J. Chem. Eng. Data **2008,** *53,* 667–669

Viscosity *B* Coefficients and Partial Molar Volumes of Tetrabutylammonium Bromide in γ-Butyrolactone + Water at Different Temperatures

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Densities and viscosities of solutions of tetrabutylammonium bromide have been measured in γ-butyrolactone + water mixtures at various temperatures, (298.15, 303.15, 308.15, 313.15, and 318.15) K. The viscosity data have been analyzed using the Jones−Dole equation. The density data have been utilized to calculate apparent molar volumes, V_φ, and partial molar volumes at infinite dilution, $V_\varphi{}^0$. The behavior of these parameters has been used to investigate the solute–solute and solute–solvent interactions.

Introduction

The volumetric and viscometric behavior of electrolytes has proved to be very useful in understanding the nature of ion–solvent interactions in aqueous and nonaqueous solutions. These properties are important in many industrial problems concerning energy transport, mass transport, and fluid flow. The apparent molar volumes and viscosity *B* coefficients of tetraalkylammonium (R_4NX) salts have been investigated extensively in aqueous and nonaqueous solutions and water−organic solvent mixtures.[1–5] In recent years, much attention has been given to the solvent γ-butyrolactone for industrial and electrochemical processes. Therefore, in this work we present the experimental density and viscosity data of tetrabutylammonium bromide in γ-butyrolactone + water mixed solvent at various temperatures, (298.15, 303.15, 308.15, 313.15, and 318.15) K. The experimental density data were used to calculate the apparent molar volumes, $V_\varphi{}^0$, and the viscosity data for determining the *A* and *B* coefficients of the Jones−Dole equation.

Experimental Section

Materials. γ-Butyrolactone (γ-BL) (0.99 mass fraction purity) was obtained from Fluka Chemie AG and used without further purification but kept over freshly activated molecular sieves of type 4A (Union Carbide) and filtered before use. Tetrabutylammonium bromide (TBAB) pure grade obtained from Fluka Chemie AG was subjected to drying over P_2O_5. The water was deionized and doubly distilled. Its specific conductivity was $< 1 \cdot 10^{-6}\ \mathrm{S \cdot cm^{-1}}$. Density and viscosity of pure γ-butyrolactone were found in good agreement with the literature values.[6,7] All the binary aqueous mixtures of γ-BL as well as the solutions of TBAB were made by weight, and molalities, *m*, were converted into molarities, *c*, using the standard expression $c = 1000\rho/(1000 + mM)$, where ρ is the solution density and *M* is the molar mass of TBAB.

Apparatus and Procedure. Densities were measured with a digital precision densimeter DMA60/602 (Anton Paar). An AVS 300 viscosity measurement unit (Schott-Gerate) equipped with an electronic counter for viscous flow time was used to measure the viscosity. Details of the two systems and the calibration procedures were adequately covered in previous work.[6] The overall precision of the density measured is estimated to be better than $\pm\ 2 \cdot 10^{-5}\ \mathrm{g \cdot cm^{-3}}$. The efflux time of the fluid was measured to ± 0.01 s. For all measurements, a Schott-Gerate CT1150 thermostat was used at a constant digital temperature control of ± 0.01 K at the desired temperature.

Table 1. Concentration, *c*, and Densities, ρ, of TBAB in γ-BL + Water at Various Temperatures

	$\rho/\mathrm{g \cdot cm^{-3}}$ at *T*/K				
$c/\mathrm{mol \cdot L^{-1}}$	298.15	303.15	308.15	313.15	318.15
	10 % γ-BL + 90 % water				
0.009	1.01211	1.00901	1.00601	1.00501	1.00312
0.019	1.01441	1.01302	1.00795	1.00682	1.00462
0.033	1.01602	1.01442	1.00954	1.00724	1.00481
0.041	1.01822	1.01599	1.01051	1.00778	1.00523
0.052	1.01985	1.01728	1.01349	1.00902	1.00729
0.061	1.02098	1.01889	1.01598	1.01112	1.00937
0.075	1.02302	1.02002	1.01812	1.01309	1.01221
0.087	1.02876	1.02208	1.01996	1.01511	1.01446
0.101	1.02885	1.02459	1.02284	1.01729	1.01655
0.139	1.03577	1.02941	1.02851	1.02239	1.01822
	20 % γ-BL + 80 % water				
0.012	1.01221	1.00901	1.00922	1.00629	1.00597
0.018	1.01332	1.01023	1.01044	1.00721	1.00698
0.032	1.01458	1.01322	1.01154	1.00855	1.00768
0.049	1.01488	1.01485	1.01401	1.01101	1.00923
0.064	1.01605	1.01525	1.01501	1.01214	1.01123
0.081	1.01722	1.01577	1.01562	1.01345	1.01199
0.095	1.01778	1.01621	1.01677	1.01466	1.01322
0.103	1.01809	1.01722	1.01724	1.01555	1.01446
0.130	1.02124	1.01933	1.01805	1.01769	1.01668
	30 % γ-BL + 70 % water				
0.016	1.01449	1.01285	1.01149	1.01109	1.01101
0.022	1.01463	1.01299	1.01163	1.01123	1.01115
0.029	1.01987	1.01485	1.01211	1.01191	1.01153
0.041	1.02001	1.01499	1.01225	1.01204	1.01167
0.045	1.02341	1.02209	1.01231	1.01201	1.01166
0.051	1.02631	1.02541	1.01244	1.01201	1.01198
0.069	1.02644	1.02555	1.01258	1.01214	1.01212
0.083	1.02998	1.02005	1.01831	1.01625	1.01407
0.092	1.03012	1.03019	1.01844	1.01639	1.01511
0.110	1.03026	1.03033	1.01858	1.01653	1.01525

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10.1021/je7004903 CCC: $40.75

Table 2. Concentration, c, and Viscosities, η, for TBAB in γ-BL + Water at Various Temperatures

	η/mPa·s at T/K				
c/mol·L^{-1}	298.15	303.15	308.15	313.15	318.15
	10 % γ-BL + 90 % water				
0.009	0.985	0.876	0.791	0.718	0.656
0.019	1.002	0.892	0.801	0.726	0.663
0.033	1.019	0.907	0.814	0.737	0.669
0.041	1.033	0.915	0.821	0.744	0.675
0.052	1.044	0.928	0.832	0.751	0.693
0.061	1.052	0.939	0.842	0.756	0.689
0.075	1.071	0.995	0.854	0.768	0.699
0.087	1.088	0.971	0.866	0.779	0.7096
0.101	1.106	0.986	0.899	0.788	0.717
0.139	1.159	1.033	0.916	0.821	0.741
	20 % γ-BL + 80 % water				
0.012	1.133	1.008	0.912	0.843	0.783
0.018	1.145	1.019	0.923	0.853	0.795
0.032	1.162	1.036	0.935	0.865	0.805
0.049	1.181	1.053	0.952	0.879	0.817
0.064	1.199	1.068	0.965	0.892	0.828
0.081	1.218	1.085	0.979	0.905	0.842
0.095	1.235	1.101	0.993	0.917	0.851
0.103	1.245	1.109	1.001	0.924	0.857
0.130	1.279	1.138	1.024	0.947	0.878
	30 % γ-BL + 70 % water				
0.016	1.269	1.129	1.009	0.913	0.831
0.022	1.278	1.138	1.021	0.919	0.839
0.029	1.293	1.149	1.027	0.929	0.845
0.041	1.308	1.161	1.039	0.935	0.853
0.045	1.319	1.176	1.043	0.939	0.856
0.051	1.333	1.186	1.049	0.946	0.861
0.069	1.355	1.207	1.065	0.961	0.872
0.083	1.377	1.216	1.084	0.975	0.884
0.092	1.391	1.239	1.093	0.984	0.889
0.110	1.411	1.258	1.107	1.000	0.901

Results and Discussion

The measured densities (ρ) and viscosities (η) for tetrabutylammonium bromide in aqueous solutions of γ-butyrolactone at various temperatures, (298.15, 303.15, 308.15, 313.15, and 318.15) K, are presented in Tables 1 and 2, respectively. The experimental data of densities were used to calculate the apparent molar volumes of TBAB in aqueous solutions of γ-BL using the following equation

$$V_\varphi = 1000(\rho_o - \rho)/c\rho_o + M/\rho_o \tag{1}$$

where ρ_o and ρ are the densities of the aqueous solutions of γ-BL and the solution of TBAB + γ-BL + water, respectively; c is the molar concentration of TBAB; and M is the molar mass. The partial molar volume, $V_\varphi{}^0$, at infinite dilution was calculated using a least-squares treatment of plots of V_φ versus $c^{1/2}$ using the following equation[2]

$$V_\varphi = V_\varphi{}^0 + S_v{}^* c^{1/2} \tag{2}$$

where $V_\varphi{}^0$ is the partial molar volume at infinite dilution and $S_v{}^*$ is the experimental slope. The obtained values of $V_\varphi{}^0$ and $S_v{}^*$ for all ternary mixtures studied at different temperatures are presented in Table 3. Table 3 shows that $V_\varphi{}^0$ values are large and positive for all ternary mixtures studied and decrease with increasing mass percent of γ-BL in the γ-BL + water mixed solvent. This is mainly attributed to the stronger hydrogen bonding between the carbonyl oxygen of γ-BL and water molecules.[8] Therefore, ion–solvent interactions are weakened with the increase in the mass % of γ-BL in the γ-BL + water solvent. However, $V_\varphi{}^0$ values increase with increasing temperature due to the reduction in electrostriction that occurs.

Table 3. Values of Partial Molar Volume, $V_\varphi{}^0$, and Experimental Slope, $S_v{}^*$ of TBAB in γ-BL + Water at Various Temperatures

T	$V_\varphi{}^0$	$S_v{}^*$
K	cm^3·mol^{-1}	cm^3·L$^{1/2}$·mol$^{-3/2}$
	10 % γ-BL + 90 % water	
298.15	130.78	1.98
303.15	147.92	1.91
308.15	166.77	1.69
313.15	213.59	1.67
318.15	225.68	1.47
	20 % γ-BL + 80 % water	
298.15	106.77	1.46
303.15	119.56	1.37
308.15	144.73	1.28
313.15	195.48	1.27
318.15	204.84	1.01
	30 % γ-BL + 70 % water	
298.15	11.58	0.88
303.15	20.88	0.64
308.15	33.62	0.58
313.15	34.11	0.44
318.15	34.84	0.28

Table 4. Values of A and B Parameters of the Jones−Dole Equation for TBAB in γ-BL + Water at Various Temperatures

T/K	A/dm^3·mol$^{-1/2}$	B/dm^3·mol^{-1}
	pure water	
298.15	0.008	1.15
303.15	0.004	1.13
308.15	0.003	1.12
	10 % γ-BL + 90 % water	
298.15	0.006	1.60
303.15	0.024	1.30
308.15	0.036	1.27
313.15	0.012	1.17
318.15	0.011	1.16
	20 % γ-BL + 80 % water	
298.15	0.012	0.96
303.15	0.014	0.90
308.15	0.020	0.78
313.15	0.027	0.75
318.15	0.042	0.42
	10 % γ-BL + 70 % water	
298.15	0.001	0.01
303.15	0.001	0.02
308.15	0.001	0.01
313.15	0.001	0.01
318.15	0.001	0.01

The $S_v{}^*$ values, given in Table 3 for all mixtures, are found to be positive but smaller than $V_\varphi{}^0$ values, suggesting the presence of weak ion–ion interactions. With an increase in temperature, the $S_v{}^*$ values decrease, and this is attributed to violent thermal agitation, resulting in diminishing of the force of ion–ion interactions, as the mass % of BL in the γ-BL + water mixed solvent increases. The trend of $S_v{}^*$ supports the behavior of $V_\varphi{}^0$.

The relative viscosities of tetrabutylammonium bromide in γ-BL + water mixtures were calculated using the Jones−Dole equation.[9]

$$\eta_{\mathrm{rel}} = \frac{\eta}{\eta_o} = 1 + Ac^{1/2} + Bc \tag{3}$$

where η and η_o are the viscosities of the solution and the solvent, respectively, and c is the concentration in molarity. A is the Falkenhagen coefficient depending on the long-range Coulombic forces related to ion–ion interactions, and B is an adjustable parameter related to the size of the ions and ion–solvent interactions.

The values of *A* and *B* coefficients obtained at various temperatures, (298.15, 303.15, 308.15, 313.15, and 318.15) K, using a least-squares method are given in Table 4. The values of the *B* coefficients are positive and larger than *A*. It is observed that *B* for TBAB in γ-BL + water is larger than *B* for TBAB in pure water,[5] and this suggests that addition of γ-BL to water enhances the solute−solvent interactions but weakens with increasing mass % of γ-BL in water, due to the strong hydrogen bonding between the carbonyl oxygen of γ-BL and water molecules. The *B* coefficients decrease as the mass % of γ-BL increases and also with a rise in temperature, thus indicating the weakest ionic solvation for the TBAB salt. On the basis of the above assumptions, the solute–solvent interactions are weakened by the most structured state of the γ-BL−water solvent.

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Received for review August 29, 2007. Accepted December 28, 2007.

JE7004903