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**CONDUCTANCE STUDIES OF SOME 1 : 1 ELECTROLYTES  
IN ACETONE + DIMETHYLSULPHOXIDE MIXTURES AT 25°C**

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Precise molar conductances of  $\text{Bu}_4\text{NBPh}_4$ ,  $\text{Bu}_4\text{NI}$ ,  $\text{Bu}_4\text{NNO}_3$ ,  $\text{AgNO}_3$ ,  $\text{LiNO}_3$ ,  $\text{NaBPh}_4$  and  $\text{KI}$  have been measured in acetone (Ac), dimethylsulphoxide (DMSO) and Ac + DMSO mixtures over the whole solvent composition range at 25°C. The conductance data has been analysed by computer using Shedlovsky conductance equation. Limiting ionic conductances have been calculated by using Gill's model. Evaluation of solvated radii of  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Ag}^+$  ions in Ac + DMSO mixtures shows strong preferential solvation for  $\text{Li}^+$  ion by DMSO.  $\text{Na}^+$  and  $\text{Ag}^+$  ions are found to be preferentially solvated by DMSO in Ac-rich region and by Ac in DMSO rich regions.  $\text{K}^+$ ,  $\text{NO}_3^-$  and  $\text{I}^-$  ions show no preferential solvation in Ac + DMSO mixtures.

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In recent studies, Gill and coworkers<sup>1,2</sup> have found that the binary mixtures of acetone (Ac) and N,N-dimethylformamide (DMF) have properties close to ideal mixtures. They have explored this extraordinary solvent system towards ion-solvent interactions by measuring equivalent conductances and viscosities of some solutions of electrolytes in Ac-DMF mixtures. Dimethylsulphoxide (DMSO) which is used in the present studies as one of the solvent components in Ac + DMSO mixtures, is known to be more basic and hence more cationophilic than DMF (ref.<sup>3</sup>). But at the same time, DMSO is also believed to possess dipole-dipole interactions to form small chains<sup>4</sup>, probably not strong enough to prevent coordination of cations by DMSO molecules. Therefore, in the present investigations, an attempt has been made to speculate a modification on cationophilic character of DMSO in the presence of Ac in Ac + DMSO mixtures.

**EXPERIMENTAL**

Ac and DMSO were purified by the methods reported elsewhere<sup>5</sup>. Binary mixtures of these solvents were prepared by weight and their properties at 25°C are summarised in Table I, where  $X_1$  is the mole fraction of DMSO in Ac + DMSO mixtures,  $D$  is permittivity,  $\eta_0 \cdot 10^{-3}$  is viscosity ( $\text{kg m}^{-1} \text{s}^{-1}$ ),  $d \cdot 10^{-3}$  is density ( $\text{kg m}^{-3}$ ) and  $q$  is Bjerrum critical distance (nm). Conduc-

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tances were repeatedly measured at 1 000 Hz frequency with a calibrated digital conductivity meter model NDC-732 manufactured by Naina Electronics, Chandigarh. The experimental data ( $C$  is concentration in  $\text{mol m}^{-3}$  and  $\Lambda$  is molar conductivities in  $\text{S cm}^2 \text{mol}^{-1}$ ) are summarized in Table II. The details of conductance cell and experimental procedure for the conductance measurements are the same as reported in literature<sup>2,5</sup>. The reproducibility of conductance, viscosity and density measurements were  $\pm 0.2\%$ ,  $\pm 0.1\%$  and  $1.0 \cdot 10^{-1} \text{ kg m}^{-3}$ , respectively.

## RESULTS AND DISCUSSION

The conductance data has been analysed with the help of a computer program using the Shedlovsky conductance equation<sup>6,7</sup>. The derived conductance parameters such as molar conductivities at infinite dilution  $\Lambda^\infty$  and ion-association constant ( $K_A$ ) for  $\text{Bu}_4\text{NBPh}_4$ ,  $\text{Bu}_4\text{NI}$ ,  $\text{Bu}_4\text{NNO}_3$ ,  $\text{NaBPh}_4$ ,  $\text{LiNO}_3$ ,  $\text{KI}$  and  $\text{AgNO}_3$  in  $\text{Ac} + \text{DMSO}$  mixtures have been reported in Table III. A reasonably good agreement between the  $\Lambda^\infty$  values obtained experimentally and the corresponding literature values as shown in Table IV indicates the accuracy of the present conductance measurements. Since our purpose was to see the solvation pattern of ions in terms of their solvated radii ( $r_i$ ) values in  $\text{Ac} + \text{DMSO}$  mixtures, which in fact depend upon the  $\Lambda^\infty$  values of electrolytes. Moreover, it has been found that the analysis of conductance data by different methods gives almost the same  $\Lambda^\infty$  values for an electrolyte but different  $K_A$  values<sup>8</sup>. Therefore, the irregular scatter of  $K_A$  values

TABLE I  
Solvent properties of  $\text{Ac} + \text{DMSO}$  mixtures at  $25^\circ\text{C}$

Solvent	$X_1$	$D^a$	$\eta_0 \cdot 10^{-3}$	$d \cdot 10^{-3}$	$q$
1	0.00	20.7	0.304	0.7834	1.354
2	0.10	22.6	0.362	0.8170	1.203
3	0.20	23.3	0.432	0.8503	1.082
4	0.30	26.5	0.507	0.8781	0.983
5	0.40	29.0	0.597	0.9142	0.901
6	0.50	31.9	0.732	0.9439	0.832
7	0.60	33.7	0.852	0.9735	0.772
8	0.70	37.4	1.077	1.005	0.720
9	0.80	40.4	1.302	1.044	0.676
10	0.90	43.3	1.589	1.072	0.636
11	1.00	46.7	1.990	1.094	0.600

<sup>a</sup> The permittivities  $D$  of  $\text{Ac} + \text{DMSO}$  mixtures reported in this table are the extrapolated values from the experimental values of Fuoss and coworkers<sup>18</sup>.

observed in our studies would not effect the  $r_i$  values of Table IV which depend only on the  $\Lambda^\infty$  values hence  $K_A$  values are of little significance to our conclusions.

### Limiting Ionic Conductances

The limiting ionic conductance ( $\lambda_i^\infty$ ) values of  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ag}^+$ ,  $\text{NO}_3^-$  and  $\text{I}^-$  ions in Ac, DMSO and Ac + DMSO mixtures have been computed in the present work from the  $\Lambda^\infty$  values of  $\text{Bu}_4\text{NNO}_3$ ,  $\text{Bu}_4\text{NI}$ ,  $\text{LiNO}_3$ ,  $\text{NaBPh}_4$ ,  $\text{KI}$  and  $\text{AgNO}_3$  (reported in Table III) by using the  $\text{Bu}_4\text{NBPh}_4$  assumption<sup>9</sup> and the Kohlrausch's law of independent ionic conductances at infinite dilution. The  $\lambda_i^\infty$  values thus obtained have been reported in Table V. No pronounced differences are observed between the present  $\lambda_i^\infty$  values in pure Ac, in pure DMSO and the literature values (literature values enclosed in parentheses) obtained by using transference number method. This, therefore, indicates a good applicability of  $\text{Bu}_4\text{NBPh}_4$  assumption in Ac + DMSO mixtures within the experimental uncertainty.

### Solvated Radii and Preferential Solvation of Ions

Recently, Gill<sup>10</sup> has proposed an empirical modification (Eq. (1)) of the Stokes law to calculate the actual solvated radii ( $r_i$ ) of ions in solution within an uncertainty of  $\pm 2\%$  by accounting for the dielectric friction effect quantitatively.

$$r_i = |z| F^2 / (6\pi N \eta_0 \lambda_i^\infty) + 0.0103D + r_y, \quad (1)$$

where the symbols have their usual significance<sup>10</sup>. Using  $\lambda_i^\infty$  values of  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ag}^+$ ,  $\text{NO}_3^-$  and  $\text{I}^-$  ions from Table V, solvated radii ( $r_i$ ) values of these ions have been calculated and have also been reported in Table V.

Plot of  $\eta_0$  vs mole % DMSO in Ac + DMSO mixtures was constructed as shown in Fig. 1 to obtain information regarding the nature of Ac + DMSO solvent system. Since viscosity shows a marked deviation from linearity between 40.0 and 90.0 mole % DMSO, therefore, a stronger solvent structural effect between 40.0 and 90.0 mole % DMSO in Ac + DMSO mixtures can be presumed as compared with those for other solvent systems.

A perusal of  $r_i$  values in Table V shows that the  $r_i$  values of  $\text{Li}^+$  ion increase continuously from 0.48 nm in pure Ac to  $\approx 0.55$  nm in 60.0 mole % DMSO with the addition of DMSO in Ac + DMSO mixture at 10.0 mole % interval. Variation of  $r_i$  values of  $\text{Na}^+$  and  $\text{Ag}^+$  ions with solvent composition is rather more interesting. The addition of DMSO in pure Ac up to  $\approx 50.0$  mole % DMSO increases the  $r_i$  value of  $\text{Na}^+$  ion from 0.45 nm to 0.48 nm whereas the addition of Ac in pure DMSO up to  $\approx 20.0$  mole % Ac increases it from 0.46 nm to 0.48 nm. Similarly,  $r_i$  value of  $\text{Ag}^+$  ion is found to be increased significantly i.e. from 0.41 nm to

TABLE II  
Conductance data of some electrolytes in Ac, DMSO and Ac + DMSO mixtures at 25°C

Electrolyte	Solvent 1		Solvent 2		Solvent 3		Solvent 4		Solvent 5	
	$C \cdot 10^{-6}$	$\Lambda$	$C \cdot 10^{-6}$	$\Lambda$	$C \cdot 10^{-6}$	$\Lambda$	$C \cdot 10^{-6}$	$\Lambda$	$C \cdot 10^{-6}$	$\Lambda$
Bu <sub>4</sub> NBPh <sub>4</sub>	0.1061	124.9	0.1061	102.5	0.2102	87.2	0.0981	79.4	0.1069	66.4
	0.2105	122.8	0.3640	99.6	0.3640	85.7	0.1948	79.2	0.2105	65.5
	0.3641	120.5	0.5139	98.7	0.5139	84.5	0.2584	78.9	0.3640	64.6
	0.5141	118.7	0.7089	97.0	0.7089	83.3	0.3839	78.3	0.5141	64.0
	0.7089	116.8	0.8508	96.3	0.8508	82.8	0.5290	77.5	0.7089	62.9
	1.0351	114.0	1.0351	95.2	1.0351	81.9	1.1562	76.4	1.0351	61.8
Bu <sub>4</sub> NNO <sub>3</sub>	0.1958	183.5	0.1958	151.4	0.1958	127.2	0.1211	117.2	0.1958	98.4
	0.3884	181.1	0.3884	148.6	0.4359	124.4	0.2250	116.4	0.3884	96.9
	0.6718	178.4	0.6718	145.6	0.6718	121.4	0.4840	114.4	0.6718	95.2
	0.9488	171.4	0.9488	143.6	0.9488	119.8	0.6761	113.2	0.9486	94.2
	1.3081	168.7	1.3081	141.3	1.3081	116.8	1.0240	112.0	1.3081	92.3
	1.5711	167.0	1.9110	137.6	1.9110	113.2	1.7640	109.0	1.5700	91.6
Bu <sub>4</sub> NI	0.1860	181.5	0.1691	146.1	0.1416	130.5	0.0681	115.2	0.2220	99.2
	0.3700	178.1	0.3348	142.2	0.2822	128.2	0.1355	144.3	0.3841	98.3
	0.6400	174.5	0.5760	137.8	0.4922	124.6	0.2683	113.2	0.5428	97.6
	0.9041	171.9	0.7842	134.7	0.6964	122.6	0.3986	112.7	0.7452	96.7
	1.2400	169.2	1.0890	131.0	0.9600	120.3	0.5893	111.7	0.9010	95.7
	1.4900	167.5	1.6560	125.6	1.4030	116.3	0.7441	110.8	1.0960	95.6
NaBPh <sub>4</sub>	0.1741	145.3	0.1371	115.3	0.1537	96.0	0.0783	83.1	0.1537	70.7
	0.3450	142.9	0.2722	113.7	0.3048	94.3	0.1555	81.8	0.3052	69.2
	0.5973	141.0	0.4708	111.5	0.7450	91.1	0.2815	80.6	0.5280	67.6
	0.8430	138.5	0.6651	110.0	1.0240	88.9	0.4066	79.6	0.7452	66.6
	1.1600	137.0	1.10000	107.5	1.2340	88.5	0.5721	78.4	1.0270	65.1
	1.6990	134.3	1.3390	106.6	1.5010	87.2	0.7339	76.9	1.5020	63.2
LiNO <sub>3</sub>	0.2250	183.6	0.2540	124.0	0.3440	115.8	0.1731	113.5	0.4309	90.2
	0.5290	176.8	0.5040	114.7	0.6754	109.0	0.3444	110.0	0.8555	86.8
	0.9610	169.8	0.8720	102.7	1.1680	102.0	0.6840	107.2	1.4790	83.0
	1.4444	164.3	1.2310	95.3	1.6490	96.8	1.0130	104.1	2.0890	80.4
	1.8490	159.6	1.4600	90.5	1.9640	93.2	1.4980	98.9	2.8720	76.4
	2.5000	156.1	1.1970	81.2	2.8720	85.0	1.9090	96.7	3.3870	74.8
KI	0.1440	189.9	0.2450	153.4	0.2390	135.9	0.1379	121.4	0.3680	106.4
	0.2890	187.0	0.4870	148.3	0.4750	131.8	0.4098	120.6	0.7300	105.0
	0.4840	183.0	0.8430	143.1	0.8220	129.9	0.8080	118.5	1.2600	103.9
	0.6760	181.1	1.6400	135.1	1.1600	125.2	1.1940	117.3	1.7800	103.0
	0.9000	178.7	1.9700	132.0	1.6000	121.7	1.5700	115.8	2.4500	101.6
	1.1560	176.0	2.3900	128.5	1.9200	120.0	2.0540	114.3	3.5900	100.2

TABLE II  
 (Continued)

Solvent 6		Solvent 7		Solvent 8		Solvent 9		Solvent 10		Solvent 11	
$C \cdot 10^{-6}$	$A$	$C \cdot 10^{-6}$	$A$	$C \cdot 10^{-6}$	$A$	$C \cdot 10^{-6}$	$A$	$C \cdot 10^{-6}$	$A$	$C \cdot 10^{-6}$	$A$
0.0529	56.3	0.1060	47.7	0.2022	39.4	0.1060	32.3	0.1060	27.0	0.1060	21.7
9.2085	55.9	0.3640	46.3	0.2348	39.2	0.2102	32.0	0.2105	26.7	0.2105	21.5
0.3094	55.6	0.5405	45.8	0.3306	39.1	0.3640	31.7	0.3640	26.4	0.3640	21.3
0.4579	55.0	0.7086	45.3	0.4541	38.9	0.7089	31.4	0.7089	26.1	0.5141	21.2
0.6019	54.8	0.8508	44.7	0.5142	38.8	0.8508	31.0	0.8508	25.9	0.8508	20.8
0.7876	54.7	1.0350	44.3	0.7161	38.4	1.0350	30.7	1.0350	25.7	1.0350	20.6
0.1031	88.9	0.1958	74.9	0.1154	63.0	0.1958	54.0	0.1958	47.1	0.1958	37.7
0.2052	88.5	0.3884	74.1	0.1975	62.9	0.3884	53.5	0.3884	46.5	0.3884	37.4
0.4063	87.9	0.6718	72.8	0.2780	62.8	0.6718	52.7	0.6718	46.2	0.9488	36.8
0.6040	87.3	0.9488	72.0	0.3810	62.5	0.9488	52.3	0.9488	45.9	1.3080	36.3
0.8920	86.9	1.3080	71.2	0.4821	62.4	1.3080	51.8	1.1910	45.5	1.5760	36.1
1.1730	86.0	1.5700	70.0	0.6022	62.3	1.9110	50.9	1.5700	45.0	1.9110	35.8
0.1422	80.4	0.1432	72.7	0.2609	58.3	0.1159	55.2	0.1770	43.1	0.1640	35.9
0.2816	79.2	0.2798	70.6	0.3898	57.6	0.3960	53.2	0.3590	42.7	0.3260	35.6
0.4813	78.3	0.4840	68.4	0.7674	56.1	0.5616	51.5	0.8213	41.9	0.5650	35.2
0.6185	77.2	0.6832	66.9	1.0150	55.5	0.7728	50.3	0.9590	41.7	0.7970	34.9
0.8130	76.4	0.9424	65.0	1.1350	55.2	0.9302	49.6	1.4210	41.1	1.1000	34.7
1.0640	75.2	1.3770	60.7	1.4910	54.6	1.1470	49.4	1.7300	40.3	1.3200	34.1
0.1955	57.0	0.1188	53.4	0.1403	41.7	0.1418	35.6	0.1640	29.0	0.1430	23.9
0.2607	56.6	0.2350	51.2	0.2094	41.5	0.2686	35.1	0.3260	28.9	0.2800	23.7
0.3558	55.9	0.4084	50.5	0.2779	41.2	0.6461	33.9	0.5716	28.6	0.4900	23.5
0.3872	55.3	0.5764	50.2	0.4128	41.0	0.9054	33.2	0.7963	28.3	0.6900	23.0
0.7526	53.4	0.7952	49.2	0.5451	40.7	1.0870	32.8	1.0900	27.9	0.9600	22.5
0.9848	52.2	1.1620	48.9	0.8022	40.2	1.3220	32.4	1.6000	27.8	1.4000	22.3
0.2199	87.1	0.3948	70.0	0.3353	60.6	0.7263	48.5	0.8640	43.3	0.8781	35.7
0.4377	86.1	0.7784	68.2	0.6672	60.2	1.4400	47.2	1.7150	41.8	2.9900	33.5
0.8667	85.9	1.3540	66.0	1.3210	59.8	2.4900	46.1	2.9590	40.2	4.2200	32.7
1.2880	85.8	1.9180	64.2	1.9620	59.5	3.5910	45.1	4.2020	38.8	5.8200	31.8
1.9030	85.2	2.6310	62.7	2.9020	59.0	4.8520	44.1	5.7790	37.3	6.9900	31.0
2.5020	84.4	3.1580	61.7	3.4810	58.5			8.4430	35.5	8.5100	30.3
0.1425	89.3	0.2860	78.2	0.2851	64.3	0.1410	55.6	0.1950	46.5	0.1910	39.3
0.2835	87.6	0.5690	76.8	0.5162	64.1	0.2800	54.9	0.4060	46.1	0.3790	38.8
0.5614	86.8	1.3900	74.2	0.8306	63.8	0.4840	54.4	0.6680	45.6	0.6570	38.5
0.8339	86.4	1.9100	73.0	1.0920	63.6	0.6840	53.7	0.9450	45.4	0.9270	38.3
1.2330	85.8	2.3000	72.2	1.7140	63.3	0.9440	53.3	1.3000	44.8	1.2800	37.7
1.6210	85.2	2.8000	71.2	1.9360	63.0	1.3700	52.2	1.904	44.6	1.8600	37.3

TABLE II  
(Continued)

Electrolyte	Solvent 1		Solvent 2		Solvent 3		Solvent 4		Solvent 5	
	$C \cdot 10^{-6}$	$\Lambda$	$C \cdot 10^{-6}$	$\Lambda$	$C \cdot 10^{-6}$	$\Lambda$	$C \cdot 10^{-6}$	$\Lambda$	$C \cdot 10^{-6}$	$\Lambda$
AgNO <sub>3</sub>	0.3610	187.7	0.3610	147.7	0.2647	119.9	0.4430	102.9	0.1831	106.6
	0.4410	184.8	0.4410	143.8	0.3955	112.8	0.7137	97.8	0.3633	91.9
	0.9610	172.5	0.9610	132.3	0.5252	108.3	0.8773	93.4	0.5408	99.2
	1.4440	163.2	1.4440	123.3	0.7180	101.7	1.0620	90.5	0.8017	96.0
	1.9360	156.3	1.9360	113.4	1.0340	94.5	1.3030	86.8	1.0570	91.6
	2.5000	149.2	2.5000	107.0	2.0250	76.0	2.5320	73.2	1.3880	88.5

TABLE III

Derived conductance parameters,  $\Lambda^\infty$  (S cm<sup>2</sup> mol<sup>-1</sup>) and  $K_A$  (m<sup>3</sup> mol<sup>-1</sup>) for Bu<sub>4</sub>NBPh<sub>4</sub>, at 25°C

Electrolyte	Solvent 1		Solvent 2		Solvent 3		Solvent 4		Solvent 5	
	$\Lambda_0$	$K_A$	$\Lambda_0$	$K_A$	$\Lambda_0$	$K_A$	$\Lambda_0$	$K_A$	$\Lambda_0$	$K_A$
Bu <sub>4</sub> NBPh <sub>4</sub>	130.0	—	107.3	—	92.3	—	80.6	—	68.8	—
Bu <sub>4</sub> NNO <sub>3</sub>	187.7	0.1	155.9	0.083	134.1	0.076	118.4	0.052	100.9	0.052
Bu <sub>4</sub> NI	183.1	0.08	154.3	0.055	135.7	0.049	116.4	0.029	101.5	—
NaBPh <sub>4</sub>	149.3	0.075	120.0	—	100.0	—	85.6	0.119	73.2	—
LiNO <sub>3</sub>	192.0	2.0	155.8	0.198	133.1	0.186	116.9	0.138	98.7	0.052
KI	195.3	0.065	164.1	0.046	143.6	0.032	123.8	0.022	108.7	—
AgNO <sub>3</sub>	209.8	3.46	170.2	1.7	141.2	0.758	125.2	0.586	107.2	0.2

0.45 nm with the addition of 20.0 mole % DMSO in pure Ac, while on the other hand, the corresponding  $r_i$  value of Ag<sup>+</sup> ion is obtained with the addition of 50.0 mole % Ac in pure DMSO. The  $r_i$  value of K<sup>+</sup> ion, however, does not change significantly with the solvent composition.

All these observations indicate that Li<sup>+</sup> ion is strongly preferentially solvated by DMSO over the entire solvent composition range of Ac + DMSO mixtures. Na<sup>+</sup> and Ag<sup>+</sup> ions are strongly preferentially solvated by DMSO in Ac rich region and weakly preferentially solvated by Ac in DMSO rich region of Ac + DMSO mixtures. K<sup>+</sup> ion does not show any preferential solvation in Ac + DMSO mixtures.

Similar results were obtained for Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup> and Ag<sup>+</sup> ions in DMF + Ac

TABLE II  
(Continued)

Solvent 6		Solvent 7		Solvent 8		Solvent 9		Solvent 10		Solvent 11	
$C \cdot 10^{-6}$	$A$	$C \cdot 10^{-6}$	$A$	$C \cdot 10^{-6}$	$A$	$C \cdot 10^{-6}$	$A$	$C \cdot 10^{-6}$	$A$	$C \cdot 10^{-6}$	$A$
0.4954	88.5	0.4313	79.0	0.2138	68.1	0.2372	60.0	0.3789	50.4	0.5828	39.8
0.9811	85.5	0.8542	75.8	0.4255	66.3	0.3500	59.6	0.7503	49.9	1.1540	38.3
1.4570	83.5	1.2690	74.3	0.8263	64.5	1.0070	58.4	1.1140	49.5	1.9900	36.5
2.1550	80.5	1.8760	71.3	1.2520	62.8	1.3890	57.8	1.6480	48.8	2.8030	35.3
2.8320	77.8	2.4660	69.1	1.8510	60.5	2.0530	57.1	2.1660	48.5	3.5920	34.1
3.7070	73.5	3.2270	66.6	2.4320	58.6	2.6990	56.1	2.8340	48.2	4.6110	32.8

TABLE III  
 $Bu_4NNO_3$ ,  $Bu_4NI$ ,  $NaBPh_4$ ,  $LiNO_3$ ,  $KI$  and  $AgNO_3$  in Ac, DMSO and Ac + DMSO mixtures

Solvent 6		Solvent 7		Solvent 8		Solvent 9		Solvent 10		Solvent 11	
$A_0$	$K_A$	$A_0$	$K_A$	$A_0$	$K_A$	$A_0$	$K_A$	$A_0$	$K_A$	$A_0$	$K_A$
56.2	—	49.2	—	39.9	—	33.2	—	27.6	—	22.3	—
89.3	0.012	76.1	—	63.7	—	55.3	—	47.4	—	38.7	—
82.8	0.074	75.8	0.030	60.2	0.060	52.4	—	43.7	—	36.1	—
59.6	0.152	52.0	—	42.1	0.047	35.0	—	29.3	—	24.4	—
87.7	—	74.4	—	60.9	—	53.6	—	46.5	—	38.2	—
88.9	0.014	80.6	—	64.4	—	56.0	—	46.7	—	39.1	—
94.8	0.103	82.3	0.104	69.2	0.096	60.0	0.024	51.1	0.015	43.0	—

mixtures. In DMSO + acetonitrile (AN) solvent mixtures<sup>5</sup>, on the other hand,  $Li^+$ ,  $Na^+$  and  $K^+$  ions have been found to be strongly preferentially solvated by DMSO through electrostatic ion-solvent interactions over the entire solvent composition range. Solvation of  $Ag^+$  ion which follows much the same pattern as that of alkali metal cations in DMSO rich region of DMSO + AN mixtures<sup>11</sup> has, however, been found to undergo selective solvation by AN through specific  $Ag^+$ -AN interaction in AN rich region of DMSO + AN solvent mixtures<sup>11</sup>. Since no such specific ion-solvent interaction is possible in Ac + DMSO mixtures, therefore, the interaction of  $Li^+$ ,  $Na^+$ ,  $K^+$  and  $Ag^+$  ions with DMSO and Ac solvent molecules in Ac + DMSO mixtures might be primarily electrostatic in nature.

Therefore, from the present investigation, it can be concluded that the exclusive electrostatic cationophilic character of DMSO in DMSO + AN mixtures is, however, competed by Ac in Ac + DMSO mixtures which probably be attributed to the localized negative charge on the Ac solvent dipole<sup>12</sup>.

On the contrary, the solvated radii of  $I^-$  and  $NO_3^-$  ions in Ac + DMSO mixtures are found to be virtually the same as in DMSO + AN (refs<sup>5,11</sup>), DMF + Ac (ref.<sup>1</sup>) and DMF + AN (ref.<sup>8</sup>) mixtures which demonstrates weak anion-solvent interaction. Anions are known to be poorly solvated in dipolar aprotic solvents<sup>4</sup>.

TABLE IV

A comparison of  $\Lambda^\infty$  ( $S\text{ cm}^2\text{ mol}^{-1}$ ) values for some electrolytes in Ac and DMSO from the present measurements with the literature values

Electrolyte	Ac		DMSO	
	$\Lambda^\infty$	Reference	$\Lambda^\infty$	Reference
$Bu_4NBPh_4$	130.0	present work	22.3	present work
	130.0	11	22.4	10
	132.5	1	22.2	10
$Bu_4NNO_3$	187.7	present work	38.7	present work
	187.1	12	38.6	10
			38.3	10
$NaBPh_4$	139.9	present work	24.4	present work
	140.1	13	24.5	5
			24.6	5
$LiNO_3$	191.5	present work	38.2	present work
	192.9	14	38.0	5
KI	196.4	present work	39.1	present work
	196.6	14	38.8	5
			38.2	15
$AgNO_3$	209.8	present work	43.2	present work
	211.0 <sup>a</sup>	—	43.1	10
			42.9	10
$Bu_4NI$	183.1	present work	36.1	present work
	184.4	13	36.0	5
			35.4	5

<sup>a</sup>  $\Lambda^\infty$  values obtained indirectly by addition i.e.  $\Lambda^\infty(AgNO_3) = \lambda_{Ag}^\infty$  (taken from ref.<sup>1</sup>) +  $\lambda_{NO_3}^\infty$  (taken from ref.<sup>12</sup>).



TABLE V

Limiting molar ionic conductivities  $\lambda_i^\infty$  ( $\text{S cm}^2 \text{mol}^{-1}$ ) and corresponding solvated radii  $r_i$  (nm) of some ions in Ac + DMSO mixed systems

Sol-vent	$\text{Li}^+$		$\text{Na}^+$		$\text{K}^+$		$\text{Ag}^+$		$\text{NO}_3^-$		$\text{I}^-$	
	$\lambda_i^\infty$	$r_i$	$\lambda_i^\infty$	$r_i$	$\lambda_i^\infty$	$r_i$	$\lambda_i^\infty$	$r_i$	$\lambda_i^\infty$	$r_i$	$\lambda_i^\infty$	$r_i$
1	71.6	·48	77.7	·45	79.1	·45	89.9	·41	119.9	·33	117.3	·34
	72.52 <sup>a</sup>		77.49 <sup>b</sup>		78.74 <sup>b</sup>		99.9 <sup>c</sup>		120.1 <sup>d</sup>		118.1 <sup>c</sup>	
2	55.4	·51	68.7	·46	65.8	·46	69.8	·44	100.4	·34	98.3	·34
3	47.2	·52	55.9	·46	56.1	·46	55.3	·45	85.9	·34	87.5	·34
4	40.0	·53	46.5	·47	48.9	·45	48.3	·45	76.9	·34	74.9	·34
5	33.8	·53	40.4	·47	43.2	·45	42.3	·45	64.9	·34	65.5	·34
6	27.8	·54	32.8	·48	35.5	·45	34.9	·45	59.9	·32	53.4	·34
7	24.0	·55	28.5	·48	30.5	·46	31.9	·44	50.4	·33	50.1	·33
8	19.1	·55	23.1	·48	25.1	·45	26.4	·43	42.8	·32	39.3	·34
9	15.7	·55	19.2	·48	21.0	·45	22.1	·44	37.9	·32	35.0	·33
10	13.6	·54	16.2	·47	17.5	·45	18.2	·44	32.9	·31	29.2	·33
11	11.2	·54	13.8	·46	14.7	·44	16.0	·42	27.0	·31	24.4	·33
	11.0 <sup>e</sup>		14.0 <sup>e</sup>		14.5 <sup>e</sup>		16.15 <sup>f</sup>		26.97 <sup>f</sup>		24.3 <sup>f</sup>	

<sup>a</sup> Ref.<sup>16</sup>; <sup>b</sup> ref.<sup>13</sup>; <sup>c</sup> ref.<sup>1</sup>; <sup>d</sup> ref.<sup>12</sup>; <sup>e</sup> ref.<sup>5</sup>; <sup>f</sup> ref.<sup>10</sup>.

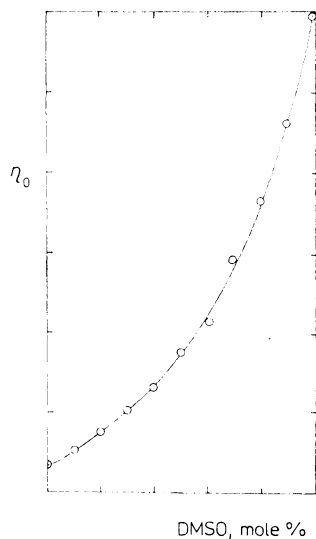


FIG. 1

Plot of viscosity ( $\eta_0$ ) vs mole % DMSO in Ac-DMSO mixtures at 25°C

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