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Densities and Viscosities of Rubidium Bromide in Dimethyl Sulfoxide + Water Mixtures in the Temperature Range $t = (25 \text{ to } 45)^\circ\text{C}$

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The viscosities and densities of rubidium bromide were determined in dimethyl sulfoxide (DMSO) + H₂O mixtures of different compositions as a function of concentration [(0.01 to 0.06) mol·L⁻¹] and temperatures [(25 to 45) °C] to obtain the Jones–Dole *B*-coefficient. The positive values indicated that the salt behaved as a structure maker in DMSO, and in DMSO + H₂O mixtures, the *B*-coefficient values were less positive, showing a weak structure-making effect. On the other hand in H₂O, *B*-coefficient values of RbBr were negative, showing the structure-breaking ability.

Introduction

The process of solvation is of central importance in chemistry and has been the subject of numerous experimental and theoretical studies. The presence of a solvent influences the outcome of a chemical reaction through the interaction of the local environment with the individual species undergoing the reactions. The solvent, on one level, provides an energy bath for the stabilization of energetic products formed during reactions and provides physical barriers to the motion of the reactive species. On a more subtle level, the solvent perturbs the potential energy curves that govern these reactions. Solvation has been shown to be of fundamental importance in such diverse areas as biological activity and atmospheric processes.^{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 the ion–solvent interactions.⁶

In our previous papers, the emphasis was on two factors: (1) the variation of temperature and (2) the variation in concentration. The ion–solvent interaction studies of lithium bromide (LiBr) and other salts in dimethyl sulfoxide (DMSO), water, and DMSO + water at 25 °C and at various temperatures with their activation energies were reported.^{7,8} In continuation of this work, in this study the densities and viscosities of RbBr in DMSO + H₂O mixtures of different compositions are reported as functions of concentration and temperature.⁹ In the present study prominence is given to the size of ions, as the size of the rubidium ion is comparatively larger than the size of lithium and sodium. Therefore, viscosity measurements of solutions of rubidium bromide in DMSO, water, and DMSO + water mixtures are reported over the concentration range of 10⁻³ mol·L⁻¹ to near saturation. The effects of temperatures on

viscosities are also studied by changing the temperatures from (25 to 45) °C.

Experimental Section

DMSO, 99 % (Fluka), was stored over well-dried 5 Å molecular sieves for several days and then filtered. The solvent was distilled in the presence of P₂O₅. DMSO (1) + water (2) mixtures of mass fraction $w_1 = (0, 0.2, 0.4, 0.5, 0.6, 0.7, \text{ and } 1)$ corresponding to mole fractions of $x_1 = (0, 0.545, 0.133, 0.1874, 0.2570, 0.3499, \text{ and } 1)$ were prepared by mixing known masses of water and DMSO in glass-stoppered flasks.

RbBr was purified by recrystallization. The recrystallized electrolyte was dried at 150 °C for several hours prior to use. Owing to the hygroscopic nature of the bromides, the salt was stored in vacuum desiccators over P₂O₅¹⁰ for viscometer measurements. Bu₄NBPh₄ (Aldrich) was precipitated with water from acetone solution and dried at 70 °C. This salt was also recovered after a set of measurements by precipitation from the DMSO solution using water. Bu₄NBr was purified by the methods reported in our previous work.⁸ Tetrabutylammonium bromide (Aldrich) with a melting point of 103 °C was recrystallized from benzene and *n*-hexane. The recrystallized salt was dried at 120 °C for several hours prior to use.

Densities of the pure solvents (DMSO and H₂O) and of solvent mixtures (DMSO + H₂O) and of salt solutions were determined by using a specific density bottle of 15 cm³ volume calibrated by the methods reported in our previous work.⁸ The estimated uncertainty in the density measurements of solutions was $\pm 0.0001 \text{ g}\cdot\text{cm}^{-3}$ as reported earlier.¹¹

For viscosity measurements, an Ubbelohde type glass capillary tube suspended-level viscometer was used for all viscosity measurements. 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 diameter of 0.45 mm and was calibrated using distilled water, hexane, methanol, and acetone. Cleaning of the viscometer using a cleaning 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 $\pm 0.01^\circ\text{C}$. A Mettler

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balance (H202) was used for weighing purposes. Viscosity values were determined using the relationship:¹²

$$\eta = d(Kt - L/t) \quad (1)$$

where η is the viscosity, d is the density of the liquid, t is the flow time, and K and L are the constants for a given viscometer. Their estimated values are $K = 2.99395 \cdot 10^{-5} \text{ cm}^2 \cdot \text{s}^{-2}$ and $L = -0.89974 \text{ cm}^2$. At first 20 cm^3 of the reference liquid of accurately known viscosity η_1 was added 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 were obtained. The overall uncertainty in viscosity measurements was estimated to be $\pm 0.1 \%$.

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:

$$\frac{\eta_1}{\eta_2} = \frac{t_1 \rho_1}{t_2 \rho_2} \quad (2)$$

The absolute viscosities of the DMSO, H_2O , DMSO + H_2O mixtures, and their solutions with rubidium bromide were determined at 25°C . Viscosities were measured over a series of concentration for rubidium bromide, the lowest concentration being $0.01 \text{ mol} \cdot \text{L}^{-1}$ and the highest concentration about $0.06 \text{ mol} \cdot \text{L}^{-1}$, 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_0 are used to determine the relative viscosities η_r of the solution. 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_0) and viscosities (η_0) for DMSO, water (H_2O), and DMSO + H_2O mixtures containing $w_1 = (0, 0.2, 0.4, 0.5, 0.6, 0.7, \text{ and } 1) \%$ DMSO for temperatures of ($25, 30, 35, 40, \text{ and } 45^\circ\text{C}$) and the values of densities of pure water of this study are compared with the literature values and are reported in Table 1. The data used in this study for densities (ρ_0) and viscosities (η_0) of the pure solvents H_2O , DMSO, and DMSO + H_2O mixtures are the same as used in our previous study.⁹

A plot of densities (ρ_0) 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,¹⁴ water + dialkylated amide,¹⁵ and water + alcohol showed a sharp maximum or minimum in the plots of viscosity versus solvent compositions. It is observed that, at $w_1 = 0.60$ of DMSO, the viscosity of the DMSO + H_2O mixture is at its maximum.

Relative viscosities, viscosities, and the densities of RbBr have been measured in the concentration range of (0.01 to 0.06) $\text{mol} \cdot \text{dm}^{-3}$ in DMSO, H_2O , and DMSO + H_2O mixtures over the entire composition range and are reported in Table 2.

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

$$\eta_r = \eta/\eta_0 = 1 + Ac^{1/2} + Bc \quad (3)$$

In this equation, η and η_0 are the viscosities of the solution and the pure solvents or solvent mixtures, respectively; c is the

Table 1. Densities (ρ_0) and Viscosities (η_0) for DMSO, H_2O , and DMSO (1) + H_2O (2) Mixtures at Various Temperatures and Mass Fractions w

w_1	lit. (ref)	$\rho/\text{g} \cdot \text{cm}^{-3}$	$\eta/\text{mPa} \cdot \text{s}$
25 °C			
1.0	1.09580 ^a	1.09541	1.9660
0.7		1.08732	2.3568
0.6		1.08231	3.4210
0.5		1.06781	2.8073
0.4		1.05347	2.2210
0.2		1.02420	1.3400
0.0	0.99710 ^a	0.99715	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 ^b	0.9970	0.8003
35 °C			
1.0		1.08538	1.6523
0.7		1.08083	2.0813
0.6		1.07280	3.1050
0.5		1.05640	2.2802
0.4		1.04530	1.9210
0.2		1.01520	1.0537
0.0	0.99410 ^b	0.98366	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	0.9922 ^b	0.96841	0.6214
45 °C			
1.0		1.07450	1.4875
0.7		1.06712	1.8650
0.6		1.05710	2.7753
0.5		1.04752	1.9373
0.4		1.03801	1.4975
0.2		0.97920	0.8482
0.0	0.99022 ^b	0.95321	0.5346

^a Ref 15. ^b Ref 36.

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 the A and B coefficients, plots of $[(\eta - \eta_0)/\eta_0]c^{1/2}$ 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 intercepts and slopes of these plots by the least-squares method.

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

Table 3 also shows the B -coefficient values obtained at various temperatures for RbBr in all solvent mixtures mentioned above. It is found that the viscosity B -coefficient of the electrolyte RbBr in pure DMSO is positive. It is also noted that the viscosities of the solutions increase with an increase in the concentration of electrolyte. This is a common feature in most

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

$c/\text{mol}\cdot\text{dm}^{-3}$	$\rho/\text{g}\cdot\text{cm}^{-3}$	$\eta/\text{mPa}\cdot\text{s}$	η_r	$c/\text{mol}\cdot\text{dm}^{-3}$	$\rho/\text{g}\cdot\text{cm}^{-3}$	$\eta/\text{mPa}\cdot\text{s}$	η_r
RbBr $t = 25\text{ }^{\circ}\text{C}$							
$w_1 = 1.0$				$w_1 = 0.4$			
0.011	1.0969	1.9969	0.1507	0.013	1.05441	2.22435	0.0132
0.020	1.0983	2.0192	0.1911	0.014	1.05453	2.22462	0.0137
0.027	1.1001	2.0394	0.2284	0.019	1.05478	2.22610	0.0165
0.030	1.1004	2.0472	0.2384	0.021	1.05492	2.22681	0.0179
0.046	1.1025	2.0851	0.2566	0.025	1.05508	2.22784	0.0194
$w_1 = 0.7$				$w_1 = 0.2$			
0.015	1.08835	2.3992	0.1469	0.015	1.02422	1.34131	0.0059
0.021	1.08847	2.4086	0.1531	0.020	1.02426	1.34172	0.0073
0.026	1.08859	2.4159	0.1562	0.024	1.02428	1.34196	0.0078
0.032	1.08871	2.4242	0.1610	0.026	1.02429	1.34204	0.0078
0.049	1.08886	2.4460	0.1701	0.033	1.02433	1.34232	0.0081
$w_1 = 0.6$				$w_1 = 0.0$			
0.011	1.08255	3.42548	0.0179	0.010	0.99669	0.89301	0.0341
0.015	1.08278	3.42954	0.0212	0.013	0.99684	0.89349	0.0331
0.021	1.08301	3.43282	0.0251	0.020	0.99703	0.89526	0.0310
0.023	1.08320	3.43559	0.0271	0.025	0.99728	0.89616	0.0299
0.028	1.08345	3.43708	0.0304	0.038	0.99779	0.89657	0.0276
$w_1 = 0.5$							
0.016	1.06453	2.90397	0.2701				
0.021	1.06470	2.91691	0.2723				
0.026	1.06489	2.93108	0.2746				
0.032	1.06495	2.94530	0.2769				
0.046	1.06508	2.97764	0.2841				
RbBr $t = 30\text{ }^{\circ}\text{C}$							
$w_1 = 1.0$				$w_1 = 0.4$			
0.011	1.09254	1.83920	0.1597	0.013	1.05449	2.22430	0.0130
0.020	1.09771	1.86052	0.2012	0.014	1.05453	2.22462	0.0137
0.026	1.10691	1.87657	0.2284	0.019	1.05478	2.22622	0.0169
0.030	1.11093	1.88439	0.2404	0.021	1.05482	2.22681	0.0179
0.056	1.13493	1.92274	0.2663	0.025	1.05502	2.22784	0.0194
$w_1 = 0.7$				$w_1 = 0.2$			
0.016	1.08733	2.36306	0.2590	0.015	1.01994	1.33214	0.0059
0.023	1.08742	2.38082	0.2652	0.020	1.02007	1.33255	0.0073
0.038	1.08754	2.41079	0.2741	0.024	1.02018	1.33278	0.0078
0.045	1.08765	2.42317	0.2787	0.026	1.02028	1.33286	0.0079
0.056	1.08778	2.44225	0.2851	0.033	1.02036	1.33315	0.0081
$w_1 = 0.6$				$w_1 = 0.0$			
0.011	1.08259	3.42753	0.0179	0.010	0.99608	0.89341	0.0328
0.015	1.08273	3.42989	0.0212	0.013	0.99608	0.89373	0.0314
0.021	1.08300	3.43381	0.0261	0.020	0.99614	0.89427	0.0301
0.023	1.08305	3.43527	0.0273	0.025	0.99617	0.89457	0.0294
0.028	1.08333	3.43849	0.0304	0.038	0.99624	0.89503	0.0272
$w_1 = 0.5$							
0.016	1.06452	2.54777	0.2655				
0.023	1.06469	2.56633	0.2690				
0.038	1.06479	2.59874	0.2773				
0.045	1.06490	2.61117	0.2800				
0.056	1.06494	2.63054	0.2842				
RbBr $t = 35\text{ }^{\circ}\text{C}$							
$w_1 = 1.0$				$w_1 = 0.4$			
0.011	1.08775	1.68165	0.1699	0.013	1.04610	1.92616	0.0235
0.024	1.08877	1.70051	0.2061	0.014	1.04613	1.92654	0.0244
0.027	1.08897	1.71230	0.2221	0.015	1.04620	1.92695	0.0249
0.030	1.08997	1.72189	0.2430	0.020	1.04634	1.92855	0.0275
0.056	1.09197	1.75852	0.2723	0.025	1.04652	1.93027	0.0305
$w_1 = 0.7$				$w_1 = 0.2$			
0.016	1.08485	2.14670	0.2483	0.014	1.01546	1.05511	0.0101
0.021	1.08490	2.15660	0.2526	0.020	1.01558	1.05539	0.0112
0.023	1.08498	2.16097	0.2541	0.024	1.01566	1.05558	0.0114
0.032	1.08512	2.17779	0.2610	0.026	1.01574	1.05568	0.0115
0.049	1.08533	2.20682	0.2712	0.033	1.01578	1.05596	0.0127
$w_1 = 0.6$				$w_1 = 0.0$			
0.011	1.07485	3.11561	0.0322	0.010	0.98987	0.76213	0.0390
0.014	1.07495	3.11866	0.0367	0.013	0.98989	0.76245	0.0380
0.020	1.07505	3.12250	0.0398	0.020	0.98999	0.76315	0.0372
0.023	1.07514	3.12469	0.0418	0.024	0.99003	0.76352	0.0370
0.028	1.07514	3.12880	0.0458	0.035	0.99013	0.76428	0.0360
$w_1 = 0.5$							
0.009	1.05461	2.30925	0.1334				
0.013	1.05478	2.31488	0.1359				
0.023	1.05482	2.32940	0.1425				
0.029	1.05499	2.38774	0.1473				
0.036	1.05535	2.34538	0.1503				

Table 2. Continued

$c/\text{mol}\cdot\text{dm}^{-3}$	$\rho/\text{g}\cdot\text{cm}^{-3}$	$\eta/\text{mPa}\cdot\text{s}$	η_r	$c/\text{mol}\cdot\text{dm}^{-3}$	$\rho/\text{g}\cdot\text{cm}^{-3}$	$\eta/\text{mPa}\cdot\text{s}$	η_r
RbBr $t = 40\text{ }^{\circ}\text{C}$							
$w_1 = 1.0$				$w_1 = 0.4$			
0.011	1.08775	1.58693	0.1726	0.013	1.04016	1.61823	0.0233
0.020	1.08877	1.60428	0.2061	0.014	1.04023	1.61824	0.0244
0.028	1.08977	1.61541	0.2221	0.015	1.04031	1.61825	0.0252
0.030	1.08997	1.61986	0.2259	0.020	1.04053	1.61826	0.0281
0.046	1.09197	1.65900	0.2722	0.025	1.04072	1.61829	0.0305
$w_1 = 0.7$				$w_1 = 0.2$			
0.016	1.07874	1.99050	0.2606	0.014	0.99904	0.95836	0.0101
0.021	1.07883	2.00037	0.2653	0.020	1.00558	0.95873	0.0112
0.024	1.07896	2.00653	0.2676	0.024	1.00966	0.95891	0.0115
0.032	1.07905	2.04893	0.2729	0.026	1.01118	0.95909	0.0122
0.049	1.07911	2.04751	0.2842	0.033	1.01707	0.95942	0.0127
$w_1 = 0.6$				$w_1 = 0.0$			
0.011	1.06885	2.85583	0.0322	0.010	0.96949	0.76213	0.0389
0.014	1.06895	2.85863	0.0367	0.013	0.96956	0.76245	0.0379
0.020	1.06905	2.86214	0.0397	0.020	0.96968	0.76315	0.0372
0.023	1.06914	2.86421	0.0419	0.024	0.96974	0.76352	0.0369
0.028	1.06924	2.86792	0.0457	0.035	0.96997	0.76418	0.0352
$w_1 = 0.5$							
0.016	1.05729	2.17601	0.1349				
0.021	1.05733	2.18156	0.1369				
0.024	1.05748	2.18565	0.1399				
0.032	1.05760	2.19467	0.1450				
0.049	1.05779	2.21190	0.1520				
RbBr $t = 45\text{ }^{\circ}\text{C}$							
$w_1 = 1.0$				$w_1 = 0.4$			
0.011	1.09642	1.51502	0.1770	0.013	1.03854	1.50158	0.0235
0.020	1.09652	1.53091	0.2061	0.014	1.03855	1.50188	0.0244
0.027	1.09658	1.54152	0.2221	0.015	1.03856	1.50219	0.0249
0.030	1.09660	1.54934	0.2384	0.020	1.03861	1.50345	0.0275
0.056	1.09690	1.58094	0.2725	0.025	1.03865	1.50495	0.0312
$w_1 = 0.7$				$w_1 = 0.2$			
0.016	1.07860	1.92492	0.2540	0.014	0.97970	0.85041	0.0216
0.021	1.07862	1.93375	0.2575	0.020	0.97987	0.85114	0.0244
0.023	1.07863	1.93786	0.2594	0.024	0.98002	0.85167	0.0263
0.032	1.07865	1.95301	0.2657	0.026	0.98014	0.85222	0.0291
0.049	1.07867	1.98003	0.2775	0.033	0.98028	0.85291	0.0304
$w_1 = 0.6$				$w_1 = 0.0$			
0.011	1.06011	2.78480	0.0322	0.010	0.95683	0.53673	0.0382
0.014	1.06031	2.78754	0.0367	0.013	0.95695	0.53700	0.0378
0.020	1.06051	2.79096	0.0398	0.020	0.95764	0.53751	0.0374
0.023	1.06071	2.79292	0.0418	0.024	0.95831	0.53777	0.0372
0.028	1.06091	2.79686	0.0463	0.034	0.95944	0.53832	0.0363
$w_1 = 0.5$							
0.019	1.04954	1.97273	0.1340				
0.025	1.04959	1.97938	0.1370				
0.032	1.04961	1.98663	0.1421				
0.041	1.04964	1.99464	0.1459				
0.049	1.04967	2.00183	0.1500				

nonaqueous solvents^{16–19} and also in the mixtures of nonaqueous solvents.^{20–22} The large and positive values of 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,²³ the structure-breaking contribution is negligible because of the positive and large values of the B -coefficients that come from the tendency of the ions to attract the solvent molecules.

The experimentally pragmatic values of the viscosity B -coefficients of RbBr in the present study are smaller than the values of the viscosity B -coefficients of the salts LiBr and NaBr observed in our previous study.⁹ The estimated values of the viscosity B -coefficients of RbBr in pure DMSO are in good agreement with the available literature values¹⁶ at (25, 35, and 45) $^\circ\text{C}$, and direct comparisons of the B -coefficient values with the literature are shown in Table 3.

The studies of B -coefficients in binary solvent (DMSO + H_2O) mixtures tabulated in Table 3 show gradual and regular decreases in the values of the B -coefficients as the DMSO

content is decreased. A decrease in B -coefficient values show that the ions cause weaker orientation effects in the solvation layer. In the water-rich region the values of B -coefficients change gradually with the solvent composition, and smaller B -values were then found in 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 mixtures²⁴ and in another study of the salts NaCl, NaBr, NaI, and KCl in H_2O + DMSO mixtures.²⁵

It was observed in Table 3 that in water the B -coefficients for RbBr have small and negative values. It is well-known that, in highly structured solvents, salts like CsBr, CsI, KBr, and KI cause B -coefficients to be negative.²⁶ The solvents in which negative B values are found^{26,27} all have molecules capable of forming hydrogen bonding in three dimensions, and water is the prime example. The values of the B -coefficients of the reference salts from our previous papers^{8,9} are presented in Table 4, which also coincide with the literature values for similar substances.²⁸

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

w_1	$A \cdot 10^2$ ($\text{dm}^{3/2} \cdot \text{mol}^{-1/2}$)	B ($\text{dm}^3 \cdot \text{mol}^{-1}$)	$B/\text{dm}^3 \cdot \text{mol}^{-1}$ (lit. ^a)
25 °C			
1.0	0.0671	0.82867	0.822
0.7	0.1194	0.22992	
0.6	−0.0034	0.19992	
0.5	0.2491	0.16121	
0.4	−0.0032	0.14284	
0.2	−0.0017	0.03696	
0.0	−0.0409	−0.06815	
30 °C			
1.0	0.0783	0.80011	
0.7	0.2292	0.23395	
0.6	−0.0036	0.20306	
0.5	0.2430	0.17423	
0.4	−0.0038	0.14710	
0.2	0.0016	0.03752	
0.0	0.0373	−0.05073	
35 °C			
1.0	0.7796	0.77957	0.779
0.7	0.2183	0.23871	
0.6	0.0108	0.20683	
0.5	0.1158	0.18084	
0.4	0.0062	0.15142	
0.2	0.0056	0.03803	
0.0	−0.0319	−0.03192	
40 °C			
1.0	0.0978	0.74503	
0.7	0.2303	0.24192	
0.6	0.2074	0.20743	
0.5	0.1115	0.18365	
0.4	0.1578	0.15779	
0.2	0.0421	0.04211	
0.0	0.0051	−0.04000	
45 °C			
1.0	0.1034	0.73208	0.744
0.7	0.2225	0.24599	
0.6	0.0100	0.21403	
0.5	0.1077	0.18928	
0.4	0.0046	0.16500	
0.2	0.0035	0.15010	
0.0	0.0403	−0.02105	

^a Bicknell et al., ref 23.**Table 4.** $B/\text{dm}^3 \cdot \text{mol}^{-1}$ of Reference Salts Bu_4NBPh_4 and Bu_4NBr in DMSO at (25, 30, 35, 40, and 45) °C \pm Standard Error^a

temperature	Bu_4NBPh_4	Bu_4NBr
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 et al., ref 8.

A solute with less positive or negative B -coefficient values in a given solvent is considered as a weak structure-making or a structure-breaking solute, respectively. The present results indicate that, in DMSO, RbBr having positive B -coefficient values behaves as a structure maker, while in DMSO– H_2O mixtures, the B -coefficient values are less positive showing the weak structure-making effect, and in H_2O B -coefficient values are negative. Therefore, RbBr has a structure-breaking effect in H_2O .

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^{29–31} 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 the tetrabutyl ammonium tetraphenyl borate and tetrabutyl ammonium bromide. In the present work Gill and Sekhri's approach,³² similar to the method of Krumgalz,²⁷ is used to resolve viscosity B -coefficients into the contributions of individual ions. Studies by Gill et al.^{31,32} confirm that the ionic radii of Bu_4N^+ and Ph_4B^- in nonaqueous solvents remain constant and are equal to (5.00 and 5.35) Å, respectively, with an average uncertainty of $\pm 2\%$.

The splitting of B into ionic B_{\pm} has been resolved by the equation

$$\frac{B\text{Ph}_4\text{B}^-}{B\text{Bu}_4\text{N}^+} = \frac{r^3\text{Ph}_4\text{B}^-}{r^3\text{Bu}_4\text{N}^+} = \frac{(5.35)^3}{(5.00)^3} \quad (4)$$

$$B(\text{exp})\text{Bu}_4\text{NBPh}_4 = B\text{Ph}_4\text{B}^- + B\text{Bu}_4\text{N}^+ \quad (5)$$

Using eqs 2 and 3, the B -coefficients have been divided into ionic B^+ and B^- . The values are shown in Table 5 which shows that the B^+ and B^- values for Bu_4N^+ , Ph_4B^- , and Br^- ions increased gradually with an increase in electrolyte concentration.

This above method of splitting of electrolyte B -coefficients into ionic contributions is not applicable in aqueous solutions. Gurney's method³³ for aqueous solution was thus used. This method simply assumes that the positive and negative ion contributions are simply equal and thus:

$$B(\text{K}^+) = B(\text{Cl}^-) = (1/2)B(\text{KCl}) \quad (6)$$

This subdivision cannot be applied in the case of organic solvents because the behavior of the ions in the nonaqueous solvents is entirely different.³⁴ 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.²⁴ Using the Gurney approach, the values of the ionic B -coefficients for the ions (Rb^+ , K^+ , and Br^-) in pure water and in DMSO– H_2O mixtures at all five temperatures were obtained and are reported in Table 6. (The reference source for the data was used to calculate the values for K^+ , and Cl^- is the viscosity B -coefficient values of KCl, determined from the relative viscosities of KCl.)

In DMSO + H_2O mixtures where the mass fraction of DMSO is 1, 0.7, 0.6, 0.5, 0.4, and 0.2, the electrolyte has small positive ionic B -coefficient values, indicating that all of these electrolytes have a structure-breaking component. This character has also come into the view because of 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. It observed that Rb^+ has a structure-disrupting influence so that the viscosity of the solution is reduced and negative ionic B -values appear. Br^- ions also maintain negative B -coefficient values in all DMSO + H_2O mixtures where water is in excess as in 0.4 and 0.2 DMSO mass fraction and in water. From this, it can be concluded that B -values of the Br^- ion are small in all solutions

Table 5. Ionic B_{\pm} Coefficients of Ions in DMSO at (25, 30, 35, 40, and 45) °C \pm Standard Error

$t/^{\circ}\text{C}$	$B_{\pm}/\text{dm}^3\cdot\text{mol}^{-1}$				
	Bu_4N^+	K^+	Rb^+	BPh_4^-	Br^-
25	0.5708 ± 0.002	0.5080 ± 0.001	0.499 ± 0.003	0.6992 ± 0.002	0.3300 ± 0.002
30	0.5685 ± 0.003	0.4974 ± 0.001	0.488 ± 0.001	0.6965 ± 0.003	0.3135 ± 0.001
35	0.5660 ± 0.001	0.4849 ± 0.001	0.469 ± 0.003	0.6933 ± 0.002	0.3100 ± 0.002
40	0.5636 ± 0.001	0.4614 ± 0.002	0.455 ± 0.003	0.6964 ± 0.001	0.2894 ± 0.003
45	0.5452 ± 0.002	0.4609 ± 0.003	0.442 ± 0.001	0.6678 ± 0.001	0.2898 ± 0.002

Table 6. Ionic B_{\pm} Coefficients of Ions in Mass Fractions w_1 at (25, 30, 35, 40, and 45) °C

$t/^{\circ}\text{C}$	$B_{\pm}/\text{dm}^3\cdot\text{mol}^{-1}$			
	K^+	Rb^+	Br^-	Cl^-
$w_1 = 0.7$				
25	0.1902	0.1866	0.0433	0.19017
30	0.1930	0.1889	0.0450	0.19308
35	0.1960	0.1920	0.0467	0.19600
40	0.1983	0.1942	0.0477	0.19833
45	0.2007	0.1967	0.0492	0.20071
$w_1 = 0.6$				
25	0.163	0.1628	0.0371	0.163
30	0.155	0.1645	0.0386	0.1655
35	0.168	0.1668	0.0400	0.168
40	0.170	0.1666	0.0409	0.170
45	0.172	0.1718	0.0422	0.172
$w_1 = 0.5$				
25	0.1620	0.1442	0.0200	0.1620
30	0.1640	0.1616	0.0126	0.1640
35	0.1665	0.1650	0.0159	0.1665
40	0.1685	0.1664	0.0173	0.1685
45	0.1712	0.1707	0.0186	0.1713
$w_1 = 0.4$				
25	0.161	0.1319	0.0109	0.1610
30	0.1625	0.1605	-0.0130	0.1625
35	0.165	0.1597	-0.0800	0.1650
40	0.167	0.1641	-0.0063	0.1670
45	0.1705	0.1705	-0.0050	0.1705
$w_1 = 0.2$				
25	0.0730	0.0594	-0.0225	0.6992
30	0.1005	0.1305	-0.0930	0.6965
35	0.1250	0.0515	-0.0130	0.6933
40	0.1850	0.0863	-0.0440	0.6964
45	0.2155	0.0669	-0.0650	0.6678
$w_1 = 0.0$				
25	0.009	-0.0362	0.0343	-0.009
30	-0.001	-0.0901	-0.0400	-0.001
35	0.004	-0.0610	0.0282	-0.040
40	0.009	-0.0604	-0.0204	-0.009
45	0.014	-0.0351	-0.0140	-0.014

at all temperatures; therefore, the Br^- ion behaves as a structure breaker in all of the solutions.

The low B_{\pm} values of alkali metal ions and Br^- ions in water given in Table 6 are due to the breakdown of the tetrahedral structural of water and the formation of strongly structured solvated ion. It is observed that this behavior is more dominant in ions with a larger ionic radius.³⁵

Conclusion

The present study indicated that, in DMSO, RbBr having positive B -coefficient values behaved as a structure maker, while in $\text{DMSO} + \text{H}_2\text{O}$, B -coefficient values are less positive, showing a weak structure-making effect. On the other hand, in water, RbBr , having negative B -coefficient values, behaved as a structure breaker in DMSO and all $\text{DMSO} + \text{H}_2\text{O}$ mixtures. The structure-making effect is decreased with the increase in the composition of water.

It is concluded that Rb^+ behaved as structure maker in DMSO because of the positive values of ionic B -coefficients, and in

all $\text{DMSO} + \text{H}_2\text{O}$ mixtures the structure-making effect is decreased with the increase in the composition of H_2O . It is observed that the Br^- ions maintain small negative B -coefficient values in all $\text{DMSO} + \text{H}_2\text{O}$ 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 $\text{DMSO} + \text{H}_2\text{O}$ mixtures except in 60 % DMSO mole fraction mixtures.

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