TRANSPORT BEHAVIOUR OF IONS IN *N*,*N*-DIMETHYLFORMAMIDE AND DIMETHYL SULFOXIDE AT DIFFERENT TEMPERATURES. CONDUCTANCE STUDIES

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Molar conductivities of Bu_4NBPh_4, $BuNNO_3$, $LiNO_3$, $NaNO_3$, KNO_3 and $AgNO_3$ have been reported in pure DMF and DMSO in the temperature range from 20 to 45 °C. The conductance data have been analyzed in terms of limiting molar conductivity Λ_0 and ion-association constant K_A. Separation of Λ_0 into ionic components λ_i^0 has been carried out on the basis of Bu_4NBPh_4 assumption in order to calculate the effective ionic radii r_i in DMF and DMSO. Examination of r_i values of K^+ and Ag^+ ions as a function of temperature revealed some specific interactions of Ag^+ ion with DMF and DMSO. In DMSO electrostatic ion–dipole interaction of Li^+, Na^+ and K^+ ions is found to be somewhat modified due to dipole–dipole interaction.

In dipolar aprotic solvents, solvation of small closed electron-shell cations like Na^+ or K^+ is attributed to electrostatic effects[1]. Solvation of Ag^+ ion, a transition metal cation of d^{10} electronic structure, is, however, also described in terms of specific interactions with electron donors like *N*,*N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), acetonitrile (AN), *N*-methylpyrrolidine (NMPy), formamide and hexamethylphosphotriamide (HMPT). Since crystallographic radius of Ag^+ ion[2] (0.126 nm) is fairly close to that of K^+ ion[2] (0.133 nm), the specific interactions of Ag^+ ion reinforce its electrostatic interaction. Ion–solvent interaction of Ag^+ ion in such solvents is thus expected to be stronger than that of K^+ ion.

It is, therefore, interesting to extend these considerations to a solvation study of ions with special reference to K^+ and Ag^+ ions in pure DMF and DMSO in temperature range of 20 to 45 °C using conductance measurements. The choice of different temperatures have been made in order to facilitate the possible difference of ion solvation with regard to the specific interactions.

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EXPERIMENTAL

Solvents

DMF and DMSO (AR grade) were purified as described earlier[3]. The middle fractions of distilled DMF and DMSO of specific conductance in the range of 1 – 7 . 10^{-8} S cm^{-1} were collected and stored with pre-dried 4 Å molecular sieves.

Salts

Lithium nitrate, sodium nitrate and potassium nitrate, all AR grade, were dried under vacuum for about 36 h at 100 – 150 °C, while silver nitrate (Merck) was dried under vacuum for about 24 h before use. Pure samples of tetrabutylammonium nitrate (Bu_4NNO_3) and tetrabutylammonium tetraphenylborate (Bu_4NBPh_4) were synthesized as suggested by Fuoss et al.[4,5] and kept under vacuum for 2 – 3 days before use.

Conductance Measurements

The concuctivity of electrolyte solutions were measured at 1 kHz with a digital conductivitymeter type NDC-732 (Naina Electronics) in two conductivity cells with the cell constants of 0.568 and 0.268 cm^{-1}, respectively. Cell constants at 25 °C were determined with aqueous potassium chloride solution in the concentration range of (5 – 100) . 10^{-4} mol l^{-1} using the method proposed by Fuoss et al.[6]. The conductivity cells with bright platinum electrodes were similar in design as cells used by Shedlovsky[7]. The conductivity measurements were carried out in a water thermostat (MLW-Baureihe U7C) with the accuracy of ±0.05 °C. The precision of conductivity data was found to be within ±0.2%.

Viscosity, Density and Dielectric Constant Measurements

Viscosity measurements were carried out in a water thermostat with accuracy of ±0.1 °C using a calibrated Ubbelohde suspended bulb viscometer. The precision of efflux times was ±0.2 s. Overall accuracy of viscosity measurements was found to be ±0.1%.

Density measurements were made in a water thermostat with the accuracy of ±0.05 °C using two different calibrated sealable pycnometers of capacity 20 and 25 ml. The average value of 4 – 5 readings at each temperature is reported. Overall accuracy of density measurements was estimated to be ±0.1%.

The dielectric constants of pure DMF and DMSO in range of temperatures from 20 to 45 °C were obtained by interpolation using data for DMF reported by Leader and Gomley[8], and for DMSO by Yao and Bennion[9].

RESULTS AND DISCUSSION

Molar concentration, C and corresponding molar conductivity, Λ of Bu_4NBPh_4, Bu_4NNO_3, $LiNO_3$, $NaNO_3$, KNO_3 and $AgNO_3$ in pure DMF and DMSO at 20, 25, 30, 35, 40 and 45 °C have been reported in Table I and Table II, respectively. The analysis of conductivity data in terms of limiting molar conductivity Λ_0 and ion-association constant K_A of electrolyte have been carried out iteratively according to the Shedlovsky equation[10,11] by the least squares treatment. Dielectric constant D and viscosity η_0 used

Table I
Molar concentration, C (mol l $^{-1}$) and the corresponding molar conductivity Λ (S cm^2 mol^{-1}) of some electrolytes in DMF at different temperatures

20 °C		25 °C		30 °C		35 °C		40 °C		45 °C	
$C \,.\, 10^4$	Λ	$C \,.\, 10^4$	Λ	$C \,.\, 10^4$	Λ	$C \,.\, 10^4$	Λ	$C \,.\, 10^4$	Λ	$C \,.\, 10^4$	Λ
					Bu_4NBPh_4						
5.17	46.5	5.806	49.7	5.17	52.3	4.80	56.4	8.210	58.2	5.170	62.4
10.21	45.1	11.50	47.6	10.21	51.1	9.50	55.1	12.20	57.5	12.20	60.7
15.14	44.6	17.96	46.4	15.14	50.1	15.26	54.3	15.14	57.0	18.03	60.1
20.89	43.8	25.25	45.6	20.89	49.0	20.88	53.9	26.48	55.4	20.89	59.6
29.22	43.0	33.19	44.6	29.22	48.2	27.44	53.0	29.22	54.6	26.48	58.9
31.92	42.5	43.44	43.8	31.92	48.0	25.91	52.2	35.46	54.1	31.92	58.2
35.46	42.4	53.31	42.9	38.07	47.3	44.08	51.5	38.07	53.8	35.46	57.6
38.07	42.0	57.00	42.4	44.04	46.9	48.09	51.1	44.04	53.1	44.04	57.2
					Bu_4NNO_3						
4.87	74.0	4.87	81.4	4.87	85.0	4.87	85.9	4.87	90.6	4.87	95.1
7.13	73.1	9.67	79.6	9.67	82.5	9.87	83.4	9.67	87.8	9.67	92.2
10.54	72.0	14.39	78.2	14.39	80.6	14.39	81.4	14.39	85.6	14.39	89.8
13.85	70.9	21.34	76.7	21.34	78.7	21.34	79.2	21.34	83.1	21.34	87.2
17.07	69.9	28.12	75.3	28.12	76.8	28.12	77.1	28.12	80.9	28.12	85.1
20.72	68.7	34.76	74.1	34.76	75.4	34.76	75.8	34.76	79.0	34.76	83.0
31.92	66.4	42.31	73.1	42.39	73.7	42.39	74.0	42.39	77.2	42.39	81.1
40.79	65.1	49.66	71.9	49.66	72.0	49.66	72.4	49.66	75.5	49.66	79.3
					$NaNO_3$						
5.87	76.9	4.84	8.12	4.84	86.1	4.84	91.2	4.84	96.4	4.84	102.9
11.53	74.7	10.00	78.5	10.00	83.5	10.00	88.0	10.00	93.00	10.00	99.0
17.13	73.2	14.89	76.7	14.89	81.6	14.89	85.6	14.89	90.5	14.89	96.2
25.33	71.4	22.08	74.8	22.08	79.4	22.08	83.1	22.08	87.3	22.08	92.7
33.30	69.9	29.10	72.8	29.10	77.7	29.10	80.9	29.10	85.0	29.10	90.4
41.04	67.7	35.96	71.2	35.96	75.9	35.96	78.9	35.96	82.9	35.96	87.8
49.80	66.6	43.77	69.8	43.77	74.1	43.77	77.1	43.77	81.1	43.77	85.5
58.29	65.3	51.38	68.4	51.38	72.6	51.38	75.3	51.38	79.2	51.38	83.6

TABLE I
(*Continued*)

20 °C		25 °C		30 °C		35 °C		40 °C		45 °C	
$C \cdot 10^4$	Λ	$C \cdot 10^4$	Λ	$C \cdot 10^4$	Λ	$C \cdot 10^4$	Λ	$C \cdot 10^4$	Λ	$C \cdot 10^4$	Λ
					KNO_3						
4.71	79.4	4.71	84.5	4.71	89.7	4.71	93.6	4.71	100.2	4.71	105.4
9.97	77.3	9.97	82.3	9.97	87.5	9.97	91.3	9.97	97.3	9.97	102.3
14.81	76.1	14.81	80.9	14.81	85.6	14.81	89.8	14.81	95.6	14.81	100.3
21.89	74.2	21.89	79.4	21.89	83.7	21.89	87.7	21.89	93.1	21.89	97.5
28.78	72.5	28.78	77.6	28.78	82.2	28.78	85.9	28.78	90.9	28.78	95.1
35.47	71.4	35.47	76.2	35.47	80.7	35.47	84.4	35.47	89.4	35.47	93.1
43.05	70.0	43.05	75.0	43.05	79.1	43.05	82.7	43.05	87.5	43.05	91.1
50.38	69.3	50.38	73.8	50.38	77.8	50.38	81.4	50.38	86.1	50.38	89.6
					$AgNO_3$						
4.93	74.8	4.93	77.7	3.71	83.7	3.71	89.0	3.71	93.4	3.71	97.3
9.79	70.0	9.79	74.6	7.37	78.4	7.37	82.8	7.37	87.0	7.37	90.5
14.57	64.2	14.57	70.7	10.99	74.6	10.99	78.8	10.99	83.1	10.99	85.6
21.60	59.4	21.60	67.1	14.57	71.0	14.57	75.4	14.57	78.7	14.57	82.2
28.47	55.2	28.47	63.4	19.28	66.5	19.28	70.1	19.28	73.8	19.28	76.7
35.19	51.3	35.19	60.0	23.91	63.3	23.91	66.1	23.91	69.8	23.91	72.6
42.83	47.3	42.83	56.4	29.60	59.6	29.60	62.7	29.60	66.4	29.60	68.5
50.28	44.4	50.28	53.2	35.19	56.5	35.19	59.4	35.19	62.7	35.19	65.1

for the analysis of the presented conductivity data are reported in Table III. The values of Λ_0 and K_A obtained for various electrolytes have been reported in Table IV.

Except for Bu_4NBPh_4 and $AgNO_3$ in DMF at 25 °C, the Λ_0 values for rest of the electrolytes reported in Table IV were in good agreement with literature.

Limiting Ionic Conductivity λ_i^0 and Effective Ionic Radii, r_i in DMF and DMSO

Separation of limiting molar conductivity Λ_0 into limiting ionic conductivity λ_i^0 has been achieved on the basis of Bu_4NBPh_4 assumption[12] using Eqs (*1*) and (*2*),

TABLE II
Molar concentration, C (mol l^{-1}) and the corresponding molar conductivity Λ (S cm^2 mol^{-1}) of some electrolytes in DMSO at different temperatures

20 °C		25 °C		30 °C		35 °C		40 °C		45 °C	
$C \cdot 10^4$	Λ	$C \cdot 10^4$	Λ	$C \cdot 10^4$	Λ	$C \cdot 10^4$	Λ	$C \cdot 10^4$	Λ	$C \cdot 10^4$	Λ
Bu_4NBPh_4											
5.07	20.2	4.62	22.2	5.07	24.5	4.66	26.7	8.06	29.0	5.07	32.1
10.02	19.5	9.15	21.8	10.02	24.0	9.23	26.0	10.02	28.7	10.02	31.1
14.85	19.2	13.59	21.5	13.90	23.7	13.71	25.5	14.85	27.9	14.85	30.2
20.50	18.7	20.09	21.2	17.69	23.2	20.26	24.9	17.70	27.5	17.70	29.6
25.99	18.5	26.42	20.8	21.42	23.0	26.69	24.5	25.99	26.8	20.50	29.5
31.32	18.3	34.57	20.2	26.89	22.9	34.86	24.0	31.32	26.4	23.26	29.1
34.80	18.2	42.42	20.0	32.20	22.7	42.78	23.6	34.80	26.0	28.67	28.7
40.73	17.9	47.45	19.9	44.03	21.8	47.53	23.5	40.73	25.6	37.36	28.1
Bu_4NNO_3											
4.87	33.4	4.87	37.5	4.87	41.3	4.87	45.1	4.87	47.0	4.87	51.3
9.55	33.0	9.67	37.0	9.67	40.7	9.67	44.2	9.67	46.3	9.67	50.6
14.18	32.1	14.39	36.5	14.39	40.2	14.39	43.5	14.39	45.6	14.39	50.1
20.96	31.4	21.34	35.9	21.34	39.6	21.34	42.6	21.34	45.0	21.34	49.5
27.56	30.8	28.12	35.4	28.12	39.2	28.12	42.0	28.12	44.6	28.12	48.9
33.56	30.5	34.76	34.9	34.76	39.0	34.76	41.5	34.76	44.0	34.76	48.5
41.22	30.0	42.36	34.5	42.31	38.6	42.31	41.0	42.31	43.6	42.31	48.0
48.25	29.4	49.66	34.2	49.66	38.3	49.66	40.5	49.66	43.2	49.66	47.5
$LiNO_3$											
4.51	33.8	5.25	36.7	5.25	40.8	4.51	44.4	4.51	49.0	4.51	51.6
8.98	33.5	10.41	36.5	10.41	40.3	8.98	43.8	8.98	48.2	8.98	51.1
15.59	33.0	15.50	36.1	15.50	39.9	15.50	43.2	15.50	47.4	15.50	50.7
22.12	32.6	22.97	35.8	22.97	39.5	22.97	42.7	22.97	46.7	22.97	50.2
30.66	32.3	30.28	35.3	30.28	39.1	30.28	42.2	30.28	46.0	30.28	49.7
39.05	31.8	37.42	35.0	37.42	38.7	37.42	41.8	37.42	45.5	37.42	49.1
49.30	31.6	45.55	34.9	45.55	38.5	45.55	41.5	45.55	45.0	45.55	48.8
59.32	31.1	53.48	34.6	53.48	38.0	53.48	41.1	53.48	44.4	53.48	48.2

TABLE II
(*Continued*)

20 °C		25 °C		30 °C		35 °C		40 °C		45 °C	
$C . 10^4$	Λ	$C . 10^4$	Λ	$C . 10^4$	Λ	$C . 10^4$	Λ	$C . 10^4$	Λ	$C . 10^4$	Λ
$NaNO_3$											
5.82	37.5	4.99	39.1	4.99	43.6	4.99	47.6	4.99	49.7	4.99	54.1
11.53	37.0	9.91	38.1	9.91	42.9	9.91	46.7	9.91	48.6	9.91	52.6
17.13	36.4	14.74	37.4	14.74	42.3	14.74	45.9	14.74	47.8	14.74	51.7
25.33	35.8	21.86	36.7	21.86	41.5	21.86	45.1	21.86	46.8	21.86	50.3
33.30	35.1	28.81	36.0	28.81	41.0	28.81	44.4	28.81	45.9	28.81	49.5
41.04	33.0	35.60	35.5	35.60	40.5	35.60	43.8	35.60	45.1	35.60	48.7
49.80	32.5	43.34	35.1	43.34	39.8	43.34	43.2	43.34	44.4	43.34	47.7
58.29	32.2	50.88	34.6	50.88	39.3	50.88	42.5	50.88	43.7	50.88	46.9
KNO_3											
5.04	37.6	4.92	40.3	4.92	44.5	4.92	48.5	4.92	52.5	4.92	56.6
9.99	37.0	9.75	39.8	9.75	43.8	9.75	47.8	9.75	51.8	9.75	56.0
14.84	36.8	14.52	39.4	14.52	43.2	14.52	47.2	14.52	51.1	14.52	55.0
21.94	36.4	21.52	38.8	21.52	42.6	21.52	46.6	21.52	50.4	21.52	54.2
28.83	36.2	28.37	38.4	28.37	42.1	28.37	46.0	28.37	49.9	28.37	53.5
35.54	34.9	35.06	38.0	35.06	41.6	35.06	45.6	35.06	49.3	35.06	53.0
43.13	34.7	42.68	37.6	42.68	41.1	42.68	45.1	42.68	48.8	42.68	52.2
50.48	34.4	50.10	37.3	50.10	40.7	50.10	44.7	50.10	48.4	50.10	52.0
$AgNO_3$											
4.99	37.5	4.99	41.8	4.99	45.4	4.99	49.8	4.99	52.7	4.99	56.8
4.90	36.9	9.90	41.2	9.90	44.6	9.90	49.0	9.90	51.6	9.90	55.8
14.74	36.4	14.74	40.5	14.74	44.1	14.74	48.3	14.74	50.7	14.74	55.1
21.85	35.8	21.85	39.9	21.85	43.2	21.85	47.4	21.85	49.9	21.85	54.4
28.80	35.3	28.80	39.4	28.80	42.6	28.80	46.8	28.80	49.2	28.80	53.3
35.59	34.9	35.59	39.0	35.59	42.1	35.59	46.2	35.59	48.7	35.59	52.5
43.32	34.4	43.32	38.4	43.32	41.6	43.32	45.7	43.32	47.9	43.32	51.8
50.85	34.0	50.85	38.0	50.85	41.1	50.85	45.1	50.85	47.2	50.85	51.2

$$\frac{\lambda^0_{\mathrm{Bu_4N^+}}}{\lambda^0_{\mathrm{Ph_4B^-}}} = \frac{0.535-(0.0103\,D+r_\mathrm{y})}{0.500-(0.0703\,D+r_\mathrm{y})} \tag{1}$$

$$\Lambda_0(\mathrm{Bu_4NBPh_4}) = \lambda^0_{\mathrm{Bu_4N^+}} + \lambda^0_{\mathrm{Ph_4B^-}}\ , \tag{2}$$

where 0.535 and 0.500 are the crystallographic radii of Ph_4B^- and Bu_4N^+ ions, respectively, D is the dielectric constant of the solvent and r_y is an adjustable parameter taken to be equal to 0.085 nm for DMF and 0.113 nm for DMSO (ref.[12]). The values of Ph_4B^- and Bu_4N^+ ions in DMF and DMSO in the range of temperature between 20 and 45 °C have been reported in Table V.

The λ_i^0 values of Li^+, Na^+, K^+, Ag^+ and NO_3^- ions shown in Table V were then obtained from the Λ_0 values (Table IV) using Kohlrausch's law of independent limiting ionic conductivity. The λ_i^0 values for NO_3^- ion in DMF for temperatures from 20 to 40 °C were determined by Gill and Bakshi[13] and are reported in Table V, as well as λ_i^0 values for Na^+ ion in DMSO in temperature range of 25 to 45 °C, determined by Yao and Bennion[9]. A good agreement between these two sets of λ_i^0 values for NO_3^- and Na^+ ions at different temperatures indicate the accuracy of the presented conductivity data.

Using λ_i^0 values for Li^+, Na^+, K^+, Ag^+, Ph_4B^-, NO_3^- and Bu_4N^+ ions from Table V, the effective ionic radii r_i in DMF and DMSO are calculated by Eq. (*3*).

TABLE III
Viscosity η_0 (kg m^{-1} S^{-1}), dielectric constant D, and density d (kg m^{-3}) of DMF and DMSO at different temperatures

Temperature °C	DMF			DMSO		
	$\eta_0 \cdot 10^3$	D^a	$d \cdot 10^{-3}$	$\eta_0 \cdot 10^3$	D^a	$d \cdot 10^{-3}$
20	0.849	37.7	0.9483	2.215	47.2	1.1012
25	0.802	36.7	0.9435	1.996	46.4	1.0949
30	0.755	35.9	0.9394	1.803	45.6	1.0914
35	0.710	35.1	0.9344	1.645	44.7	1.0846
40	0.669	34.4	0.9300	1.488	44.1	1.0800
45	0.633	33.4	0.9252	1.385	43.3	1.0758

[a] Interpolated using data from ref.[8] for DMF and from ref.[9] for DMSO.

TABLE IV
Molar conductivity Λ_0 (S cm^2 mol^{-1}) and ion-association constant K_A (l mol^{-1}) for electrolytes in DMF and DMSO at different temperatures

Electrolyte	20 °C		25 °C		30 °C		35 °C		40 °C		45 °C	
	Λ_0	K_A	Λ_0	K_A	Λ_0	K_A	Λ_0	K_A	Λ_0	K_A	Λ_0	K_A
DMF												
Bu_4NBPh_4	49.2	–	52.2 (50.7)[a]	–	55.4	–	59.0	–	62.8	–	66.2	–
Bu_4NNO_3	79.1	12	83.0 (82.6)[a]	23	87.1	33	92.2	36	97.2	43	102.1	45
$LiNO_3$	78.0	11	82.0 (82.3)[b]	20	86.2	27	92.2	29	104.0	31	110.1	31
$NaNO_3$	82.1	29	87.5 (87.2)[b]	31	91.1	36	97.3	37	103.3	38	110.2	44
KNO_3	83.3	15	88.5 (88.1)[b]	24	94.2	29	99.0	29	106.0	30	111.9	34
$AgNO_3$	87.3	230	91.3 (89.3)[a]	235	96.0	238	101.6	238	106.9	245	111.6	245
DMSO												
Bu_4NBPh_4	20.9	–	23.3 (22.24)[c]	–	25.7	–	28.2 (27.7)[e]	21	31.1	22	33.5	23
Bu_4NNO_3	34.8	–	38.5 (38.7)[d]	13	42.3	13	46.5	14	48.6	14	53.0	15
$LiNO_3$	34.2	–	37.8 (38.2)[d]	10	41.7	12	45.8	13	50.5	16	52.5	18
$NaNO_3$	36.8	17	40.7 (40.8)[b]	21	45.0	21	49.5	22	52.0	23	56.6	27
KNO_3	38.0	11	41.2 (41.5)[b]	14	45.5	17	49.8	18	53.8	19	58.4	20
$AgNO_3$	38.7	–	43.1 (43.2)[d]	–	47.0	–	51.5	14	54.6	14	59.1	16

[a] Ref.[17]; [b] ref.[18]; [c] ref.[19]; [d] ref.[20]; [e] ref.[21].

TABLE V
The λ_i^0 (S cm^2 mol^{-1}) values for ions in DMF and DMSO at different temperatures (°C)

Ion	DMF						DMSO					
	20	25	30	35	40	45	20	25	30	35	40	45
Li^+	24.2	26.8	30.9	35.2	39.6	42.5	10.4	11.5	12.9	14.1	15.5	17.1
Na^+	28.7	31.0	32.9	35.9	38.9	42.6	13.0	14.4 (14.34)[a]	16.2	17.8 (17.43)[a]	19.7	21.1 (20.67)[a]
K^+	29.9	32.8	36.0	37.6	41.6	44.3	13.4	14.8	16.7	18.1	21.5	23.0
Ag^+	33.9	35.6	37.8	40.2	42.5	44.0	14.9	16.8	18.2	19.8	22.3	23.7
NO_3^-	53.4 (52.6)[b]	55.7 (55.4)[b]	58.2 (59.1)[b]	61.4 (62.8)[b]	64.4 (65.0)[b]	67.6	23.8	26.3	28.8	31.7	32.2	35.4
Bu_4N^+	25.7	27.3	28.9	30.8	32.8	34.5	11.0	12.2	13.5	14.8	16.3	17.6
Ph_4B^-	23.5	24.9	26.5	28.2	30.0	31.7	9.9	11.1	12.2	13.4	14.8	15.9

[a] Ref.[9]; [b] ref.[13].

TABLE VI
The r_i (nm) values for ions in DMF and DMSO at different temperatures (°C)

Ion	DMF						DMSO					
	20	25	30	35	40	45	20	25	30	35	40	45
Li^+	0.50	0.50	0.47	0.45	0.43	0.43	0.52	0.52	0.52	0.51	0.51	0.50
Na^+	0.46	0.45	0.45	0.44	0.44	0.42	0.45	0.45	0.44	0.44	0.44	0.44
K^+	0.45	0.43	0.43	0.43	0.42	0.41	0.44	0.44	0.44	0.43	0.44	0.43
Ag^+	0.41	0.41	0.41	0.41	0.41	0.41	0.41	0.41	0.41	0.41	0.41	0.41

$$r_i = 0.82/\lambda_i^0\,\eta_0 + (0.0103\,D + r_y) \qquad (3)$$

Equation (*3*) is an empirical modification of the Stokes' law suggested by Gill[14] to obtain the effective ionic radii in non-aqueous solvents by addition of a term proportional to dielectric constant D of the solvent. The r_i values for Li^+, Na^+, K^+ and Ag^+ ions are reported in Table VI.

Solvation of Li^+, Na^+, K^+ and Ag^+ Ions in DMF and DMSO

The crystallographic radii of Li^+, Na^+, K^+ and Ag^+ ions are equal to 0.06, 0.095, 0.133 and 0.126 nm, respectively[2]. They decrease in the order $K^+ > Ag^+ > Na^+ > Li^+$. From simple electrostatic considerations it is, therefore, expected that the effective ionic radii r_i of these ions in DMF and DMSO should decrease in the order $Li^+ > Na^+ > Ag^+ > K^+$. However, a pursual of Table VI indicates that at all temperatures the r_i values of these ions decrease in the order: $Li^+ > Na^+ \approx K^+ > Ag^+$ contrary to expectations.

Another striking feature of Table VI is that the r_i value of Ag^+ ion, equal to 0.41 nm, is independent on temperature in both DMF and DMSO. Similarly r_i values of Li^+ ion (≈ 0.51 nm) Na^+ and K^+ ions (≈ 0.44 nm) were found to be independent on temperature in DMSO. In DMF, however, r_i values of Li^+, Na^+ and K^+ ions decrease with rising temperature.

If we take an account of free energy of solvation, $\Delta G_S(M^+)$ of K^+ and Ag^+ ions in DMF and DMSO ($\Delta G_S(K^+) = -82.8$ kcal/g ion* in DMF and −83.5 kcal/g ion in DMSO, ref.[15]) and free energy of transfer $\Delta G_{tr}(M^+)$ of K^+ ion from water to DMF and DMSO ($\Delta G_{tr}(K^+) = -2.2$ kcal/g ion in DMF and −2.5 kcal/g ion in DMSO, ref.[15]) one finds that K^+ ion follows the same pattern of solvation in both DMF and DMSO. It is therefore interesting to note that like Ag^+ ion, r_i value of K^+ ion is independent on temperature in DMSO.

Parker et al.[15] have shown that the solvents which solvate cations through oxygen, the main factors influencing solvation of K^+ and Ag^+ ions are primarily of electrostatic nature modified by structural effects due to the solvent–solvent interaction. Since there is an evidence for molecular association in DMSO due to the dipole–dipole interaction[1], constant r_i value of K^+ ion in DMSO thus supports this conjecture. Similar arguments holds with respect to constant r_i for Li^+ and Na^+ in DMSO.

From free energy of solvation, $\Delta G_S(M^+)$ for Ag^+ ion in DMF and DMSO ($\Delta G_S(Ag^+) = -118.6$ kcal/gramion in DMF and −122.5 kcal/gramion in DMSO, ref.[15]) and that of

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* 1 kcal = 4.184 kJ.

K^+ ion as reported above, it is further evident that Ag^+ ion, as compared to K^+ ion, is much more solvated by DMF and DMSO. Moreover, a comparison of $\Delta G_{tr}(M^+)$ for K^+ ion with Ag^+ ion from water to dimethylthioformamide (SDMF), DMSO and HMPT indicate some specific interactions of Ag^+ ion but not of K^+ ion with these solvents[15]. Constant r_i value of Ag^+ ion in DMF and DMSO over the entire temperature range reported in Table VI appears to indicate that in addition to electrostatic effects, Ag^+ ion undergoes some specific interactions with DMF and DMSO.

Now, turning to the effective ionic radii of NO_3^-, Bu_4N^+ and Ph_4B^- ions, it has been found that their r_i values in DMF and DMSO are equal to ≈ 0.32 nm, ≈ 0.50 nm and ≈ 0.53 nm, respectively, in the temperature range of 20 to 45 °C. Moreover, these values have been found to be very close to their crystallographic size[9,12]. It can be therefore concluded that these ions are unsolvated in DMF and DMSO. Anions and large ions are known to be unsolvated in dipolar aprotic solvents[1,16].

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