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Viscosity Studies on Lithium Bromide in Water + Dimethyl Sulfoxide Mixtures at 278.15 K and 293.15 K

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Viscosities of dilute solutions of lithium bromide in binary mixtures of water + dimethyl sulfoxide (DMSO) have been measured in the composition range 0−85 mass % DMSO at 278.15 K and 0−100 mass % DMSO at 293.15 K. The viscosity data have been analyzed by the Jones−Dole equation. The viscosity *B* coefficients of LiBr are positive at both temperatures in the whole composition range of the mixed solvent. The ion−solvent interactions have been discussed.

1. Introduction

Viscosimetric measurements of electrolyte solutions have been widely used in order to obtain information regarding solute−solvent interactions. While ion−solvent interactions have been studied in water and some organic solvents, less consideration has been given to such effects in solvent mixtures. For such studies, the solvent mixture of water + DMSO has special importance because of the wide use of DMSO and its aqueous solutions as solvents and reaction media.[1] Also, this solvent mixture is of extreme interest from the point of view of their structural properties. Extensive studies of the physical properties of the binary system water (1) + DMSO (2) have been made to investigate the changes which occur in the molecular structure and motion of the liquid as a function of the composition. At ambient pressure, DMSO exists in the liquid state over a wide temperature range (T_f = 18 °C and T_b = 189 °C) and is completely miscible with water. The high boiling temperature has been attributed to the large dipole moment of the DMSO molecule (μ = 3.90 D at 25 °C). In the strongly polar S═O bond, oxygen is the most electronegative site of DMSO. Dipole or ionic interactions are responsible for self-association DMSO molecules. Acting as a proton acceptor, it can alter the structure of water. From thermodynamic considerations, Lindberg[2] has argued that the water−DMSO hydrogen bond is stronger than the water−water hydrogen bond. Results of neutron inelastic scattering (NIS) and X-ray[3] diffraction techniques show that small quantities of DMSO ($x_2 \leq 0.1$) added to water produce a cooperative ordering of water molecules, increasing the long-range structure of water. At higher concentrations of DMSO, the NIS, infrared spectroscopy, and X-ray results show that the water structure is broken down by the increased formation of hydrogen-bonded DMSO−water complexes.

On the other hand, infrared spectroscopy[4] as well as density[5] measurements, shows that small quantities of DMSO have little effect on the water structure. Other methods[6,7] even lead to the conclusion that small amounts of DMSO act as a "stucture breaker" in water. The dielectric spectra[8] of water (1) + DMSO (2) mixtures showed two maxima (one each on the water rich region and DMSO rich region) in the distribution of relaxation times against concentration and a minimum around x_2 = 0.33, indicating more homogeneity around this mole fraction. The existence of stoichiometrically well-defined hydrogen-bonded DMSO−water aggregates is suggested thereby.

Table 1. Densities (*ρ*) and Viscosities (*η*) of Water (1) + DMSO (2) Mixtures at 278.15 K and 293.15 K

	T = 278.15 K		*T* = 293.15 K	
100w_2	*ρ*/g·cm^{-3}	*η*/mPa·s	*ρ*/g·cm^{-3}	*η*/mPa·s
0.00	0.999 96	1.524	0.998 20	0.999
2.50	1.003 32	1.589	1.001 32	1.053
5.00	1.006 89	1.727	1.004 52	1.112
10.00	1.014 31	1.948	1.011 20	1.264
14.97	1.022 00	2.178	1.018 20	1.402
18.15	1.027 27	2.354	1.022 83	1.515
20.00	1.030 38	2.463	1.025 53	1.559
30.00	1.047 50	3.203	1.040 96	2.009
40.00	1.065 05	4.230	1.056 62	2.589
42.75	1.070 15	4.625	1.061 69	2.743
50.00	1.082 53	5.570	1.072 40	3.319
65.00	1.104 44	7.330	1.092 33	4.296
70.00	1.109 25	7.326	1.096 70	4.385
78.00	1.115 47	6.666	1.102 16	4.091
85.00	1.117 61	5.450	1.103 81	3.498
89.00	1.117 88	4.904	1.103 71	3.211
93.00	1.117 48	4.035	1.102 91	2.743
96.00	1.117 02	3.630	1.102 12	2.514
100.00			1.100 41	2.194
			1.100 40[a]	2.216[a]

[a] Reference 31.

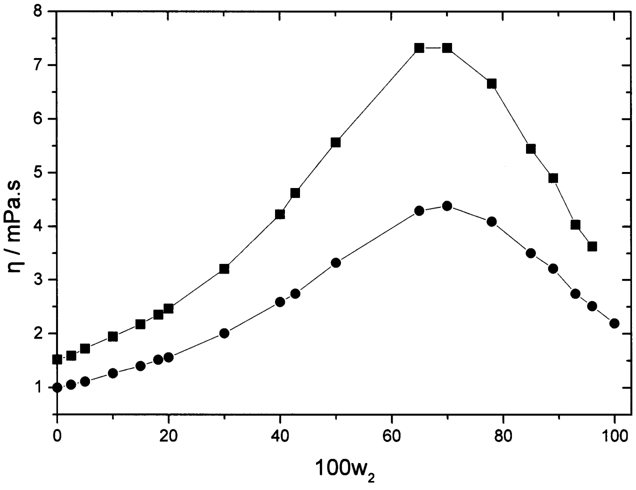

Figure 1. Viscosity of water (1) + DMSO (2) mixtures: ■, 278.15 K; ●, 293.15 K.

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Table 2. Experimental Densities (ρ) and Viscosities (η) of LiBr in Water (1) + DMSO (2) Mixtures at 278.15 K and 293.15 K

c/mol·dm^{-3}	ρ/g·cm^{-3}	η/mPa·s	c/mol·dm^{-3}	ρ/g·cm^{-3}	η/mPa·s
278.15 K					
$100w_2 = 0.00$					
0.0098	1.000 60	1.500	0.0453	1.002 86	1.506
0.0146	1.000 91	1.501	0.0543	1.003 45	1.507
0.0199	1.001 25	1.502	0.0802	1.005 07	1.511
0.0280	1.001 75	1.503	0.0996	1.006 36	1.514
0.0350	1.002 20	1.504	0.1222	1.007 81	1.516
$100w_2 = 2.50$					
0.0149	1.004 28	1.592	0.0558	1.006 90	1.599
0.0235	1.004 83	1.594	0.0808	1.008 48	1.603
0.0284	1.005 24	1.595	0.1018	1.009 82	1.606
0.0350	1.005 65	1.596	0.1176	1.010 84	1.609
0.0456	1.006 24	1.598			
$100w_2 = 5.00$					
0.0186	1.008 07	1.718	0.0749	1.011 63	1.730
0.0257	1.008 53	1.720	0.0955	1.012 95	1.733
0.0316	1.008 92	1.721	0.1207	1.014 49	1.738
0.0484	1.009 97	1.724			
$100w_2 = 10.00$					
0.0050	1.014 64	1.949	0.0320	1.016 32	1.954
0.0104	1.014 96	1.950	0.0364	1.016 59	1.955
0.0137	1.015 19	1.951	0.0445	1.017 12	1.957
0.0172	1.015 41	1.952	0.0508	1.017 49	1.958
0.0265	1.015 99	1.953	0.1062	1.020 90	1.969
$100w_2 = 15.00$					
0.0154	1.022 96	2.181	0.0809	1.026 41	2.198
0.0207	1.023 17	2.184	0.1025	1.027 57	2.204
0.0263	1.023 49	2.185	0.1526	1.030 24	2.214
0.0518	1.024 87	1.192			
$100w_2 = 18.15$					
0.0164	1.028 11	2.361	0.0846	1.032 10	2.381
0.0214	1.028 52	2.363	0.1024	1.033 13	2.388
0.0274	1.028 86	2.365	0.1219	1.034 17	2.393
0.0523	1.030 31	2.373			
$100w_2 = 20.00$					
0.0181	1.031 48	2.470	0.0425	1.033 03	2.480
0.0199	1.031 56	2.471	0.0481	1.033 38	2.482
0.0301	1.032 17	2.474	0.1015	1.036 63	2.502
0.0396	1.032 78	2.478	0.1532	1.039 93	2.521
$100w_2 = 30.00$					
0.0150	1.048 33	3.215	0.1017	1.053 12	3.263
0.0207	1.048 58	3.217	0.1212	1.054 19	3.275
0.0504	1.050 32	3.236	0.1524	1.055 96	3.296
0.0818	1.052 02	3.255			
$100w_2 = 40.00$					
0.0120	1.065 77	4.249	0.0463	1.067 84	4.284
0.0154	1.065 98	4.252	0.0575	1.068 73	4.302
0.0203	1.066 28	4.256	0.0845	1.070 17	4.327
0.0292	1.066 84	4.266	0.1045	1.071 35	4.345
0.0367	1.067 43	4.276	0.1309	1.072 94	4.376
$100w_2 = 42.75$					
0.0062	1.070 40	4.643	0.1139	1.077 25	4.805
0.0164	1.071 33	4.660	0.1481	1.079 15	4.839
0.0490	1.073 07	4.709	0.1930	1.082 45	4.884
0.0897	1.073 80	4.755			
$100w_2 = 49.95$					
0.0142	1.083 43	5.608	0.0594	1.086 24	5.702
0.0194	1.083 80	5.619	0.0855	1.087 77	5.748
0.0259	1.084 12	5.632	0.1071	1.089 09	5.791
0.0315	1.084 45	5.644	0.1286	1.090 32	5.828
0.0371	1.084 75	5.654	0.1616	1.092 33	5.896
0.0492	1.085 51	5.674			
$100w_2 = 65.00$					
0.0152	1.105 19	7.383	0.1042	1.109 84	7.709
0.0200	1.105 47	7.399	0.1254	1.111 00	7.769
0.0249	1.105 66	7.416	0.1572	1.112 61	7.875
0.0509	1.107 07	7.511	0.2095	1.115 39	8.077
0.0814	1.108 74	7.628	0.2574	1.117 59	8.240
$100w_2 = 84.98$					
0.0156	1.118 52	5.516	0.0827	1.122 54	5.833
0.0209	1.118 89	5.545	0.1042	1.123 91	5.937
0.0259	1.119 16	5.577	0.1581	1.127 17	6.212
0.0520	1.120 79	5.687	0.2074	1.130 11	6.467
293.15 K					
$100w_2 = 0.00$					
0.0146	0.999 14	1.001	0.0453	1.001 07	1.005
0.0198	0.999 46	1.002	0.0542	1.001 63	1.006
0.0279	0.999 97	1.003	0.0801	1.003 25	1.009
0.349	1.000 43	1.004	0.1000	1.004 51	1.012
$100w_2 = 2.50$					
0.0149	1.002 28	1.055	0.0557	1.004 82	1.060
0.0235	1.002 81	1.056	0.0812	1.006 38	1.063
0.0283	1.003 22	1.057	0.1016	1.007 75	1.066
0.0349	1.003 57	1.058	0.1173	1.008 72	1.068
0.0455	1.004 20	1.059			
$100w_2 = 5.00$					
0.0135	1.005 38	1.115	0.0415	1.007 10	1.119
0.0178	1.005 63	1.116	0.0470	1.007 46	1.120
0.0200	1.005 77	1.116	0.0584	1.008 09	1.122
0.0308	1.006 45	1.117	0.1246	1.012 28	1.130
0.0386	1.006 92	1.118			
$100w_2 = 10.00$					
0.0104	1.011 85	1.267	0.0363	1.013 46	1.273
0.0137	1.012 06	1.268	0.0443	1.013 94	1.275
0.0171	1.012 27	1.269	0.0506	1.014 33	1.276
0.0264	1.012 82	1.271	0.1059	1.017 71	1.285
0.0320	1.013 19	1.272			
$100w_2 = 15.00$					
0.0153	1.019 02	1.405	0.0806	1.022 48	1.418
0.0206	1.019 60	1.407	0.1021	1.023 67	1.421
0.0262	1.019 60	1.408	0.1520	1.026 41	1.429
0.0516	1.020 99	1.412			
$100w_2 = 18.15$					
0.0207	1.024 11	1.522	0.1020	1.028 77	1.541
0.0273	1.024 58	1.524	0.1214	1.029 77	1.544
0.0521	1.025 87	1.530	0.2003	1.034 36	1.562
$100w_2 = 20.00$					
0.0063	1.025 95	1.562	0.0423	1.028 17	1.572
0.0180	1.026 66	1.565	0.0479	1.028 55	1.573
0.0198	1.026 80	1.566	0.0605	1.029 31	1.577
0.0300	1.027 40	1.568	0.1011	1.031 82	1.588
0.0394	1.028 02	1.571			
$100w_2 = 30.00$					
0.0150	1.041 89	2.015	0.1011	1.046 62	2.049
0.0206	1.042 16	2.018	0.1204	1.047 73	2.058
0.0501	1.043 84	2.030	0.1515	1.049 53	2.070
0.0813	1.045 56	2.042			
$100w_2 = 40.00$					
0.0202	1.057 91	2.607	0.0570	1.060 18	2.632
0.0289	1.058 45	2.612	0.0838	1.061 80	2.651
0.0364	1.058 90	2.617	0.1037	1.063 00	2.664
0.0459	1.059 49	2.625	0.1299	1.064 68	2.681
$100w_2 = 42.75$					
0.0061	1.062 00	2.753	0.0970	1.066 52	2.830
0.0162	1.062 44	2.761	0.1139	1.068 67	2.850
0.0221	1.063 18	2.767	0.1469	1.070 63	2.872
0.0488	1.064 70	2.789	0.1892	1.073 96	2.914
$100w_2 = 49.95$					
0.0106	1.073 00	3.332	0.0487	1.075 39	3.375
0.0141	1.073 28	3.337	0.0589	1.076 06	3.388
0.0193	1.073 58	3.342	0.0847	1.077 60	3.414
0.0258	1.073 98	3.350	0.1061	1.078 92	3.438
0.0313	1.074 32	3.356	0.1283	1.080 22	3.460
0.0367	1.074 64	3.362			
$100w_2 = 65.00$					
0.0151	1.093 13	4.327	0.1030	1.097 83	4.488
0.0198	1.093 40	4.336	0.1241	1.099 01	4.526
0.0247	1.093 69	4.347	0.1555	1.100 66	4.584
0.0504	1.095 06	4.390	0.2073	1.103 43	4.677
0.0805	1.096 70	4.447	0.2546	1.105 65	4.758
$100w_2 = 85.00$					
0.0154	1.104 78	3.539	0.1029	1.110 18	3.773
0.0206	1.105 40	3.558	0.1245	1.111 49	3.842
0.0256	1.105 42	3.564	0.1562	1.113 42	3.934
0.0515	1.107 00	3.642	0.2048	1.116 40	4.075
0.0817	1.108 84	3.723			
$100w_2 = 100.00$					
0.0112	1.101 23	2.216	0.0487	1.103 97	2.297
0.0159	1.101 58	2.226	0.0596	1.104 76	2.320
0.0221	1.102 02	2.239	0.0690	1.105 45	2.342
0.0303	1.102 62	2.257	0.1083	1.108 31	2.430
0.0379	1.103 18	2.273			

Table 3. Viscosity *A* and *B* Coefficients of the Jones−Dole Equation (Eq 1) for LiBr in Water (1) + DMSO (2) Mixtures at 278.15 and 293.15 K

	$A/(\mathrm{dm^3 \cdot mol^{-1}})^{1/2}$		$B/\mathrm{dm^3 \cdot mol^{-1}}$	
$100w_2$	T = 278.15 K	T = 293.15 K	T = 278.15 K	T = 293.15 K
0.00	0.0012 ± 0.0001	0.0053 ± 0.0005	0.093 ± 0.002	0.104 ± 0.002
2.50	0.0040 ± 0.0004	0.0075 ± 0.0008	0.092 ± 0.002	0.102 ± 0.002
5.00	0.0112 ± 0.0011	0.0107 ± 0.0011	0.089 ± 0.002	0.096 ± 0.002
10.00	0.0006 ± 0.0001	0.0209 ± 0.0021	0.098 ± 0.002	0.098 ± 0.002
15.00	0.0030 ± 0.0003	0.0094 ± 0.0009	0.102 ± 0.002	0.105 ± 0.002
18.15	0.0110 ± 0.0011	0.0166 ± 0.0017	0.104 ± 0.002	0.114 ± 0.002
20.00	−0.0003 ± 0.0001	0.0050 ± 0.0005	0.158 ± 0.003	0.163 ± 0.003
30.00	0.0070 ± 0.0007	0.0020 ± 0.0002	0.170 ± 0.003	0.196 ± 0.004
40.00	0.0150 ± 0.0015	0.0142 ± 0.0014	0.219 ± 0.004	0.234 ± 0.004
42.75	0.0310 ± 0.0031	0.0193 ± 0.0019	0.228 ± 0.004	0.276 ± 0.005
49.95	0.0189 ± 0.0019	0.0076 ± 0.0008	0.311 ± 0.006	0.312 ± 0.006
65.00	0.0007 ± 0.0001	0.0091 ± 0.0009	0.483 ± 0.010	0.406 ± 0.008
85.00	−0.0131 ± 0.0013	−0.0053 ± 0.0005	0.917 ± 0.018	0.807 ± 0.016
100.00		−0.0151 ± 0.0015		1.036 ± 0.021
				0.907 ± 0.003[a]

[a] Value at 298.15 K.[40]

The studies indicate a strong interaction between DMSO and water, and the general conclusion is that in the mole fraction range $x_2 = 0.3$ to 0.4 the interactions due to hydrogen bonds are at a maximum. When plotted against concentration, properties of the mixtures such as density,[9] viscosity,[9] spin lattice relaxation rates,[10] enthalpy of mixing,[11] and surface tension[12] pass through minima or maxima at about $x_2 = 0.35$. There is some disagreement as to whether actual hydrogen-bonded complexes are formed,[3,13,14] what the water to DMSO ratio is in the complex,[15] and how long such complexes exist.[10,16] For example, measurements of the neutron spin−lattice relaxation time in the water + DMSO system have suggested that the reorientation of the DMSO·3H_2O complex is the dominant motion causing relaxation.[15] Also, from phase diagram studies, it is concluded that a complex of one DMSO and three water molecules is formed.[17]

Other dielectric studies have also shown that a DMSO molecule reorients together with two water molecules.[16] This is in agreement with enthalpy of mixing,[11] density,[9] and viscosity[9] data, where the results also indicate a DMSO·2H_2O complex.

From a phase diagram of the supercooled aqueous solutions[18] of DMSO it is suggested that a stable complex of DMSO·2H_2O exists the near glass transition temperature (T_g) in DMSO.

The existence of strongly hydrogen bonded DMSO·2H_2O aggregates has been proved through molecular dynamical simulations of these solvent mixtures.[19] The behavior of the principal relaxation time of the mixture shows a maximum at a value corresponding to a mixture with 30 mass % water.[20]

A survey of the literature shows that ionic viscosity *B* coefficients have been investigated for electrolyte solutions in water,[21−23] in DMSO,[24−26] and in water + DMSO mixtures.[27−30] This work involves the study of the *B* coefficient of lithium bromide in water + DMSO mixtures in the whole mole fraction region at 278.15 K and 293.15 K.

2. Experimental Section

Dimethyl sulfoxide (Riedel−de Häen, 99.9%) with density 1.100 41 g·cm^{-3} and refractive index 1.4795 at 293.15 K was used without further purification. These physical constants are in agreement with the literature values ρ = 1.100 401 g·cm^{-3} and n_D = 1.4793.[31] Water was deionized by an ion-exchange resin and doubly distilled. The specific conductance was found to be better than 0.50 μS·cm^{-1} at 293.15 K. Anhydrous lithium bromide (Fluka 99.0%) was dried before use at 413.15 K for 24 h. All solutions were prepared by mass from a stock solution. The weighings were uncertain to less than ±0.0001 g (salt) and ±0.01 g (solvent mixtures). Molar concentrations were obtained from molality and density values with an uncertainty ±0.0001 mol·dm^{-3}.

Densities (ρ) were measured with an Anton Paar (DMA 58) microcomputer-controlled precision densimeter, with a build-in solid state thermostat. The precision of the sample thermostat was ±0.01 K. The DMA cell was calibrated with air and doubly distilled water at atmospheric pressure. The uncertainty in the density was ±0.000 01 g·cm^{-3}.

The viscosities have been measured in the concentration range 0.0010−0.1500 mol·dm^{-3} with a viscosity measuring unit (Schott Geräte AVS 310) equipped with an Ubbelohde capillary viscometer. The viscometer was calibrated with doubly distilled water. The time measurement tolerance was ±0.005%, and the display accuracy was ±0.01 s. The temperature was maintained constant within ±0.03 K. The viscosities (η) were averaged from four readings. The uncertainty in the viscosity measurements was ±0.001 mPa·s.

3. Results and Discussion

Densities and viscosities of pure water, DMSO, and water + DMSO mixtures are reported in Table 1. Inspection of density values shows that the density passes through a maximum between 80 and 90 mass % DMSO for both temperatures. The viscosity−concentration curves, plotted in Figure 1, exhibit very pronounced maxima, which occur at a concentration corresponding to the formula DMSO/2H_2O ($100w_2 = 68$). These maxima in the viscosity water + DMSO system can be attributed to the strong interaction of DMSO with water. These results agree well with the literature values.[9, 32−34]

Densities and viscosities of LiBr in water + DMSO mixtures are reported in Table 2.

The viscosities of electrolytic solutions were analyzed using the Jones−Dole[35] equation:

$$\eta_r = 1 + Ac^{1/2} + Bc \qquad (1)$$

where η_r is the relative viscosity of the solution, the *A* coefficient is a measure of ion−ion interactions, and the *B*

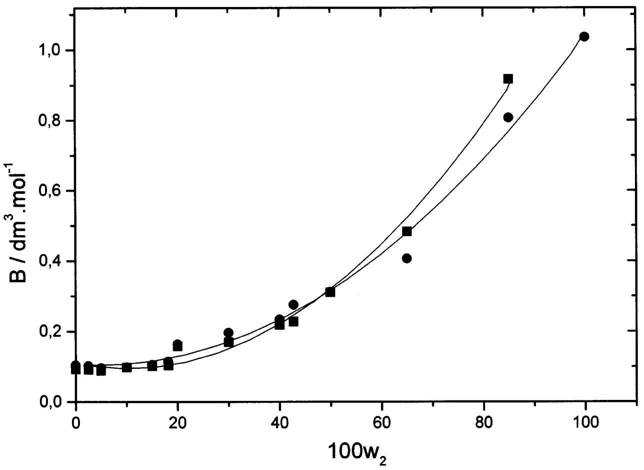

Figure 2. Viscosity *B* coefficients for LiBr in water (1) + DMSO (2) mixtures: ■, 278.15 K; ●, 293.15 K.

coefficient depends on the specific electrolyte and temperature and consequently is a measure of ion−solvent interactions.

The viscosity *A* and *B* coefficients have been calculated as the intercept and the slope, respectively, from plots of $(\eta/\eta_0 - 1)/c^{1/2}$ against $c^{1/2}$. The *A* and *B* values derived from eq 1 are given with their standard deviations in Table 3.

It is seen that the viscosity *A* coefficient is negative in some cases, but this has no physical significance.[36]

The values of the *B* coefficient for both temperatures are presented graphically in Figure 2. The *B* coefficient is positive throughout all solvent mixtures, indicating a structure making behavior of LiBr. In pure water the Li^+ ion is considered to be a structure making ion whereas the Br^- ion is considered to be a structure breaking ion.[23]

As is shown in Figure 2, the change of the *B* coefficient at both temperatures is very small up to $100w_2 \sim 18.15$, within the experimental uncertainty, with a small decrease from water to $100w_2 = 10$. This change of the *B* values in the water rich region may be due to the weakening of the ion−solvent interactions, because of the domination of the solvent−solvent interactions between unlike solvent molecules. Above $100w_2 = 18.15$ there is a marked increase in the *B* values. This increase may be attributed to the stronger solvation of Li^+ by DMSO molecules because of their greater basicity (donor number = 29.8 $kJ{\cdot}mol^{-1}$).[37] On the other hand, the Br^- ion exhibits weaker solvation because the positive end of the DMSO dipole is sterically hindered. The preference solvation of Li^+ and the small solvation of Br^- by DMSO are also confirmed from the free energies of transfer[38] of ions from water to water + DMSO mixtures and from the limiting ionic conductivities[39] in DMSO. Therefore, the structure making behavior of the salt can be attributed mainly to Li^+.

In conclusion, the *B* coefficient is positive throughout the solvent mixtures for both temperatures, showing a structure maker behavior of LiBr. The thermal coefficient (dB/dT) is positive up to $100w_2 = 50$, and above this composition turns to negative values. This change may be due to the strongest solvent−solvent interactions in the lower temperature. Though at higher concentration of DMSO the solvent−solvent interactions are less strong, the effect of long-range ordering of the solvent around the ions decreases with the increasing thermal energy.[23]

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