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Viscosities, Densities, and Ultrasonic Velocities of Binary Mixtures of Ethylbenzene with Ethanol, 1-Propanol, and 1-Butanol at (298.15 and 308.15)K

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The viscosities, densities, and ultrasonic velocities of binary mixtures of ethylbenzene with ethanol, 1-propanol, and 1-butanol have been determined at 298.15 and 308.15 K over the whole composition range. Excess compressibility (K_s^E) and deviations in viscosity ($\Delta\eta$) were evaluated and presented as functions of composition.

Introduction

The studies of viscosity, density, and ultrasonic velocities are being increasingly used as tools for investigation of the properties of pure components and the nature of intermolecular interactions between the liquid mixture constituents.

Earlier we have reported the ultrasonic, density. and viscosity studies of binaries of some *n*-alkanols with isopropylbenzene and ethylbenzene,[1−3] where densities, ultrasonic velocities, and viscosities were measured for four of these systems at two temperatures, 298.15 and 308.15 K. As part of the experimental investigation of the excess thermodynamic properties of industrially significant liquid mixtures, in the present study, measurements of densities, viscosities, and ultrasonic velocities of three binary mixtures of ethylbenzene with ethanol, 1-propanol, and 1-butanol have also been made at two temperatures, 298.15 and 308.15 K. This forms a part of a program to study the properties of *n*-alkanol mixtures with a C_8 or C_9 aromatic hydrocarbon as one of the components.

Experimental Section

Ethylbenzene (Koch-Light Lab, England), 1- propanol (E. Merck A. G. Germany), and 1-butanol (BDH, India) were purified by standard procedures[4] and stored over molecular sieves. Ethanol (99.8% of Fluka Puriss) was used as received. The purity of the samples was checked by comparing measured densities and viscosities with those reported in the literature, as shown in Table 1. The densities were measured by using a calibrated bicapillary pycnometer having an accuracy of $\pm 1.0 \times 10^{-4}$ g·cm^{-3}. The mol fraction of each mixture was obtained to an accuracy of $\pm 1.0 \times 10^{-4}$.

Viscosities were measured by using a modified Ubbelhode viscometer, as described earlier.[5] From the measured values of density ρ and efflux time t, the viscosity was calculated using the relation

$$\eta/\rho = At + B/t \qquad (1)$$

where A and B are viscometer constants. The values of these constants A and B were obtained by measuring the flow time with triply distilled water and twice-distilled benzene. The flow measurements were made with an electronic stopwatch with a precision of ±0.01 s. For the purpose of calculation of viscosity, an average of three to four sets of flow times of each liquid mixture was taken. The reproducibility of the viscosity estimates is found to be within ±0.003 mPa·s.

Table 1. Physical Properties of the Pure Components at Different Temperatures

		ρ/g·cm^{-3}		η/mPa·s	
component	T/K	exp	lit	exp	lit
ethylbenzene	298.15	0.8620	0.86264[4]	0.628	0.6373[4]
	308.15	0.8555	0.85386[4]	0.553	0.5688[4]
ethanol	298.15	0.7855	0.78509[11]	1.117	1.0826[4]
	308.15	0.7763	0.77639[4]	0.935	0.903[4]
1-propanol	298.15	0.7996	0.79960[4]	2.042	1.943[4]
	308.15	0.7920	0.79158[4]	1.565	1.537[11]
1-butanol	298.15	0.8077	0.80600[11]	2.564	2.571[4]
	308.15	0.8001	0.79815[4]	2.000	2.000[11]

Ultrasonic velocities were determined by using an interferometer (Belen Model UI-751) with an accuracy of ±1.0 m·s^{-1}. All the measurements were made at constant temperature with the help of a circulating-type cryostat (MK70-MLW) where the temperature was controlled to ±0.02 K.

Experimental Results and Correlations:

The experimental values of viscosity, η, density, ρ, and ultrasonic velocity, u, are reported in Table 2. Deviations in viscosity, $\Delta\eta$, were obtained by using the relation

$$\Delta\eta = \eta_m - (x_1\eta_1 + x_2\eta_2) \qquad (2)$$

where η_m is the viscosity of the mixture and η_1 and η_2 are the viscosities of pure components 1 and 2, respectively.

The values of the ultrasonic velocities, u, and mixture densities, ρ_m, were used to calculate the isentropic compressibility, K_s, by using the relation

$$K_s = u^{-2}\rho_m^{\ -1} \qquad (3)$$

The excess isentropic compressibility, K_s^E, was obtained from the relation

$$K_s^E = K_s - K_s^{id} \qquad (4)$$

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Table 2. Density, ρ, Viscosity, η, Ultrasonic Velocity, u, and Compressibility, k_s, for Ethylbenzene (1) + n-Alkanols (2) at 298.15 and 308.15 K

x_1	ρ/kg·m^{-3}	η/mPa·s	u/m·s^{-1}	$K_s \times 10^{12}$/Pa^{-1}
Ethylbenzene (1) + Ethanol (2)				
298.15 K				
0.0000	785.5	1.117	1160	947.3
0.0712	795.0	1.026	1170	918.0
0.1551	807.2	0.947	1185	882.2
0.2404	817.6	0.864	1203	845.1
0.3520	827.0	0.789	1228	801.9
0.4053	836.0	0.764	1235	784.3
0.5530	842.3	0.684	1261	746.6
0.7382	853.6	0.639	1278	717.3
0.8805	858.5	0.623	1291	698.8
1.0000	862.0	0.628	1312	673.9
308.15 K				
0.0000	776.3	0.935	1112	1041.7
0.0712	789.6	0.856	1133	986.6
0.1551	801.6	0.788	1155	935.1
0.2404	811.7	0.719	1173	895.4
0.3520	820.0	0.656	1195	854.8
0.4053	823.2	0.629	1203	839.4
0.5530	835.8	0.587	1223	799.9
0.7382	842.8	0.548	1250	759.4
0.8805	851.2	0.544	1266	732.9
1.0000	855.5	0.553	1276	717.9
Ethylbenzene (1) + 1-Propanol (2)				
298.15 K				
0.0000	799.6	2.042	1213	850.0
0.1090	811.4	1.543	1227	815.6
0.1677	817.3	1.375	1233	804.8
0.3777	828.5	0.976	1257	763.8
0.5006	837.9	0.839	1266	744.5
0.6429	845.1	0.712	1277	725.6
0.8074	853.3	0.638	1287	707.5
0.8951	857.0	0.606	1299	691.5
1.0000	862.0	0.628	1312	673.9
308.15 K				
0.0000	792.0	1.565	1182	903.7
0.1090	803.7	1.226	1194	872.8
0.1677	807.1	1.098	1202	857.5
0.3777	823.5	0.809	1224	810.5
0.5006	833.1	0.702	1233	789.5
0.6429	839.0	0.616	1245	768.5
0.8074	844.3	0.562	1258	748.4
0.8951	850.0	0.542	1264	735.6
1.0000	855.5	0.553	1276	717.9
Ethylbenzene (1) + 1-Butanol (2)				
298.15 K				
0.0000	807.7	2.564	1238	807.8
0.1035	816.7	1.985	1246	788.6
0.2050	821.2	1.565	1256	771.9
0.3221	828.1	1.236	1264	755.8
0.3650	831.1	1.147	1267	749.5
0.5071	839.6	0.916	1277	730.3
0.6494	845.7	0.764	1288	712.7
0.8136	854.5	0.693	1301	691.4
0.9100	858.6	0.649	1307	681.8
1.0000	862.0	0.628	1312	673.9
308.15 K				
0.0000	800.1	2.000	1211	851.5
0.1035	808.9	1.569	1217	834.6
0.2050	815.3	1.253	1223	820.0
0.3221	822.0	1.102	1229	805.4
0.3650	824.5	0.941	1231	800.4
0.5071	832.1	0.765	1239	782.8
0.6494	839.1	0.651	1249	763.9
0.8136	846.0	0.577	1262	742.1
0.9100	852.6	0.566	1268	729.4
1.0000	855.5	0.553	1276	717.9

Table 3. Value of the Coefficients of the Redlich−Kister Equation 6 and Standard Deviations (Equation 7)

T/K	A_0	A_1	A_2	A_3	A_4	σ
Ethylbenzene (1) + Ethanol (2)						
$\Delta\eta$/mPa·s						
298.15	−0.6422	0.0910	−0.1105			0.004
308.15	−0.5858	0.1263	−0.0887			0.003
$K_s^E \times 10^{12}$/Pa^{-1}						
298.15	−209.8991	57.7164	149.3772			0.520
308.15	−265.6467	143.3654	−137.6521			0.760
Ethylbenzene (1) + 1-Propanol (2)						
$\Delta\eta$/mPa·s						
298.15	−1.9629	1.0562	−1.1583			0.011
308.15	−1.4045	0.6904	−0.6708			0.005
$K_s^E \times 10^{12}$/Pa^{-1}						
298.15	−66.8738	70.7241	−4.2337			0.470
308.15	−84.3861	57.2097	29.8451			0.370
Ethylbenzene (1) + 1-Butanol (2)						
$\Delta\eta$/mPa·s						
298.15	−2.6933	1.3717	−0.4361			0.007
308.15	−2.0213	0.9403	−0.4197			0.005
$K_s^E \times 10^{12}$/Pa^{-1}						
298.15	−36.6658	4.4774	−31.1957			0.400
308.15	−4.02785	13.5917	−39.0898	8.0130	24.0339	0.140

where K_s is the experimental compressibility and K_s^{id} is the isentropic compressibility of an ideal mixture of the components. The values of K_s are also reported in Table 2.

K_s^{id} was determined by using the Kiyohara and Benson equation[6]

$$K_S^{id} = \sum \phi_i [k_{s,i}{}^0 + TV_i{}^0(\alpha_i{}^0)^2/C_{Pi}{}^0] - T(\sum x_i V_i{}^0)(\sum \phi_i \alpha_i{}^0)^2/\sum x_{iCPi}{}^0 \quad (5)$$

where ϕ_i is the volume fraction of component i in the mixture stated in terms of the unmixed components, T is the temperature, and $k_{s,i}{}^0$, $V_i{}^0$, $\alpha_i{}^0$, and $C_{Pi}{}^0$ are the isentropic compressibility, molar volume, coefficient of thermal expansion, and molar heat capacity for the pure component i. The values of $\alpha_i{}^0$ were obtained from the density values at two different temperatures. The values of the molar heat capacity were taken from the literature.[4,7,8] The excess properties (K_s^E) and deviations in viscosity ($\Delta\eta$) were fitted to a Redlich−Kister-type[9] equation

$$A = x_1 x_2 \sum_{j=1}^{n} A_{j-1}(x_1 - x_2)^{(j-1)} \quad (6)$$

where A is the property, A_{j-1} is the polynomial coefficient, and n is the polynomial degree.

The standard deviation in each case is calculated using the relation

$$\sigma(X) = \left[\frac{(\sum X_{expt} - X_{calc})^2}{N - n}\right]^{1/2} \quad (7)$$

where N is the number of data points and n is the number of coefficients. The values of the coefficients of eq 6 as determined by the method of least squares along with the standard deviations for all three systems are reported in Table 3.

Discussion

The data for all the three systems studied show a smooth nonlinear variation of density, viscosity, and ultrasonic

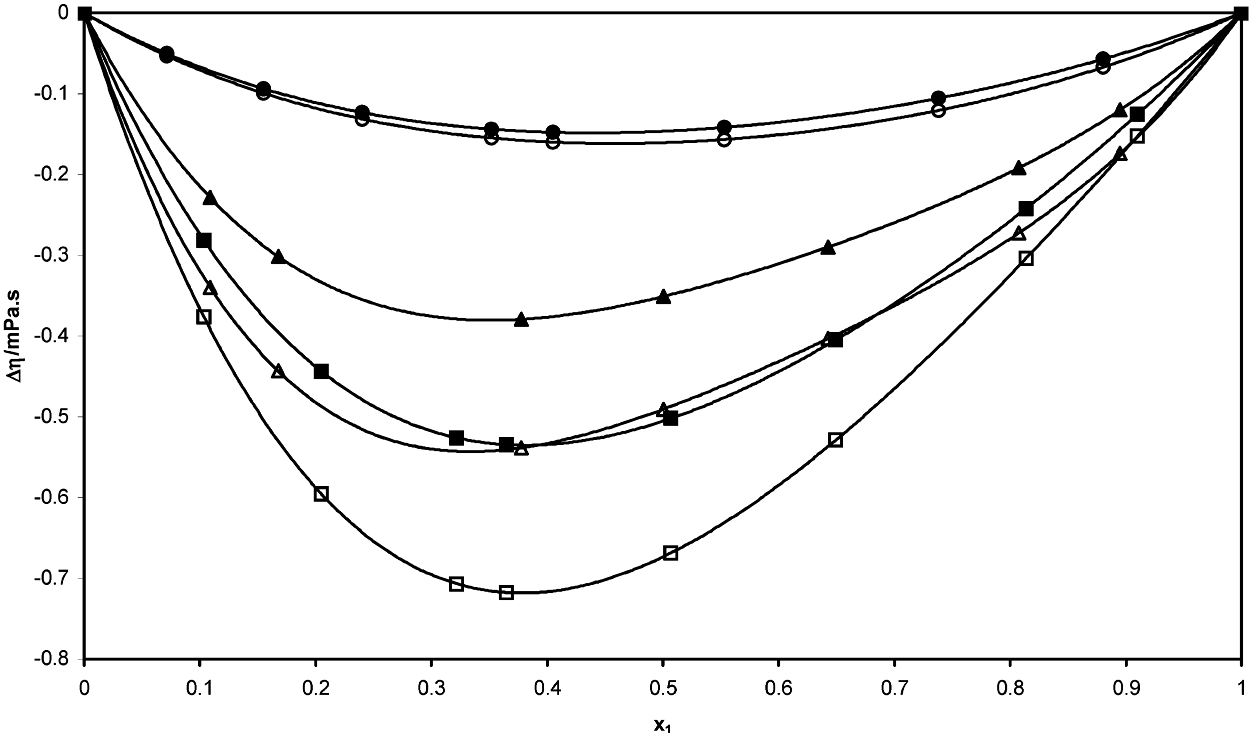

Figure 1. Viscosity deviations, $\Delta\eta$ (mP·s), for the systems of ethylbenzene with ethanol (○, ●), 1-propanol (△, ▲), and 1-butanol (□, ■) at (298.15 and 308.15) K, respectively.

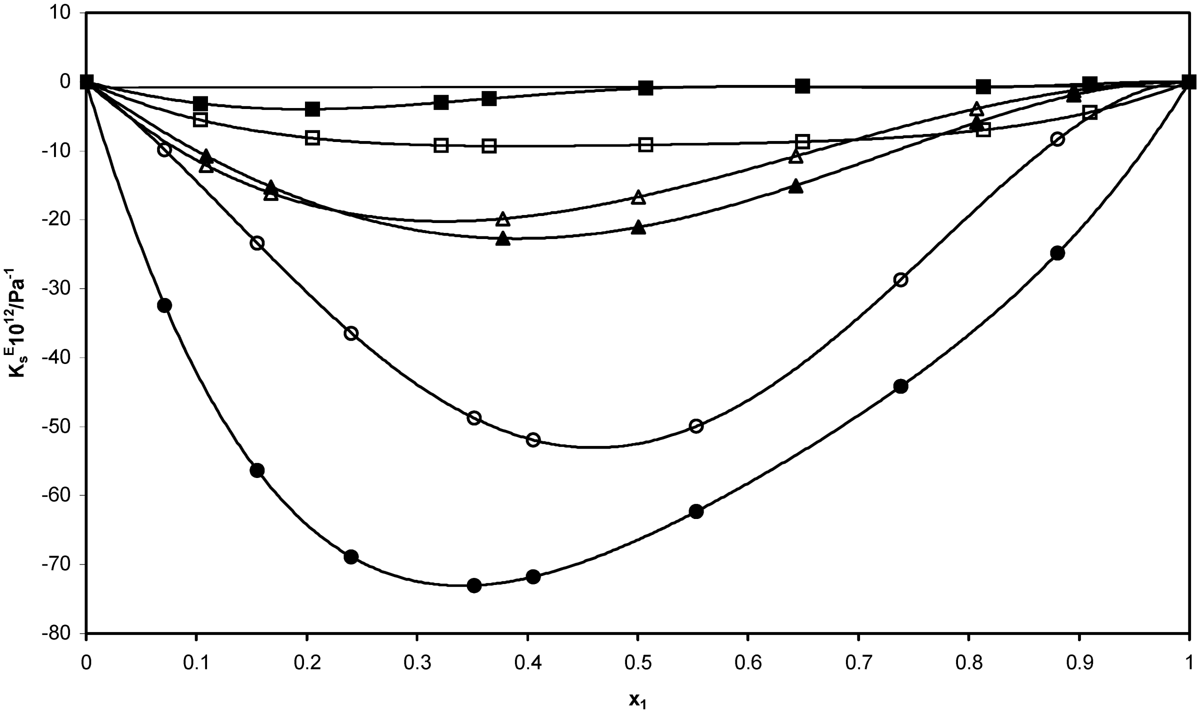

Figure 2. Excess compressibility, K_s^E (Pa^{-1}), for the systems of ethylbenzene with ethanol (○, ●), 1-propanol (△, ▲), and 1-butanol (□, ■) at (298.15 and 308.15) K, respectively.

velocity with composition over the complete range at 298.15 and 308.15 K. The deviations in viscosity (Figure 1) for all the three systems are negative and the $\Delta\eta$ values decrease with an increase in temperature, which may be due to the reduction in dispersion forces.

The values of excess compressibility K_s^E (Figure 2) are negative for all three systems at both temperatures. Fort and Moore[10] have reported that K_s^E becomes increasingly negative as the strength of interaction increases. The results indicate the interactions to be stronger in case of ethylbenzene + ethanol mixtures. These interactions grow weaker as the alcohol chain length increases.

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