13	8·44	44·37	9·65	36·78	10·22
	76·41	8·91	72·65	10·34	63·39	10·82	84·90	12·64	70·37	13·02
	109·84	10·43	104·44	12·11	91·12	12·55	122·04	14·73	101·15	15·44
Bu_4NNO_3	140·60	11·74	133·68	13·62	116·63	13·94	156·21	16·62	129·47	17·04
	168·99	12·60	160·68	14·76	140·48	15·13	187·75	18·01	155·62	18·55
	195·28	13·61	185·67	15·66	161·99	16·12	216·96	19·20	179·82	19·60
	40·24	5·81	41·59	7·14	48·77	8·84	52·72	9·80	30·55	9·14
	76·98	7·93	79·56	9·33	93·30	11·61	100·86	12·93	71·49	12·94
KNO_3	110·66	9·32	114·37	11·07	134·12	13·64	144·99	15·25	107·52	15·42
	141·64	10·54	146·39	12·32	171·67	15·25	185·58	17·21	129·23	16·71
	170·24	11·33	175·95	13·43	206·34	16·62	223·06	18·55	158·84	18·25
	196·72	12·11	203·32	14·44	238·43	17·63	257·76	19·82	185·38	19·55
	41·75	5·81	40·17	6·89	23·20	7·24	44·46	8·32	44·08	10·04
	80·10	7·82	77·07	9·35	45·34	8·92	85·28	11·24	84·56	13·22
	115·43	9·22	111·07	10·92	66·50	10·41	128·91	13·43	121·87	15·61
$AgNO_3$	148·10	10·43	142·50	12·25	86·74	11·43	157·70	15·20	156·36	17·55
	178·39	11·45	171·65	13·44	159·60	14·56	189·95	16·61	158·35	19·04
	206·56	12·34	190·75	14·28	221·66	16·87	219·94	17·82	218·08	20·42

TABLE V
(*Continued*)

Electrolyte	Solvent (mole % DMSO)									
	100		90		75		60		45	
	$C \cdot 10^4$	$\psi \cdot 10^2$	$C \cdot 10^4$	$\psi \cdot 10^2$	$C \cdot 10^4$	$\psi \cdot 10^2$	$C \cdot 10^4$	$\psi \cdot 10^2$	$C \cdot 10^4$	$\psi \cdot 10^2$
	49·22	6·80	41·04	8·35	42·36	10·08	42·29	11·94	43·29	11·64
	94·42	9·03	78·51	10·84	81·03	13·34	80·90	15·74	82·82	15·85
$LiNO_3$	136·07	10·84	112·85	12·65	116·48	15·75	116·30	18·50	119·05	18·91
	174·59	12·05	144·45	14·13	149·09	17·45	148·86	20·63	152·38	21·26
	210·30	13·22	172·62	15·39	179·20	19·02	178·92	22·44	183·15	23·22
	243·50	14·13	200·63	16·45	232·96	20·33	206·75	23·90	211·64	25·04
	24·46	5·45	44·61	7·04	23·20	7·24	19·55	6·92	36·77	9·71
	47·81	7·03	85·34	9·25	45·34	8·92	38·21	8·84	70·34	12·63
NaBr	91·47	9·23	122·68	10·89	66·50	10·41	73·09	11·15	101·12	14·42
	131·49	10·82	157·03	12·15	86·74	11·43	105·07	12·92	129·43	16·15
	168·30	12·04	188·74	13·15	159·60	14·56	134·49	14·44	155·57	17·44
	202·29	12·91	218·10	14·09	221·66	16·87	161·64	15·63	179·77	18·40

The plots of ψ versus $\sqrt{C}$ have been found linear over the whole studied concentration range of the electrolytes and are shown for some electrolytes in Fig. 4.

The positve A-coefficients of the electrolytes obtained from the plots have been found in agreement with the theoretically calculated A_η-coefficients (reported in Table VI) using Falkenhagen–Vernon equation[24]:

$$A_\eta = \frac{0{\cdot}2577 \Lambda_0}{\eta_0 (DT)^{1/2} \lambda_1^0 \lambda_2^0} \left[1 - 0{\cdot}6863 \left(\frac{\lambda_1^0 - \lambda_2^0}{\Lambda_0}\right)\right]^2, \qquad (7)$$

where the symbols have their usual meanings. For the calculation of A_η from Eq. (7), η_0 and D values have been taken from Table I. The Λ_0, λ_1^0 and λ_2^0 values for electrolytes and ions in DMSO and DMSO + dioxane mixtures have been taken from Table III and IV.

The calculated B-coefficients from the plots with the help of least square method are given in Table VI with the literature values in DMSO. The close agreement between the two sets of B values shows the accuracy of viscosity data. From Table VI, it is clear that viscosity B-coefficients are large, positive and increase with the increase of dioxane content in DMSO + dioxane mixtures for all the electrolytes. Gill and Coworkers[6,7] have also reported that as the DMF composition is increased

in DMF + AC and DMF + AN mixtures, the viscosity B-coefficients increased. Syal et al.[3] have also observed that B-coefficients increased with the increase of DMSO concentration in DMSO + AN mixtures.

TABLE VI

Falkenhagen–Vernon coefficient A_η ($dm^{3/2}\ mol^{-1/2}$) and Jones–Dole viscosity coefficient[a] B ($dm^3\ mol^{-1}$) for some electrolytes in DMSO and DMSO + dioxane mixtures at 25°C

Electrolyte	Solvent (mole % DMSO)									
	100		90		75		60		45	
	$A_\eta \cdot 10^2$	B	$A_\eta \cdot 10^2$	B	$A_\eta \cdot 10^2$	B	$A_\eta \cdot 10^2$	B	$A_\eta \cdot 10^2$	B
Bu_4NBPh_4	1·98	1·46 1·43[b]	1·71	1·50	2·25	1·55	2·64	1·58	3·26	1·66
Bu_4NI	1·30	0·95 0·95[b]	1·39	1·00	1·50	1·08	1·77	1·16	2·17	1·22
$NaBPh_4$	1·75	1·35 1·32[b]	1·84	1·40	2·10	1·45	2·36	1·53	2·95	1·62
Pr_4NI	1·22	0·85	1·30	0·93	1·40	1·04	1·69	1·15	2·14	1·28
Et_4NI	1·09	0·76	1·20	0·82	1·30	0·90	1·56	1·02	1·96	1·10
Me_4NI	1·03	0·69	1·14	0·76	1·24	0·87	1·47	1·00	1·89	1·10
KI	1·16	0·84 0·85[b]	1·31	0·91	1·36	1·00	1·63	1·14	2·10	1·23
$KClO_4$	1·12	0·81 0·81[b]	1·21	0·89	1·33	0·98	1·57	1·09	2·06	1·19
$NaClO_4$	1·17	0·80 0·81[b]	1·25	0·87	1·37	0·95	1·56	1·06	2·05	1·17
Bu_4NNO_3	1·20	0·90 0·92[b]	1·28	1·03	1·41	1·13	1·65	1·20	2·05	1·28
KNO_3	1·09	0·81	1·17	0·93	1·35	1·05	1·54	1·15	1·99	1·28
$AgNO_3$	1·04	0·82 0·82[b]	1·13	0·95	1·25	1·08	1·44	1·18	1·94	1·28
$LiNO_3$	1·21	0·86 0·86[b]	1·27	1·05	1·38	1·30	1·60	1·53	2·04	1·68
NaBr	1·18	0·82	1·27	0·88	1·41	0·95	1·66	1·05	2·18	1·17

[a] The maximum uncertainty of the B values in this Table is $\pm 0{\cdot}03\ dm^3\ mol^{-1}$. [b] Taken from ref.[3].

From Table VI, it has been found that *B*-coefficient values generally decreas with the increasing size of the alkali metal and Ag cations in all studied solvent mixtures. This observation is also in agreement with literatures studies.

Ionic $B_{\pm}$ Values and Solvation Behaviour

To understand ionic solute–solvent interactions, it is necessary that *B*-coefficients of electrolytes are split up into its single ion contribution. The *B*-coefficient of Bu_4NBPh_4 have been split up into ionic $B_{\pm}$ values using the following equations as proposed by Gill[6]:

$$\frac{B_-}{B_+} = \left(\frac{5{\cdot}35}{5{\cdot}00}\right)^3 \tag{8}$$

and

$$B_{(Bu_4NBPh_4)} = B_+ + B_- , \tag{9}$$

where $B_{(Bu_4NBPh_4)}$ is the experimentally determined *B*-coefficient for Bu_4NBPh_4. Using these $B_{\pm}$ (B_+ and B_-) values, the *B* values (Table VI) of the electrolytes are

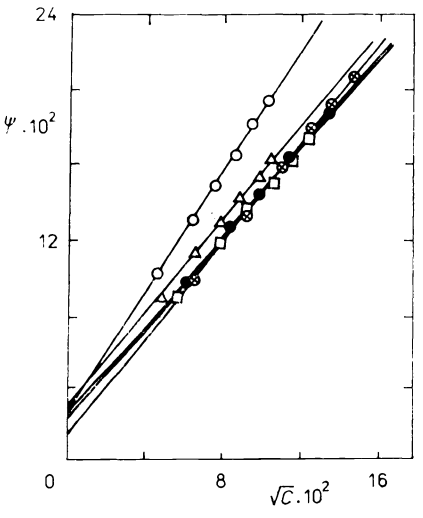

FIG. 4

Plot of ψ vs $\sqrt{C}$ for some electrolytes in DMSO containing 55 mole % dioxane at 25°C: ○ $NaBPH_4$, △ Bu_4NI, □ $KClO_4$, ⊗ $AgNO_3$, ● NaBr

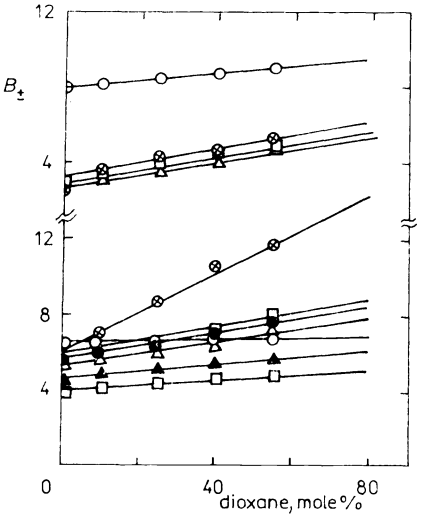

FIG. 5

Plot of $B_{\pm}$ coefficients for some ions vs mole % dioxane in DMSO + dioxane mixtures at 25°C: ○ Ph_4B, △ Br^-, □ I^-, ⊗ NO_3^- (*A*); ○ Bu_4N^+, △ Et_4N^+, □ Me_4N^+, ⊗ Li^+, ▲ Na^+, ● K^+, ■ Ag^+ (*B*)

resolved into their ionic contributions with the help of additive relationship and these are presented in Table VII.

The ionic $B_{\pm}$ values in DMSO are in good agreement with literature values as given in brackets in Table VII.

TABLE VII

Ionic $B_{\pm}$ ($dm^3\ mol^{-1}$) coefficients [a] in DMSO and DMSO + dioxane mixtures at 25°C

Ion	Solvent (mole % DMSO)				
	100	90	75	60	45
Bu_4N^+	0·66 0·65[b]	0·67	0·70	0·71	0·75
Pr_4N^+	0·56 0·54[c]	0·60	0·66	0·71	0·81
Et_4N^+	0·47 0·46[c]	0·49	0·52	0·57	0·63
Me_4N^+	0·40	0·43	0·49	0·56	0·63
Li^+	0·60 0·59[b]	0·70	0·87	1·07	1·17
Na^+	0·55 0·54[b]	0·57	0·60	0·66	0·71
K^+	0·55 0·55[b]	0·58	0·62	0·69	0·76
Ag^+	0·56 0·55[b]	0·60	0·65	0·72	0·77
Ph_4B^-	0·80 0·78[b]	0·83	0·85	0·87	0·91
ClO_4^-	0·26 0·26[b]	0·31	0·36	0·40	0·43
NO_3^-	0·26 0·27[b]	0·35	0·43	0·46	0·51
Br^-	0·27 0·31[b]	0·31	0·35	0·39	0·46
I^-	0·29 0·30[b]	0·33	0·38	0·45	0·47

[a] The maximum uncertainty of $B_{\pm}$ values in this table is $\pm 0{\cdot}03\ dm^3\ mol^{-1}$. Taken from [b] ref.[3]; [c] ref.[4].

Plot of $B_{\pm}$-coefficients vs mole % of dioxane in DMSO + dioxane mixtures are given in Fig. 5.

From Table VII, it is clear that B_+ values for tetraalkylammonium cations increase with the increase of size of the cation. One also finds that B_+ value for Li^+ ion is greater than Na^+, K^+ or Ag^+ ion. But B_- value increases in the following order:

$$Ph_4B^- > I^- > Br^- > ClO_4^- \geqq NO_3^- .$$

The ordering of $B_{\pm}$ values opposite to the ordering obtained for $\lambda_{\pm}^0$ values is in confirmity with the relation between conductance and viscosity property.

The solvation behaviour of an ion in a solvent can be explained on the basis of variation of $B_{\pm}$ value of an ion as a function of solvent composition and preferential solvation is inferred by non-linear variation of $B_{\pm}$. It is evident from Table VII that $B_{\pm}$ values of all studied ions increase linearly with the increase of dioxane content in DMSO + dioxane mixtures.

The linear variation of B_+ values of Li^+, Na^+, K^+ and Ag^+ ions with the decrease of dielectric constant of the medium is in contrast with the conclusions derived from studies in DMSO + AN by Syal et al.[3], DMF + AN and DMF + AC by Gill and coworkers[6,7]. Thus, this can be inferred that these ions show different behaviour in DMSO + dioxane mixtures than in DMF + AN, DMF + AC and DMSO + AN mixture systems.

Thus, from above observations it can be stated that either all studied ions show no change in preferential solvation or show no solvation due to the addition of dioxane to the DMSO in DMSO + dioxane mixtures.

It is known from the following viscosity $B_{\pm}$ coefficient equation[25] (which has been obtained from the combination of Einstein viscosity equation with that of Jones and Dole):

$$B_{\pm} = (\tfrac{4}{3}N\pi r_{\pm}^3 + nV_1)/400 , \qquad (10)$$

(where N is Avogadro's number, $r_{\pm}$ the ionic radii, n the solvation number and V_1 is the volume of first solvation shell), that $B_{\pm}$ coefficients are directly related to crystal radii and hence effective solvated radii of the ions.

From the conductance measurements it has been observed that r_i values for all ions either increase or remain practically constant with the increase of dioxane content in the solvent mixture. The same results have been obtained for $B_{\pm}$ values. Hence the results obtained from conductance and viscosity studies are in complete agreement with each other.

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REFERENCES

1. Syal V. K., Ranowt P. C.: Indian J. Chem., A *24* 16 (1985).
2. Syal V. K., Bisht P., Chauhan M. S.: Proc. Natl. Acad. Sci. (India), in press.
3. Syal V. K., Chauhan S., Chauhan M. S.: Z. Phys. Chem. (N.F.) *159*, 49 (1988).
4. Syal V. K., Chauhan S., Chauhan M. S.: Indian J. Chem., A *29* 69 (1989).
5. Gill D. S., Sharma A. N., Schneider H.: J. Chem. Soc., Faraday Trans. 1 *78*, 465 (1982).
6. Gill D. S., Sharma A. N.: J. Chem. Soc., Faraday Trans. 1 *78*, 475 (1982).
7. Gill D. S., Cheema J. S.: Z. Phys. Chem. (N.F.) *134*, 205 (1983).
8. Gill D. S., Sekheri M. B.: J. Chem. Soc., Faraday Trans. 1 *78*, 119 (1982).
9. Gill D. S., Nording R.: Z. Phys. Chem. (N.F.) *136*, 117 (1983).
10. Swindels J. F., Coe J. R. jr, Goodfrey T. B.: J. Res. Natl. Bur. Stand. (U.S.) *48*, 1 (1952).
11. Weissberger A., Rossiter B. W.: *Physical Methods of Chemistry*, Part IV. Wiley, New York 1972.
12. Fuoss R. M., Shedlovsky T.: J. Am. Chem. Soc. *71*, 1496 (1949).
13. Fuoss R. M., Accascina F.: *Electrolytic Conductance*. Wiley Interscience, New York 1959.
14. Salomon M.: *Computer Program, Shedlovsky Conductance Equation*, U.S. Army ET and DL (LABCOM) FT. MONMOUTH, NJ 07703-5000 (U.S.A.).
15. Beronious P.: Acta Chem. Scand., A *28* 77 (1974); A *29* 289 (1975); A *30* 115 (1976).
16. Gill D. S.: J. Chem. Soc., Faraday Trans. 1 *77*, 751 (1981).
17. Kinsinger J. B., Tannahill M. M., Greenberg M. S., Popov A. I.: J. Phys. Chem. *77*, 2444 (1973).
18. Szmant H. H. in: *Dimethylsulphoxide* (S. W. Jacob, E. E. Rosenbaum and D. C. Wood, Eds). Dekker, New York I 1971.
19. Fuoss R. M.: Proc. Natl. Acad. Sci. (U.S.A.) *45*, 807 (1959).
20. Chauhan S.: *Thesis*. H. P. University, Shimla (India) 1988.
21. Gill D. S.: Electrochim. Acta *22*, 491 (1977); *24*, 701 (1979).
22. Parker A. J.: Q. Rev., Chem. Soc. *16*, 163 (1962).
23. Jones G., Dole M.: J. Am. Chem. Soc. *51*, 2950 (1929).
24. Falkenhagen J., Vernon E. L.: Phys. Z. *33*, 1401 (1932).
25. Bicknell R. T. M., Lawerence K. G., Feakins D.: J. Chem. Soc., Faraday Trans. 1 *76*, 637 (1980).
26. Atalani C., Justice J. C., Quintin M., Dubois J. E.: J. Chim. Phys. Physicochim. Biol. *66*, 180 (1969); J. Solution Chem. *4*, 955 (1975).
27. Sears P. G., Lester G. R., Dawson L. R.: J. Phys. Chem. *60*, 1433 (1956).
28. Arrington D. E., Griswold E.: J. Phys. Chem. *74*, 123 (1970).
29. Spiro M.: *Physical Chemistry of Organic Systems*. Plenum, London 1973.
30. Gill D. S., Chauhan S., Chauhan M. S.: Z. Phys. Chem. (N.F.) *150*, 113 (1986).