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Viscosities and Densities of Halide Salts in Dimethylsulfoxide + Water from $t =$ (25 to 45) °C

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The relative viscosities and densities for lithium bromide (LiBr) and sodium bromide (NaBr) were measured in dimethylsulfoxide (DMSO), water, and DMSO + water at temperatures from (25 to 45) °C. The estimated uncertainty of the measurements was ± 0.003 for relative viscosities and ± 0.0004 for densities. The data have been analyzed using the Jones−Dole equation. The Jones−Dole *B*-coefficients of these electrolytes were derived and the estimated uncertainty was ± 0.002. The values of the *B*-coefficients indicated that the salts behave as structure makers in DMSO, while in H_2O and DMSO + H_2O mixtures, the *B*-coefficient values were less positive showing a weaker structure-making effect.

Introduction

Ion solvation is a phenomenon of primary interest in many contexts of chemistry because solvated ions are omnipresent on Earth. Hydrated ions occur in aqueous solution in many chemical and biological systems.[1,2] Solvated ions appear in high concentrations in living organisms, where their presence or absence can fundamentally alter the functions of life. Ions solvated in organic solvents or mixtures of water and organic solvents are also very common.[3,4] The exchange of solvent molecules around ions in solutions is fundamental to the understanding of the reactivity of ions in solution.[5] Solvated ions also play a key role in electrochemical applications, where for instance the conductivity of electrolytes depends on ion−solvent interactions.[6]

Dimethylsulfoxide (DMSO) is an aprotic solvent which has useful properties for application in organic synthesis[7,8] and in electrochemical systems.[9] The dipolar character of DMSO makes the solvent a good nucleophilic agent and tends to enhance the reaction rates and yields of many organic syntheses by stabilizing charged intermediates in the reaction.[7] The polarity and physical properties of DMSO coupled with the stability of some potentially useful electrode materials makes the solvent theoretically promising for high-energy density battery applications. The transport behavior of ions in DMSO required for battery applications and the function of DMSO in organic reactions both require an understanding of the nature of ion−solvent interaction. Transport properties of electrolyte solutions such as ionic conductance and viscosity can provide information concerning the nature of kinetic entities.

In previous papers, ion−solvent interaction studies of lithium bromide (LiBr) and other salts in DMSO, water, and DMSO + water at 25 °C and at various temperatures with their activation energies were reported.[10,11] In continuation of the previous paper, the results of viscosity measurements on solutions of lithium bromide and sodium bromide in DMSO, water, and DMSO + water are reported over the concentration range of 10^{-3} mol·L^{-1} to near saturation. The effect*s* of temperature on viscosities are also studied in the present paper by changing the temperatures from (25 to 45) °C.

Experimental Section

The purification of DMSO for electrochemical studies has been surveyed on behalf of the IUPAC Commission. Water is the principal impurity in DMSO, and the recommended procedure is to remove water with molecular sieves (type 5A), followed by distillation.

Dimethylsulfoxide (Fluka) was stored over well-dried 5 Å molecular sieves for several days and then filtered. The solvent was distilled in the presence of P_2O_5. Dimethylsulfoxide (1) + water (2) mixtures of mass fraction $w_1 =$ (0, 20, 40, 50, 60, 70 and 100) % (corresponding to mole fractions of $x_1 =$ (0, 0.545, 0.133, 0.1874, 0.2570, 0.3499, and 1) were prepared by mixing known masses of water and dimethylsulfoxide in glass-stoppered flasks.

LiBr and NaBr were purified by recrystallization. These recrystallized electrolytes were dried at (130 to 150) °C for several hours prior to use. Owing to the hygroscopic nature of the bromides, these salts were stored in a vacuum desiccator over P_2O_5[12] for the viscosity measurements.

Densities of the pure solvents (DMSO and H_2O) and of solvent mixtures (DMSO + H_2O) and of salt solutions were determined by using a specific density bottle of volume 15 cm^3 calibrated using double-distilled water and benzene at 25 °C. The specific density bottle filled with air- or bubble-free experimental liquid was kept in a transparent-walled water bath for (10 to 15) min to attain thermal equilibrium. When the level of the meniscus remained unchanged for 15 min, the system was considered to be at equilibrium. The specific density bottle was removed from the thermostatic water bath, dried, and weighed. The density of the solution was calculated by dividing the mass in grams of the liquid by the volume in milliliters of the density bottle. The estimated uncertainty in density measurements of solutions was ± 0.00001 g·cm^{-3}.

For all viscosity measurements, an Ubbelhode-type glass capillary tube suspended level viscometer was used. A flow time of 450 s was obtained for distilled water at 25 °C. The viscometer had a capillary length of 12.2 cm and a capillary

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Table 1. Densities (ρ_o) and Viscosities (η_o) for DMSO, H_2O, and DMSO (1) + H_2O (2) Mixtures at Various Temperatures and Mass Fractions w

	ρ/g·cm^{-3}		η/MPa·s	
w_1	lit. (ref)	our work	lit. (ref)	our work
25 °C				
1.0	1.09580[b]	1.09541	1.9600[b]	1.9660
0.7		1.08732	3.7300[b]	2.3568
0.6		1.08231	3.4200[b]	3.4210
0.5		1.06781	2.8300[b]	2.8073
0.4		1.05347	2.2205[b]	2.2210
0.2		1.02420	1.3400[b]	1.3400
0.0	0.99710[b]	0.99715	0.8925[b]	0.8900
30 °C				
1.0		1.09013		1.8090
0.7		1.08492		2.8881
0.6		1.08111		3.4210
0.5		1.06243		2.4650
0.4		1.05247		2.2210
0.2		1.01970		1.3117
0.0	0.99570[a]	0.99570	0.7990[a]	0.8003
35 °C				
1.0	1.08538[c]	1.08538	1.6520[c]	1.6523
0.7		1.08083		2.0813
0.6		1.07280		3.1050
0.5		1.06640		2.2802
0.4		1.04530		1.9210
0.2		1.01520		1.0537
0.0	0.99410[a]	0.99366	0.7220[a]	0.7591
40 °C				
1.0		1.08058		1.5588
0.7		1.07523		1.9272
0.6		1.06521		2.8461
0.5		1.04828		2.1398
0.4		1.04012		1.6182
0.2		0.99840		0.9572
0.0	0.99222[a]	0.96841	0.6550[a]	0.6214
45 °C				
1.0	1.07537[c]	1.07450	1.3930[c]	1.4875
0.7		1.06712		1.8650
0.6		1.06500		2.7753
0.5		1.04752		1.9373
0.4		1.03801		1.4975
0.2		0.97920		0.8482
0.0	0.99022[a]	0.95321	0.5950[a]	0.5346

[a] Ref 14. [b] Ref 15. [c] Ref 16.

diameter of 0.45 mm and was calibrated using distilled water, hexane, methanol, and acetone. Cleaning of the viscometer with a clean mixture (chromic acid) was done at frequent intervals to ensure proper drainage of the solution.

The viscometer was suspended in a water thermostat maintained at 25 °C with an uncertainty of ± 0.01 °C. At first, 20 cm^3 of the reference liquid of accurately known viscosity η_1 was added from a pipet to the viscometer, and its flow time t_1 was obtained. The same procedure was repeated for the liquid of interest to obtain the viscosity η_2 by its rate of flow t_2. At least three replicates of each data set reproducible to 0.05 s was obtained; results were averaged; and standard deviation and errors were determined. The overall uncertainty in viscosity measurements was estimated to be ± 0.01.

Viscosity values η_2 were determined from measurements of flow times t_1 and t_2 of liquids of the respective densities ρ_1 and ρ_2 using the following relation

$$\frac{\eta_1}{\eta_2} = \frac{t1\rho_1}{t2\rho_2} \qquad (1)$$

The absolute viscosities of DMSO, H_2O, DMSO + H_2O mixtures, and their solutions with lithium bromide were determined at 25 °C. Viscosities were measured at a series of concentrations for lithium bromide, the lowest concentration being 0.01 mol·L^{-1} and the highest concentration being about 0.4 mol·L^{-1}, which was found empirically to be the practical limit of the linear relationship that is the Jones−Dole equation.[13] Experimental values of viscosities of the solution η_1 and of solvents (H_2O, DMSO, H_2O + DMSO mixtures) as η_o are used to determine the relative viscosities η_r of the solution which was used in the Jones−Dole equation. Experimental values of densities and viscosities were used to calculate the *A*- and *B*-coefficients in the Jones−Dole equation.

Results and Discussion

The measured physical parameters like densities (ρ_o) and viscosities (η_o) for dimethyl sulfoxide (DMSO), water (H_2O), and DMSO + H_2O mixtures containing w_1 = (100, 70, 60, 50, 40, 20, and 0) % DMSO are reported in Table 1 for temperatures of (25, 30, 35, 40, and 45) °C. The data obtained in this study for densities (ρ_o) and viscosities (η_o) of the pure solvents H_2O and DMSO at 25 °C coincide with the values obtained by other authors.[14−16]

The plot of densities (ρ_o) versus mass fraction of DMSO showed small deviations from linearity in the mixture w_1 = 0.60 of DMSO. The same trend is observed in the plot of viscosities versus mass fraction of DMSO. Similar changes in viscosity were also found by other researchers. The viscosity of water + dioxane,[17] water + dialkylated amide,[18,19] and water + alcohol showed a sharp maximum or minimum in the plots of viscosity versus solvent composition. It is observed that with w_1 = 0.60 of DMSO the viscosity of the DMSO + H_2O mixture is at its maximum.

Relative viscosities, viscosities, and the densities of LiBr and NaBr have been measured in the concentration range (15 to 1000)·10^{-4} mol·dm^{-3} in DMSO, H_2O, and DMSO + H_2O mixtures over the entire composition range and are reported in Table 2.

The results of the measurements of the relative viscosities η_r for nonaqueous electrolyte solutions are found to fit the Jones−Dole equation.[13]

$$\eta_r = \eta/\eta_o = 1 + Ac^{1/2} + BC$$
$$\eta_r = \frac{\eta - \eta_o}{\eta_o C^{1/2}} = A + BC^{1/2} \qquad (2)$$

In this equation, η and η_o are the viscosities of the solution and the pure solvents or solvent mixtures respectively; c is the concentration; and *A* and *B* are the constants at a given temperature and are characteristic of the solvent and the salt. The *A*-coefficient accounts for ion−ion interactions, and the *B* parameter is a measure of the ion−solvent interactions. For evaluation of *A*- and *B*-coefficients, plots of $(\eta - \eta_o)/\eta_o \cdot c^{1/2}$ versus $c^{1/2}$ have been constructed and found to be linear over the whole concentration range studied. The *A*- and *B*-coefficients in each case were obtained from the intercepts and slopes of these plots by the method of least-squares.

The values of the *A*-coefficients obtained at various temperatures are listed in Table 3, and a variation is observed in the *A*-coefficient for various compositions of solvent mixtures. The *A*-coefficient values vary with composition of the solvent and temperature of solution. Smaller values of the *A* coefficient at higher composition of water in binary solvent mixtures imply that ion hydration is greater than ion−ion interaction.

The *B*-coefficient values obtained at various temperatures for LiBr and NaBr in the different solvent mixtures are listed in

Table 2. Density (ρ), Viscosity (η), and Relative Viscosity (η_r) of Salts in Dimethyl Sulfoxide (1) + Water (2)

c / mol·dm^{-3}	ρ / g·cm^{-3}	η / MPa·s	η_r	c / mol·dm^{-3}	ρ / g·cm^{-3}	η / MPa·s	η_r
LiBr							
t = 25 °C							
$w_1 = 1.0$				$w_1 = 0.4$			
0.019	1.0969	2.0086	0.1573	0.016	1.0723	2.29664	0.2670
0.025	1.0973	2.0182	0.1664	0.021	1.0748	2.3072	0.2709
0.033	1.0978	2.0385	0.2047	0.026	1.0769	2.3191	0.2733
0.040	1.0985	2.0536	0.2228	0.032	1.0800	2.3306	0.2774
0.049	1.0990	2.0655	0.2277	0.046	1.0801	2.3545	0.2814
$w_1 = 0.7$				$w_1 = 0.2$			
0.015	1.0942	2.4306	0.2554	0.013	1.0263	1.3639	0.1518
0.021	1.0957	2.4452	0.2610	0.019	1.0270	1.3687	0.1540
0.026	1.0961	2.4579	0.2672	0.026	1.0276	1.3739	0.1568
0.032	1.0968	2.4709	0.2725	0.036	1.0286	1.3809	0.1603
0.049	1.0983	2.5053	0.2834	0.044	1.0296	1.3859	0.1630
$w_1 = 0.6$				$w_1 = 0.0$			
0.016	1.0923	3.5416	0.2765	0.014	0.9982	0.9061	0.1518
0.021	1.0948	3.5594	0.2822	0.019	0.9994	0.9090	0.1539
0.026	1.0969	3.5796	0.2887	0.025	0.9996	0.9131	0.1547
0.032	1.0999	3.5979	0.2911	0.035	0.9998	0.9171	0.1599
0.046	1.1099	3.6471	0.2972	0.045	1.0007	0.9211	0.1627
$w_1 = 0.5$							
0.015	1.0801	2.9030	0.2785				
0.021	1.0824	2.9206	0.2816				
0.026	1.0852	2.9358	0.2852				
0.032	1.0880	2.9504	0.2872				
0.049	1.0902	2.9922	0.2963				
t = 30 °C							
$w_1 = 1.0$				$w_1 = 0.4$			
0.016	1.0926	1.8583	0.2152	0.016	1.0722	2.2956	0.2676
0.022	1.0961	1.8712	0.2317	0.020	1.0745	2.3051	0.2699
0.029	1.0979	1.8894	0.2621	0.026	1.0769	2.3185	0.2733
0.045	1.0999	1.9204	0.2889	0.031	1.0797	2.3288	0.2766
0.049	1.1008	1.9283	0.2993	0.046	1.0800	2.3555	0.2834
$w_1 = 0.7$				$w_1 = 0.2$			
0.016	1.09252	2.3621	0.2556	0.013	1.0218	1.3323	0.1778
0.023	1.09431	2.3799	0.2624	0.018	1.0255	1.3326	0.1809
0.038	1.09610	2.4115	0.2757	0.024	1.0265	1.3328	0.1834
0.045	1.09772	2.4243	0.2810	0.034	1.0276	1.3332	0.1875
0.056	1.09924	2.4440	0.2882	0.042	1.3556	1.3334	0.1900
$w_1 = 0.6$				$w_1 = 0.0$			
0.016	1.09230	3.54074	0.2789	0.013	0.9986	0.8140	0.1528
0.021	1.09482	3.56092	0.2832	0.016	0.9994	0.8158	0.1553
0.027	1.09689	3.58289	0.2875	0.021	0.9996	0.8183	0.1570
0.031	1.09999	3.59571	0.2898	0.030	0.9998	0.8226	0.1599
0.049	1.10992	3.64904	0.2998	0.035	1.0007	0.8247	0.1617
$w_1 = 0.5$							
0.016	1.0823	2.5491	0.2697				
0.023	1.0842	2.5681	0.2736				
0.038	1.0859	2.6002	0.2804				
0.045	1.0875	2.6134	0.2842				
0.056	1.0900	2.6355	0.2926				
t = 35 °C							
$w_1 = 1.0$				$w_1 = 0.4$			
0.019	1.0867	1.7010	0.2154	0.016	1.0623	1.9825	0.2511
0.025	1.0872	1.7157	0.2416	0.021	1.0643	1.9909	0.2541
0.032	1.0877	1.7330	0.2721	0.026	1.0663	2.0007	0.2568
0.041	1.0885	1.7458	0.2785	0.032	1.0673	2.0007	0.2607
0.049	1.0890	1.7589	0.2900	0.046	1.0693	2.0308	0.2678
$w_1 = 07$				$w_1 = 0.2$			
0.016	1.08100	2.1464	0.2473	0.013	1.0173	1.0753	0.1764
0.021	1.82776	2.1563	0.2516	0.019	1.0180	1.0799	0.1808
0.023	1.84010	2.1618	0.2568	0.026	1.0181	1.0847	0.1841
0.032	1.08662	2.1793	0.2651	0.036	1.0187	1.0909	0.1869
0.049	1.08800	2.2101	0.2783	0.044	1.0183	1.0953	0.1905
$w_1 = 0.6$				$w_1 = 0.0$			
0.016	1.0738	3.2052	0.2550	0.014	0.9914	0.7711	0.1366
0.021	1.0748	3.2197	0.2580	0.019	0.9917	0.7733	0.1379
0.023	1.0765	3.2266	0.2599	0.020	0.9923	0.7744	0.1412
0.032	1.0768	3.2515	0.2656	0.030	0.9924	0.7781	0.1433
0.049	1.0778	3.2955	0.2760	0.036	0.9926	0.7829	0.1470
$w_1 = 0.5$							
0.016	1.07001	2.3538	0.2550				
0.021	1.07112	2.3645	0.2580				
0.023	1.07242	2.3695	0.2599				
0.032	1.07368	2.3878	0.2656				
0.049	1.07686	2.4195	0.2747				

Table 2 Continued

$\frac{c}{\mathrm{mol \cdot dm^{-3}}}$	$\frac{\rho}{\mathrm{g \cdot cm^{-3}}}$	$\frac{\eta}{\mathrm{MPa \cdot s}}$	η_r	$\frac{c}{\mathrm{mol \cdot dm^{-3}}}$	$\frac{\rho}{\mathrm{g \cdot cm^{-3}}}$	$\frac{\eta}{\mathrm{MPa \cdot s}}$	η_r
$t = 40$ °C							
	$w_1 = 1.0$				$w_1 = 0.4$		
0.019	1.0869	1.6052	0.2176	0.044	1.0113	0.9957	0.1926
0.025	1.0873	1.6186	0.2414	0.021	1.0443	1.6773	0.2550
0.032	1.0877	1.6294	0.2521	0.026	1.0463	1.6856	0.2577
0.041	1.0885	1.6467	0.2775	0.032	1.0473	1.6934	0.2614
0.049	1.0890	1.6590	0.2889	0.046	1.0493	1.7110	0.2686
	$w_1 = 0.7$				$w_1 = 0.2$		
0.016	1.0777	1.9876	0.2486	0.013	1.0014	0.9768	0.1764
0.021	1.0785	1.9993	0.2613	0.019	1.0044	0.9810	0.1807
0.024	1.0795	2.0068	0.2684	0.026	1.0081	0.9854	0.1841
0.032	1.0833	2.0245	0.2843	0.036	1.0112	0.9913	0.1887
0.049	1.0822	2.0475	0.2809	0.044	1.0113	0.9957	0.1926
	$w_1 = 0.6$				$w_1 = 0.0$		
0.016	1.0654	2.9378	0.2547	0.014	0.9687	0.6313	0.1366
0.021	1.0656	2.9512	0.2578	0.019	0.9690	0.6331	0.1385
0.023	1.0659	2.9575	0.2599	0.020	0.9693	0.6339	0.1412
0.032	1.0662	2.9807	0.2662	0.030	0.9697	0.6369	0.1433
0.049	1.0668	3.0211	0.2765	0.036	0.9699	0.6409	0.1475
	$w_1 = 0.5$						
0.016	1.0567	2.2083	0.2531				
0.021	1.0578	2.2181	0.2554				
0.024	1.0588	2.2248	0.2581				
0.032	1.0592	2.2411	0.2669				
0.049	1.0613	2.2692	0.2725				
$t = 45$ °C							
	$w_1 = 1.0$				$w_1 = 0.4$		
0.019	0.9544	1.5277	0.1974	0.016	1.0385	1.5353	0.2514
0.026	0.9546	1.5411	0.2267	0.021	1.0385	1.5420	0.2551
0.032	0.9548	1.5522	0.2421	0.026	1.0386	1.5496	0.2579
0.041	0.9550	1.5638	0.2525	0.032	1.0387	1.5568	0.2618
0.049	0.9551	1.5775	0.2720	0.046	1.0389	1.5733	0.2697
	$w_1 = 0.7$				$w_1 = 0.2$		
0.016	1.03231	1.9196	0.2509	0.013	0.9796	0.8653	0.1741
0.021	1.04321	1.9331	0.2575	0.019	0.9801	0.8693	0.1808
0.023	1.05432	1.9409	0.2594	0.019	0.9801	0.8693	0.1808
0.032	1.05523	1.9557	0.2687	0.036	0.9822	0.8784	0.1885
0.049	1.05643	1.9755	0.2864	0.044	0.9838	0.8821	0.1917
	$w_1 = 0.6$				$w_1 = 0.0$		
0.016	1.06261	2.8645	0.2540	0.014	0.9566	0.54319	0.1372
0.021	1.06351	2.8774	0.2570	0.019	0.9575	0.54485	0.1400
0.023	1.06421	2.8843	0.2606	0.020	0.9578	0.54537	0.1402
0.032	1.06651	2.9063	0.2657	0.030	0.9603	0.54818	0.1441
0.049	1.07131	2.9378	0.2770	0.045	0.9623	0.55158	0.1485
	$w_1 = 0.5$						
0.016	1.0482	1.9999	0.2527				
0.021	1.0494	2.0083	0.2561				
0.023	1.0500	2.0129	0.2592				
0.032	1.0502	2.0283	0.2645				
0.049	1.0512	2.0554	0.2743				
NaBr							
$t = 25$ °C							
	$w_1 = 1.0$				$w_1 = 0.4$		
0.009	1.0962	1.8391	0.1700	0.0167	1.0823	3.3617	0.2383
0.013	1.0976	2.8470	0.2079	0.0206	1.0848	3.3802	0.2439
0.033	1.0999	2.8899	0.2406	0.0257	1.0869	3.3995	0.2456
0.049	1.1008	2.9238	0.2689	0.0315	1.0900	3.4193	0.2468
0.056	1.1021	2.9355	0.3136	0.0428	1.0901	3.4541	0.2499
	$w_1 = 0.7$				$w_1 = 0.2$		
0.0150	1.0952	2.3999	0.1492	0.0159	1.0276	1.3573	0.0777
0.0206	1.0965	2.4083	0.1522	0.0189	1.0280	1.3623	0.0828
0.0256	1.0974	2.4167	0.1582	0.0235	1.0287	1.3679	0.0839
0.0315	1.0986	2.4246	0.1619	0.0323	1.0296	1.3740	0.0889
0.0494	1.0995	2.4486	0.1751	0.0419	1.0315	1.3783	0.0915
	$w_1 = 0.6$				$w_1 = 0.0$		
0.01627	1.0944	2.2894	0.3031	0.0106	0.9994	0.8956	0.0576
0.02058	1.0949	2.2989	0.3046	0.0136	0.9996	0.8964	0.0599
0.02582	1.0969	2.3085	0.3081	0.0245	0.9998	0.8988	0.0612
0.03155	1.1000	2.3083	0.3108	0.0354	1.0007	0.9008	0.0628
0.04563	1.1099	2.3358	0.3203	0.0484	1.0036	0.9029	0.0643
	$w_1 = 0.5$						
0.0163	1.0883	2.8974	0.2707				
0.0206	1.0894	2.9177	0.2743				
0.0258	1.0900	2.9321	0.2708				
0.0315	1.0911	2.9463	0.2788				
0.0456	1.0922	2.9785	0.2855				

Table 2 Continued

c / mol·dm^{-3}	ρ / g·cm^{-3}	η / MPa·s	η_r	c / mol·dm^{-3}	ρ / g·cm^{-3}	η / MPa·s	η_r
			t = 30 °C				
	w_1 = 1.0				w_1 = 0.4		
0.011	0.96860	1.8391	0.1848	0.016	1.0843	2.2881	0.2413
0.013	0.96873	1.8470	0.1930	0.019	1.0868	2.2947	0.2429
0.020	0.96891	1.8899	0.2506	0.022	1.0889	2.3010	0.2445
0.034	0.96939	1.9238	0.2886	0.031	1.0920	2.3175	0.2488
0.048	0.96998	1.9355	0.2977	0.041	1.0941	2.3346	0.2532
	w_1 = 0.7				w_1 = 0.2		
0.0160	1.10258	2.36237	0.2566	0.014	1.0276	1.3446	0.0853
0.0234	1.11345	2.38079	0.2650	0.017	1.0280	1.3462	0.0869
0.0383	1.12460	2.41106	0.2747	0.026	1.0287	1.3488	0.0883
0.0448	1.14011	2.42384	0.2801	0.032	1.0296	1.3528	0.0915
0.0558	1.15670	2.44344	0.2872	0.041	1.0315	1.3565	0.0940
	w_1 = 0.6				w_1 = 0.0		
0.0153	1.09530	3.54872	0.3021	0.011	0.9994	0.8051	0.0582
0.0196	1.09631	3.56677	0.3046	0.014	0.9996	0.8058	0.0589
0.0228	1.09789	3.58017	0.3081	0.024	0.9998	0.8080	0.0612
0.0305	1.10383	3.60681	0.3108	0.035	0.1001	0.8098	0.0628
0.0356	1.11359	3.62550	0.3167	0.048	1.0036	0.8116	0.0643
	w_1 = 0.5						
0.016	1.8898	2.5485	0.2677				
0.023	1.8987	2.5682	0.2740				
0.038	1.9005	2.6002	0.2803				
0.045	1.9108	2.6138	0.2850				
0.056	1.9229	2.6327	0.2878				
			t = 35 °C				
	w_1 = 1.0				w_1 = 0.4		
0.009	1.0886	1.6699	0.1118	0.016	1.0553	1.9439	0.0952
0.013	1.0888	1.6765	0.1306	0.020	1.0568	1.9479	0.0975
0.023	1.0892	1.6932	0.1635	0.026	1.0568	1.9517	0.0995
0.029	1.0903	1.7008	0.1715	0.031	1.0581	1.9554	0.1025
0.036	1.0953	1.7117	0.1890	0.042	1.0599	1.9628	0.1070
	w_1 = 0.7				w_1 = 0.2		
0.016	1.0799	2.14697	0.2493	0.014	1.0175	1.0622	0.0676
0.021	1.0800	2.15690	0.2536	0.019	1.0180	1.0638	0.0696
0.023	1.0802	2.16245	0.2588	0.024	1.0189	1.0653	0.0715
0.032	1.0812	2.17893	0.2641	0.032	1.0193	1.0678	0.0746
0.049	1.0824	2.20918	0.2763	0.042	1.0215	1.0704	0.0773
	w_1 = 0.6				w_1 = 0.0		
0.016	1.0739	3.1740	0.1736	0.011	0.9899	0.76213	0.0384
0.021	1.0739	3.1834	0.1763	0.013	0.9901	0.76269	0.0418
0.025	1.0768	3.1927	0.1794	0.020	0.9908	0.76385	0.0435
0.029	1.0791	3.2019	0.1815	0.034	0.9921	0.76548	0.0451
0.041	1.0799	3.2238	0.1899	0.048	0.9929	0.76677	0.0458
	w_1 = 0.5						
0.009	1.0652	2.3095	0.1344				
0.013	1.0665	2.3151	0.1369				
0.023	1.0678	2.3284	0.1395				
0.029	1.0688	2.3381	0.1483				
0.036	1.0700	2.3463	0.1524				
			t = 40 °C				
	w_1 = 1.0				w_1 = 0.4		
0.009	1.0886	1.5762	0.1166	0.016	1.0443	1.6374	0.0945
0.013	1.0888	1.5816	0.1306	0.021	1.0461	1.6406	0.0966
0.023	1.0892	1.5972	0.1627	0.026	1.0477	1.6443	0.1005
0.029	1.0903	1.6052	0.1739	0.031	1.0488	1.6478	0.1048
0.036	1.0953	1.6146	0.1880	0.042	1.0519	1.6538	0.1071
	w_1 = 0.7				w_1 = 0.2		
0.016	1.0776	1.9898	0.2576	0.014	1.0018	0.9648	0.0666
0.021	1.0779	1.9998	0.2633	0.019	1.0046	0.9662	0.0686
0.024	1.0781	2.0071	0.2695	0.024	1.0089	0.9677	0.0715
0.032	1.0789	2.0199	0.2711	0.032	1.0118	0.9703	0.0762
0.049	1.0792	2.0497	0.2859	0.042	1.0144	0.9726	0.0788
	w_1 = 0.6				w_1 = 0.0		
0.016	1.0654	2.9093	0.1736	0.011	0.9686	0.6239	0.0404
0.021	1.0655	2.9184	0.1775	0.013	0.9687	0.6242	0.0408
0.025	1.0658	2.9265	0.1794	0.020	0.9689	0.6253	0.0435
0.030	1.0659	2.9361	0.1839	0.034	0.9394	0.6267	0.0459
0.041	1.0662	2.9551	0.1900	0.048	0.9699	0.6279	0.0478
	w_1 = 0.5						
0.016	1.0543	2.1758	0.1341				
0.021	1.0560	2.1816	0.1370				
0.024	1.0571	2.1857	0.1399				
0.032	1.0582	2.1947	0.1452				
0.049	1.0593	2.2122	0.1526				

Table 2 Continued

c / mol·dm^{-3}	ρ / g·cm^{-3}	η / MPa·s	η_r	c / mol·dm^{-3}	ρ / g·cm^{-3}	η / MPa·s	η_r
			$t = 45$ °C				
	$w_1 = 1.0$				$w_1 = 0.4$		
0.009	1.0756	1.5043	0.1181	0.016	1.0381	1.5051	0.0942
0.013	1.0759	1.5093	0.1306	0.020	1.0381	1.5081	0.0965
0.023	1.0760	1.5244	0.1635	0.026	1.0381	1.5115	0.1005
0.029	1.0764	1.5312	0.1715	0.031	1.0382	1.5142	0.1025
0.036	1.0768	1.5409	0.1890	0.042	1.0382	1.5204	0.1076
	$w_1 = 0.7$				$w_1 = 0.2$		
0.016	1.06840	1.9244	0.2520	0.014	0.9796	0.8551	0.0676
0.021	1.07132	1.9340	0.2585	0.019	0.9799	0.8563	0.0696
0.023	1.07658	1.9381	0.2604	0.023	0.9802	0.8576	0.0725
0.032	1.07991	1.9520	0.2627	0.032	0.9805	0.8599	0.0766
0.049	1.08121	1.9821	0.2824	0.042	0.9809	0.8621	0.0800
	$w_1 = 0.6$				$w_1 = 0.0$		
0.016	1.0601	2.8369	0.1733	0.009	1.0756	0.5368	0.0385
0.021	1.0601	2.8454	0.1763	0.013	1.0759	0.5372	0.0419
0.025	1.0601	2.8537	0.1794	0.023	1.0760	0.5380	0.0436
0.029	1.0601	2.8619	0.1815	0.029	1.0764	0.5391	0.0450
0.040	1.0602	2.8815	0.1899	0.036	1.0768	0.5402	0.0475
	$w_1 = 0.5$						
0.019	1.0481	1.9727	0.1337				
0.025	1.0486	1.9792	0.1364				
0.032	1.0491	1.9859	0.1399				
0.041	1.0495	1.9946	0.1456				
0.049	1.0503	2.0020	0.1504				

Table 3. Viscosity $A \cdot 10^2$ (dm$^{3/2}$·mol$^{-1/2}$) Coefficients of the Jones–Dole Equation for Some Electrolytes in DMSO, H_2O, and DMSO (1) + H_2O (2) Mixtures at Various Temperatures and Mass Fraction *w*

w_1	LiBr	NaBr	LiBr	NaBr
	25 °C		30 °C	
1.0	0.0287	0.9860	0.1050	0.1087
0.7	0.2215	0.1153	0.2171	0.2225
0.6	0.2519	0.2716	0.2519	0.2756
0.5	0.2562	0.2499	0.2434	0.2451
0.4	0.2465	0.2231	0.2445	0.2217
0.2	0.1507	0.0639	0.1624	0.0733
0.0	0.1379	0.0530	0.1411	0.0530
	35 °C		40 °C	
1.0	0.1041	0.0402	0.1059	0.2464
0.7	0.2063	0.2149	0.2133	0.2234
0.6	0.2266	0.1451	0.2256	0.1452
0.5	0.2286	0.1158	0.2258	0.1095
0.4	0.2261	0.0762	0.2258	0.0731
0.2	0.1605	0.0538	0.1569	0.0485
0.0	−0.0319	0.0444	0.1242	0.0395
	45 °C			
1.0	0.0923	0.0485		
0.7	0.2043	0.2144		
0.6	0.2234	0.1444		
0.5	0.2244	0.1058		
0.4	0.2246	0.0726		
0.2	0.1546	0.0494		
0.0	0.1240	0.0330		

Table 4. Viscosity *B* (dm^3·mol^{-1}) Coefficients of the Jones-Dole Equation for LiBr and NaBr in DMSO, H_2O, and DMSO (1) + H_2O (2) Mixtures at Various Temperatures and Mass Fraction *w*

w_1	LiBr	NaBr	LiBr	NaBr
	25 °C		30 °C	
1.0	0.92944	0.83699	0.87964	0.80682
0.7	0.28130	0.26633	0.30064	0.27230
0.6	0.21167	0.20173	0.21560	0.21100
0.5	0.17868	0.16590	0.19890	0.18034
0.4	0.16664	0.13318	0.18203	0.15567
0.2	0.12651	0.08782	0.13643	0.10225
0.0	0.11482	0.05205	0.10913	0.05304
	35 °C		40 °C	
1.0	0.86298	0.78512	0.83111	0.75006
0.7	0.32641	0.27750	0.34250	0.28012
0.6	0.22087	0.21857	0.23022	0.22210
0.5	0.20745	0.18400	0.21496	0.19611
0.4	0.19405	0.14944	0.20003	0.17009
0.2	0.14354	0.11508	0.17006	0.15003
0.0	0.10752	0.05340	0.11009	0.0640
	45 °C			
1.0	0.81008	0.73681		
0.7	0.36740	0.29763		
0.6	0.24040	0.22222		
0.5	0.22550	0.19675		
0.4	0.21010	0.17080		
0.2	0.18000	0.15008		
0.0	0.11500	0.06401		

Table 4. It is found that the viscosity *B*-coefficient of the electrolytes in pure DMSO is large and positive. It is also noted that the viscosities of the solutions increase with an increase in the concentration of electrolytes. This is a common feature in most nonaqueous solvents like sulfolane (TMS);[20] hexamethylphosphotriamide (HMPT);[21] acetonitrile (AN);[22] propylene carbonate (PC);[23] tetramethylurea (TMU);[22] methanol;[24] *N*-methylformamide;[25] and ethylenecarbonate (EC);[26] and also in the mixtures of nonaqueous solvents.[27−29] The large and positive values of the viscosity *B*-coefficients indicate the structure-making effect of ions on the DMSO solvent. It is clear from the literature that in dipolar aprotic solvents[30] the structure breaking contribution is negligible due to the positive and large values of the *B*-coefficients that come from the tendency of the ions to attract the solvent molecules around themselves centrosymmetrically.

According to the literature,[31] the interaction energy between a small alkali metal ion and the solvent dipole in DMSO is at least six times greater than the solvent−solvent (DMSO−DMSO) interaction. The same effect is observed in the present study which shows that the interaction of small alkali metal ions, especially Li^+ and Na^+ with DMSO, is much stronger than the DMSO−DMSO interaction. These strong interactions immobilize neighboring DMSO molecules and produce large obstructions to their flow, which results in an increase in solution viscosity and causes large *B*-coefficient values which measure the structure-making contribution. The experimentally observed values of the viscosity *B*-coefficients (0.929 and 0.83699) dm^3·mol^{-1} for the salts LiBr and NaBr, respectively, in pure

Table 5. Comparison of Viscosity B/dm^3·mol^{-1} of electrolytes in DMSO with Literature Values at (25, 35, and 45) °C

	25 °C		35 °C		45 °C	
ions	lit.[a]	our	lit.[a]	our	lit.[a]	our
LiBr	0.907	0.929 ± 0.004	0.860	0.863 ± 0.002	0.82	0.810 ± 0.003
NaBr	0.833	0.837 ± 0.004	0.783	0.785 ± 0.001	0.739	0.737 ± 0.002

[a] Bicknell et al., ref 30.

Table 6. B/dm^3·mol^{-1} of Reference Salts Bu_4 $NBPh_4$ and Bu_4 NBr in DMSO at (25, 30, 35, 40, and 45) °C ± Standard Errors[a]

temperature	Bu_4 $NBPh_4$	Bu_4 NBr
25 °C	1.270 ± 0.001	0.901 ± 0.003
30 °C	1.265 ± 0.003	0.882 ± 0.002
35 °C	1.259 ± 0.002	0.876 ± 0.002
40 °C	1.254 ± 0.003	0.853 ± 0.002
45 °C	1.213 ± 0.002	0.835 ± 0.003

[a] Zamir, T. et al., ref 11.

DMSO are in good agreement with available literature values[32] at (25, 35, and 45) °C, and the direct comparisons of the B-coefficient values with literature data are shown in Table 5.

Studies of B-coefficients in binary solvent (DMSO + H_2O) mixtures tabulated in Table 4 show gradual and regular decreases in the values of the B-coefficients as the DMSO content is decreased. A decrease in B-coefficient values shows that the ions cause weaker orientation effects in the solvation layer. In the water-rich region, the values of the B-coefficients changed gradually with the solvent composition, and smaller B-values were then found in the DMSO−H_2O system. The same trend was observed in the study of KCl and KBr dissolved in H_2O−HMPT (hexamethyl phosphoric triamide) binary mixtures[16] and in another study of the salts NaCl, NaBr, NaI, and KCl in H_2O + DMSO mixtures.[33]

It was observed in Table 4 that in water the B-coefficients for LiBr and NaBr have small and positive values, which increase with an increase in the concentration of the electrolyte. This trend was also observed during the literature survey.[34] The present measurement of B-coefficients [(0.1148 ± 0.001) dm^3·mol^{-1}] for lithium bromide in pure water was in good agreement with 0.113 dm^3·mol^{-1}.[35,36] The values of the B-coefficients of the reference salts from our previous papers[10,11] are presented in Table 6, which also coincide with the literature values for similar substances.[37]

The values of B-coefficients for lithium bromide and sodium bromide in different compositions of DMSO were found to be positive and much higher than water. A solute with positive B-coefficients in a given solvent is considered to have a structure-making effect. On the other hand, it was observed that the values of the B-coefficients of lithium bromide and sodium bromide in different compositions of binary solvent mixtures and in pure water are less positive. A solute with less positive or negative B-coefficient values in a given solvent is considered as a structure-breaking solute. The present results indicate that in DMSO, LiBr and NaBr have positive B-coefficient values and behave as structure makers, while in H_2O and DMSO−H_2O mixtures, the B-coefficient values are less positive showing a weak structure-making effect.

Ionic B-Coefficients. To achieve a better understanding of ion−solvent interactions, it is necessary to split the B-coefficients into the individual ionic B-coefficients, B_+ and B_-. However, there is no experimental method related to viscosity, which separately determines the ionic B-coefficients. A number of methods have been suggested by various workers[31,35,36] to split B-coefficients of electrolytes into the contributions of the individual ions.

Most of these methods depend upon the choice of the reference salts for which cation−solvent and anion−solvent interactions may be considered equal. This criterion is realized for large polyatomic ions that are minimally solvated, so we chose tetrabutyl ammonium tetraphenyl borate and tetrabutyl ammonium bromide. In the present work, Gill and Sharma's approach,[37] similar to the method of Krumgalz,[35] was used to resolve viscosity B-coefficients into the contributions of individual ions. Studies by Gill et al.[38,39] confirm that the ionic radii of Bu_4N^+ and Ph_4B^- in nonaqueous solvents remain constant and equal to (5.00 and 5.35) Å, respectively, with an average uncertainty of ± 2 %.

The splitting of B into ionic $B_\pm$ have been resolved by the equation

$$\frac{B\mathrm{Ph_4B^-}}{B\mathrm{Bu_4N^+}} = \frac{r^3\mathrm{Ph_4B^-}}{r^3\mathrm{Bu_4N^+}} = \frac{(5.35)^3}{(5.00)^3} \qquad (3)$$

$$B(\exp)\mathrm{Bu_4NBPh_4} = B\mathrm{Ph_4B^-} + B\mathrm{Bu_4N^+} \qquad (4)$$

Using eqs 3 and 4, the B-coefficients have been divided into ionic B^+ and B^-. The values are shown in Table 7 which shows that the B^+ and B^- values for Bu_4N^+, Ph_4B^-, and Br^- ions increase gradually with an increase in electrolyte concentration.

The above method of splitting of electrolyte B-coefficients into ionic contributions is not applicable in aqueous solutions. Thus, Gurney's method[40] for aqueous solutions was used. This method simply assumes that the positive and negative ion contributions are simply equal and thus

$$B(\mathrm{K^+}) = B(\mathrm{Cl^-}) = 1/2B(\mathrm{KCl}) \qquad (5)$$

This subdivision cannot be applied in the case of organic solvents because the behavior of the ions in the nonaqueous solvents is entirely different.[41] The Gurney approach is used in the present study whenever water-rich solutions are involved. Many other researchers have adopted the same practice in their studies for water-rich solvent mixtures.[32] Using the Gurney approach, the values of the ionic B-coefficients for the ions (Li^+, Na^+, K^+, and Br^-) in pure water and in DMSO−H_2O mixtures at all five temperatures were obtained and are reported in Table 8.

In the DMSO + H_2O mixtures where the mass fraction of DMSO is 0.7, 0.6, 0.5, 0.4, and 0.2, the electrolyte has small positive ionic B-coefficient values indicating that all these electrolytes have a structure-breaking component. This character is due to the Br^- ion because it has smaller and negative ionic B-coefficient values in 0.4 and 0.2 DMSO + H_2O mixtures.

A complete comparison of the present study with the literature is not possible because of meager published ionic B-coefficient values for alkali bromides in DMSO + H_2O. The measured ionic B-coefficient values of the ions in water are in good agreement with the values already reported in the literature. In this study, it was observed that all the values of ionic B-coefficient of (Li^+ and Na^+) were positive and small showing the weak structure-making effects associated with the increase in ionic radius in DMSO + H_2O mixtures. It was observed that Br^- ions maintain negative B-coefficient values in all DMSO + H_2O mixtures, except in the 0.6 DMSO mass fraction. From this, it can be concluded that the Br^- ion behaved as a structure

Table 7. Ionic $B_\pm$ Coefficients of Ions in DMSO at (25, 30, 35, 40, and 45) °C ± Standard Error

	$B_\pm$/dm^3·mol^{-1}					
t/°C	$Bu_4\ N^+$	Li^+	Na^+	K^+	BPh_4^-	Br^-
25	0.5708 ± 0.002	0.5994 ± 0.001	0.5070 ± 0.002	0.5080 ± 0.001	0.6992 ± 0.002	0.3300 ± 0.002
30	0.5685 ± 0.003	0.5662 ± 0.003	0.4934 ± 0.002	0.4974 ± 0.001	0.6965 ± 0.003	0.3135 ± 0.001
35	0.5660 ± 0.001	0.5530 ± 0.003	0.4751 ± 0.004	0.4849 ± 0.001	0.6933 ± 0.002	0.3100 ± 0.002
40	0.5636 ± 0.001	0.54171 ± 0.003	0.4607 ± 0.002	0.4614 ± 0.002	0.6964 ± 0.001	0.2894 ± 0.003
45	0.5452 ± 0.002	0.5202 ± 0.002	0.4470 ± 0.002	0.4609 ± 0.003	0.6678 ± 0.001	0.2898 ± 0.002

Table 8. Ionic $B_\pm$ Coefficients of Ions in Mass Fractions w_1 at (25, 30, 35, 40, and 45) °C

	$B_\pm$/dm^3·mol^{-1}				
t/°C	Li^+	Na^+	K^+	Br^-	Cl^-
			$w_1 = 0.7$		
25	0.2380	0.2230	0.1902	0.0433	0.19017
30	0.2556	0.2272	0.1930	0.0450	0.19308
35	0.2797	0.2308	0.1960	0.0467	0.19600
40	0.2948	0.2324	0.1983	0.0477	0.19833
45	0.3182	0.2484	0.2007	0.0492	0.20071
			$w_1 = 0.6$		
25	0.1745	0.1646	0.163	0.03713	0.163
30	0.1771	0.1724	0.155	0.0386	0.1655
35	0.1809	0.1786	0.168	0.0400	0.168
40	0.1894	0.1812	0.170	0.0409	0.170
45	0.1982	0.1800	0.172	0.0422	0.172
			$w_1 = 0.5$		
25	0.1587	0.1459	0.1620	0.0200	0.1620
30	0.1863	0.1677	0.1640	0.0126	0.1640
35	0.1916	0.1681	0.1665	0.0159	0.1665
40	0.1976	0.1788	0.1685	0.0173	0.1685
45	0.2069	0.1782	0.1712	0.0186	0.1713
			$w_1 = 0.4$		
25	0.1557	0.12224	0.161	0.01094	0.1610
30	0.1956	0.1691	0.1625	−0.01300	0.1625
35	0.2023	0.1577	0.165	−0.08000	0.1650
40	0.2000	0.1764	0.167	−0.00629	0.1670
45	0.2156	0.1763	0.1705	−0.00500	0.1705
			$w_1 = 0.2$		
25	0.1490	0.11029	0.0730	−0.0225	0.6992
30	0.2294	0.19525	0.1005	−0.0930	0.6965
35	0.1570	0.1285	0.1250	−0.0130	0.6933
40	0.2143	0.1942	0.1850	−0.0440	0.6964
45	0.2454	0.2155	0.2155	−0.0650	0.6678
			$w_1 = 0.0$		
25	0.1491	0.08632	0.009	−0.0343	−0.009
30	0.1492	0.09307	−0.001	−0.0400	−0.001
35	0.1357	0.08160	0.004	0.0282	−0.040
40	0.1305	0.08443	0.009	−0.0204	−0.009
45	0.1290	0.07801	0.014	−0.0140	−0.014

breaker in water and in all DMSO + H_2O mixtures except in 0.6 DMSO mass fraction mixtures.

The low $B_\pm$ values of alkali metal ions and Br^- ions in water given in Table 8 are due to the breakdown of the tetrahedral structural of water and the formation of strongly structured solvated ion. It was observed that this behavior is more dominant in ions with larger ionic radius.[42]

Conclusion

The present study indicated that in DMSO, LiBr and NaBr having positive *B*-coefficient values behaved as a structure maker, while in water and DMSO + H_2O, *B*-coefficient values are less positive showing weak structure-making effect.

From this study, it is also concluded that Li^+ and Na^+ behaved as structure-makers in DMSO and all DMSO + H_2O mixtures, and in water, the structure-making effect is decreased with the increase in the composition of water. It was also observed that the Br^- ions maintain negative *B*-coefficient values in all DMSO + H_2O mixtures except in 60 % DMSO mole fraction. From this, it is concluded that the Br^- ion behaved as a structure breaker in H_2O and in all DMSO + H_2O mixtures except in 60 % DMSO mole fraction mixtures.

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