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Densities, Viscosities, and Speeds of Sound of Binary Liquid Mixtures of Sulfolane with Ethyl Acetate, *n*-Propyl Acetate, and *n*-Butyl Acetate at Temperature of (303.15, 308.15, and 313.15) K

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Density, viscosity, and speed of sound data for (sulfolane + ethyl acetate (EA)), (sulfolane + *n*-propyl acetate (PA)), and (sulfolane + *n*-butyl acetate (BA)) were determined at $T = (303.15 \text{ to } 313.15)$ K. From this data, excess molar volume and deviation in isentropic compressibility, $\Delta\kappa_s$, have been calculated. The computed properties were fit to a Redlich−Kister polynomial.

Introduction

Physical properties of liquid mixtures are required in most of the engineering calculations where fluid flow or mixing is an important factor in many practical problems concerning mass transport applications. Sulfolane is an important industrial solvent that has several advantageous physicochemical properties and the ability to extract monocyclic aromatic hydrocarbons from petroleum products. Mixtures of sulfolane with other solvents are also of particular interest. An understanding of the mixing behavior of sulfolane with esters is therefore important and has applications in many engineering areas. To the best of our knowledge, no extensive studies have been made on the mixtures of sulfolane with esters. In a continuation of our ongoing program of research,[1–3] we now report the results of density, viscosity, and speed of sound for the binary mixtures of sulfolane with ethyl acetate, *n*-propyl acetate, and *n*-butyl acetate over the entire range of composition at $T = (303.15 \text{ to } 313.15)$ K. With this data, the excess molar volume and deviation in isentropic compressibility have been computed. These results have been fitted to the Redlich−Kister polynomial equation using a multiparametric nonlinear regression analysis technique to derive the binary coefficients and to estimate the standard deviation (σ) between experimental and calculated data.

Experimental Procedure

Materials. Ethyl acetate, *n*-propyl acetate, and *n*-butyl acetate that were all supplied by Sigma-Aldrich with stated purities of better than 99 % were stored over molecular sieves (0.3 nm Merck, India). Sulfolane with a purity of 99 % was provided by Sigma-Aldrich Chemicals and was used without further purification. To minimize the contact of this deliquescent reagent with moist air, the product was kept in sealed bottles in a desiccator. The purity of the substances was determined by GLC. Densities and viscosities of pure substances and their comparison with literature values are listed in Table 1.[4–14]

Apparatus and Procedure. Binary mixtures were prepared by mass in airtight bottles. The mass measurements were performed on a Dhona 100 DS (India) single-pan analytical balance with a resolution of $\pm\ 0.01 \cdot 10^{-6}$ kg. The required properties of the mixture were measured on the same day. The uncertainty in mole fraction was estimated to be less than $\pm\ 1 \cdot 10^{-4}$. The detailed procedures for measuring density and viscosity have been described in our previous publication.[15]

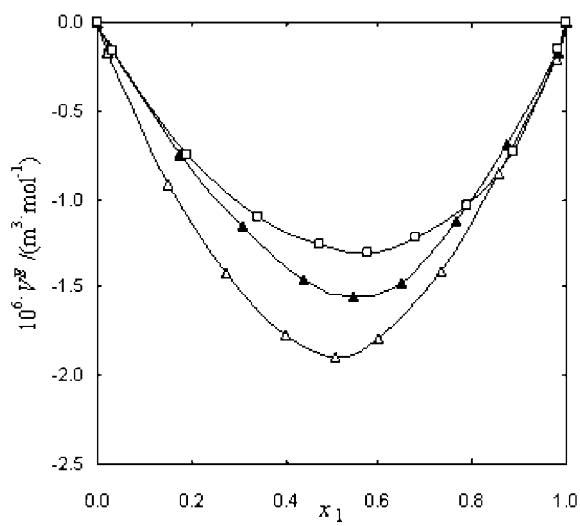

Figure 1. Plots of excess molar volume, V^E, of the sulfolane (1) + esters (2) system as a function of mole fraction at $T = 308.15$ K: △, ethyl acetate; ▲, *n*-propyl acetate; □, *n*-butyl acetate. The symbols represent experimental values.

The speed of sound was measured with a single-crystal variable-path interferometer (Mittal Enterprises, India) operating at a frequency of 2 MHz that had been calibrated with water and benzene. The detailed procedure was described in our previous papers.[2,3] The uncertainty in speed of sound was found to be ± 0.2 %. In all property measurements, the temperature was controlled within ± 0.01 K using a constant temperature bath (INSREF model IRI-016 C, India) by circulating water from the thermostat.

Results and Discussion

Experimental values of densities, ρ, viscosities, η, speeds of sound, u, and excess molar volumes, V^E, for the binary mixtures

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Table 1. Comparison of Experimental Densities, ρ, Viscosities, η, and Speeds of Sound, u, of Pure Components with Available Literature at Different Temperatures

		$\rho \cdot 10^{-3}$/kg·m^{-3}		$\eta \cdot 10^3$/mPa·s		u/m·s^{-1}	
component	T/K	exptl	lit.	exptl	lit.	exptl	lit.
sulfolane	298.15	1.2639	1.2640[14]			1601	
	303.15	1.2618	1.2618[4]	10.0304	10.0742[5]	1588	1588.8[13]
	313.15	1.2516	1.2519[5]	7.8365		1558	
ethyl acetate	298.15	0.8951	0.8946[6]	1.3716	1.3710[7]	1142	
	303.15	0.8894	0.8896[11]	0.3806		1122	1119[11]
	308.15	0.8839	0.8832[9]	0.3622		1101	
n-propyl acetate	298.15	0.8837	0.8831[7]	1.3838	1.3835[7]	1156	
n-butyl acetate	298.15	0.8756	0.8759[7]	1.3934	1.3931[7]	1203	1201[12]
	303.15	0.8716	0.8713[8]	0.6072	0.6080[10]	1176	1176[11]
	313.15	0.8620	0.8618[10]	0.5340		1135	

of sulfolane with ethyl acetate, n-propyl acetate, and n-butyl acetate at T = (303.15 to 313.15) K are listed as a function of the mole fraction of sulfolane in Table 2.

The density values have been used to calculate excess molar volumes, V^E, using the following equation

$$V^E/(\text{m}^3\cdot\text{mol}^{-1}) = (x_1M_1 + x_2M_2)/\rho_m - (x_1M_1/\rho_1 + x_2M_2/\rho_2) \quad (1)$$

where ρ_m is the density of the mixture and x_1, M_1, ρ_1 and x_2, M_2, and ρ_2 are the mole fraction, molar mass, and density of pure components, respectively.

The speed of sound, u, was used to calculate the isentropic compressibility, κ_s, using

$$\kappa_s = 1/u^2\rho \quad (2)$$

The deviation from isentropic compressibility, $\Delta\kappa_s$, has been evaluated using the equation

$$\Delta\kappa_s/(\text{m}^2\cdot\text{N}^{-1}) = \kappa_s - (\Phi_1\kappa_{s1} + \Phi_2\kappa_{s2}) \quad (3)$$

where κ_{s1}, κ_{s2}, and κ_s are the isentropic compressibility of the pure components and observed isentropic compressibility of liquid mixture, respectively. In eq 4, Φ_i is the volume fraction and is calculated from the individual pure molar volumes, V_i, with the relation

$$\Phi_i = x_iV_i/(\Sigma x_iV_i) \quad (4)$$

The excess or deviation properties, Y^E, were fitted by the method of nonlinear least-squares to a Redlich−Kister-type polynomial[16]

$$Y^E = x_1x_2\Sigma A_i(x_1 - x_2)^i \quad (5)$$

In each case, the optimum number of coefficients, A_i, was determined from an examination of the variation of standard deviation, σ, as calculated by

$$\sigma(Y^E) = [\Sigma(Y^E_{\text{obsd}} - Y^E_{\text{calcd}})^2/(n - m)]^{1/2} \quad (6)$$

where n represents the number of experimental points and m is the number of coefficients. It is found that for the solution of the fifth degree polynomial, the agreement between the experimental values and the calculated values is satisfactory. The derived parameters, A_i, and the estimated standard deviation, σ, for V^E and $\Delta\kappa_s$ are given in Table 3.

Excess Molar Volume. Excess molar volumes of (sulfolane + esters) at T = 308.15 K are shown in Figure 1. The values of V^E are negative for all (sulfolane + EA), (sulfolane + PA), and (sulfolane + BA) over the whole mole fraction range and are less negative with increasing chain length of the ester molecules. The negative values of V^E vary in the following order: EA < PA < BA < 0. The V^E values are less negative with increasing temperature in the case of BA, whereas no particular trend was observed in the case of EA and PA. These plots are not furnished to avoid overcrowding.

Deviation in Isentropic Compressibility. The $\Delta\kappa_s$ values are negative over the whole composition range for all mixtures and become more negative at higher temperatures. It can be pointed out that the influence of the structure of the homologous series of esters on the isentropic compressibility behavior is very marked. An inspection of Figure 2 reveals that the $\Delta\kappa_s$ values become more negative with decreasing chain length of the ester.

In the present study, the behavior of V^E and $\Delta\kappa_s$ are similar in nature. The sign of $\Delta\kappa_s$ supports the postulates used to interpret the sign of excess molar volume. The negative V^E and $\Delta\kappa_s$ values may result from dipole−dipole and dipole-induced dipole interactions[13,17–19] that enhance the solvent structure in the mixture, in turn making negative contributions to V^E and $\Delta\kappa_s$.

Conclusions

The experimental values of density, viscosity, and speed of sound and calculated excess molar volume and deviation in

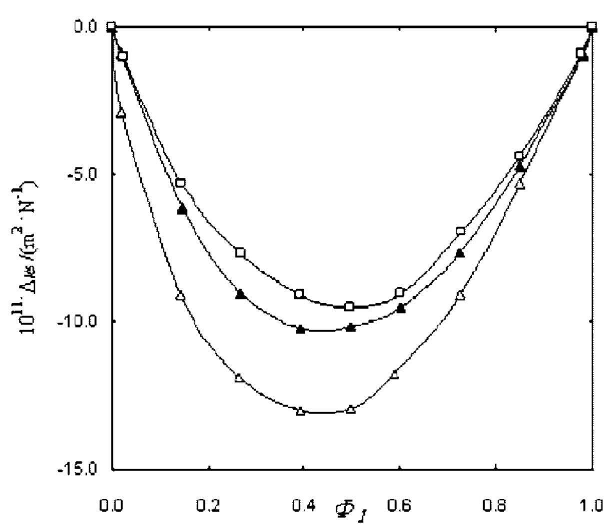

Figure 2. Plots of deviation in isentropic compressibility, $\Delta\kappa_s$, of the sulfolane (1) + esters (2) system as a function of volume fraction at T = 308.15 K: △, ethyl acetate; ▲, n-propyl acetate; □, n-butyl acetate. The symbols represent experimental values.

Table 2. Values of Density, ρ, Viscosity, η, Speed of Sound, u, and Excess Molar Volume, V^E, for the Binary Liquid Mixtures at Temperature T

x_1	$\rho \cdot 10^{-3}$ / $kg \cdot m^{-3}$	$\eta \cdot 10^3$ / $mPa \cdot s$	u / $m \cdot s^{-1}$	$V^E \cdot 10^6$ / $m^3 \cdot mol^{-1}$	x_1	$\rho \cdot 10^{-3}$ / $kg \cdot m^{-3}$	$\eta \cdot 10^3$ / $mPa \cdot s$	u / $m \cdot s^{-1}$	$V^E \cdot 10^6$ / $m^3 \cdot mol^{-1}$
Sulfolane (1) + Ethyl Acetate (2)									
T/K = 303.15									
0.0000	0.8894	0.3806	1122	0.000	0.5980	1.1276	2.0539	1408	−1.633
0.0218	0.8978	0.4006	1134	−0.065	0.7331	1.1754	3.2106	1472	−1.300
0.1511	0.9507	0.5566	1196	−0.705	0.8548	1.2155	5.2851	1524	−0.757
0.2748	1.0011	0.7832	1251	−1.197	0.9799	1.2555	9.2053	1579	−0.114
0.4012	1.0523	1.1179	1313	−1.573	1.0000	1.2618	10.0304	1588	0.000
0.5068	1.0940	1.4995	1366	−1.735					
T/K = 308.15									
0.0000	0.8839	0.3622	1101	0.000	0.5980	1.1239	1.8819	1398	−1.787
0.0218	0.8932	0.3819	1121	−0.170	0.7331	1.1715	2.9230	1465	−1.414
0.1511	0.9471	0.5275	1185	−0.921	0.8548	1.2116	4.7555	1515	−0.856
0.2748	0.9977	0.7300	1241	−1.418	0.9799	1.2519	8.0778	1569	−0.207
0.4012	1.0488	1.0424	1301	−1.771	1.0000	1.2570	8.7947	1576	0.000
0.5068	1.0903	1.3942	1355	−1.897					
T/K = 313.15									
0.0000	0.8758	0.3426	1082	0.000	0.5980	1.1167	1.7516	1397	−1.789
0.0218	0.8851	0.3633	1092	−0.167	0.7331	1.1647	2.6995	1464	−1.410
0.1511	0.9395	0.4961	1154	−0.971	0.8548	1.2055	4.2809	1513	−0.857
0.2748	0.9899	0.6874	1216	−1.434	0.9799	1.2458	7.0920	1555	−0.163
0.4012	1.0405	0.9781	1283	−1.721	1.0000	1.2516	7.8365	1558	0.000
0.5068	1.0821	1.2925	1346	−1.838					
Sulfolane (1) + *n*-Propyl Acetate (2)									
T/K = 303.15									
0.0000	0.8777	0.4878	1149	0.000	0.6489	1.1249	2.6244	1419	−1.457
0.0247	0.8869	0.5146	1154	−0.182	0.7639	1.1695	3.9199	1474	−1.113
0.1746	0.9414	0.7260	1214	−0.841	0.8733	1.2123	5.8629	1530	−0.671
0.3110	0.9929	1.0193	1266	−1.285	0.9823	1.2554	9.3047	1579	−0.140
0.4416	1.0431	1.4384	1322	−1.485	1.0000	1.2618	10.0304	1588	0.000
0.5468	1.0846	1.9225	1368	−1.551					
T/K = 308.15									
0.0000	0.8731	0.4595	1139	0.000	0.6489	1.1201	2.3752	1410	−1.474
0.0247	0.8819	0.4827	1147	−0.134	0.7639	1.1647	3.5015	1469	−1.127
0.1746	0.9358	0.6764	1203	−0.745	0.8733	1.2076	5.2167	1521	−0.692
0.3110	0.9869	0.9439	1257	−1.156	0.9823	1.2510	8.1319	1573	−0.175
0.4416	1.0379	1.3250	1312	−1.459	1.0000	1.2570	8.7947	1576	0.000
0.5468	1.0796	1.7617	1359	−1.550					
T/K = 313.15									
0.0000	0.8667	0.4329	1126	0.000	0.6489	1.1141	2.1758	1401	−1.498
0.0247	0.8757	0.4554	1134	−0.163	0.7639	1.1594	3.1853	1458	−1.191
0.1746	0.9298	0.6342	1189	−0.798	0.8733	1.2022	4.6616	1510	−0.724
0.3110	0.9813	0.8781	1243	−1.257	0.9823	1.2454	7.2221	1555	−0.165
0.4416	1.0324	1.2220	1301	−1.555	1.0000	1.2516	7.8365	1558	0.000
0.5468	1.0740	1.6173	1352	−1.623					
Sulfolane (1) + *n*-Butyl Acetate (2)									
T/K = 303.15									
0.0000	0.8716	0.6072	1176	0.000	0.6793	1.1205	3.0273	1424	−1.336
0.0311	0.8808	0.6426	1182	−0.068	0.7887	1.1682	4.2748	1477	−1.131
0.1903	0.9323	0.8950	1232	−0.624	0.8876	1.2122	6.1997	1528	−0.750
0.3402	0.9852	1.2425	1280	−1.040	0.9836	1.2542	9.0492	1577	−0.098
0.4740	1.0361	1.7220	1327	−1.291	1.0000	1.2618	10.0304	1588	0.000
0.5789	1.0785	2.2995	1372	−1.396					
T/K = 308.15									
0.0000	0.8671	0.5687	1155	0.000	0.6793	1.1144	2.7172	1418	−1.224
0.0311	0.8769	0.6016	1164	−0.162	0.7887	1.1621	3.8367	1468	−1.028
0.1903	0.9286	0.8248	1212	−0.746	0.8876	1.2071	5.4987	1520	−0.733
0.3402	0.9809	1.1452	1261	−1.100	0.9836	1.2501	7.9251	1572	−0.154
0.4740	1.0309	1.5770	1316	−1.258	1.0000	1.2570	8.7947	1576	0.000
0.5789	1.0727	2.0816	1366	−1.303					
T/K = 313.15									
0.0000	0.8620	0.5340	1135	0.000	0.6793	1.1088	2.4714	1408	−1.219
0.0311	0.8718	0.5637	1146	−0.167	0.7887	1.1566	3.4359	1466	−1.033
0.1903	0.9235	0.7699	1193	−0.772	0.8876	1.2015	4.9020	1510	−0.726
0.3402	0.9754	1.0664	1245	−1.088	0.9836	1.2448	6.9875	1556	−0.164
0.4740	1.0254	1.4573	1301	−1.256	1.0000	1.2516	7.8365	1558	0.000
0.5789	1.0671	1.9028	1354	−1.295					

Table 3. Binary Coefficients (A_i) and Standard Errors (σ) of Sulfolane (1) + Esters (2)

function	T/K	A_0	A_1	A_2	A_3	A_4	σ
Sulfolane (1) + Ethyl Acetate (2)							
$V^E \cdot 10^6$/ $m^3 \cdot mol^{-1}$	303.15	−6.824	−0.68	2.38	0.20	−0.4	0.021
	308.15	−7.556	−0.13	3.05	0.36	−4.4	0.024
	313.15	−7.345	−0.42	1.08	1.62	−1.8	0.018
$\Delta\kappa_s \cdot 10^{11}$/ $m^2 \cdot N^{-1}$	303.15	−45.65	10.46	1.9	9.3	−10	0.070
	308.15	−51.78	11.2	7.5	25.2	−43	0.30
	313.15	−57.76	6.61	4.9	8.9	−11.7	0.083
Sulfolane (1) + *n*-Propyl Acetate (2)							
$V^E \cdot 10^6$/ $m^3 \cdot mol^{-1}$	303.15	−6.216	−0.72	1.2	1.27	−2.0	0.022
	308.15	−6.166	−1.44	2.57	1.22	−3.5	0.027
	313.15	−6.477	−1.06	2.44	0.66	−3.47	0.017
$\Delta\kappa_s \cdot 10^{11}$/ $m^2 \cdot N^{-1}$	303.15	−39.07	9	−10.1	−0.8	13	0.20
	308.15	−40.96	8.38	−6	−1.3	3.4	0.096
	313.15	−44.83	7.39	1.8	−0.7	−8.1	0.042
Sulfolane (1) + *n*-Butyl Acetate (2)							
$V^E \cdot 10^6$/ $m^3 \cdot mol^{-1}$	303.15	−5.293	−2.12	−0.99	−0.69	1.36	0.017
	308.15	−5.140	−0.913	−0.42	−0.95	−2.14	0.0088
	313.15	−5.103	−0.94	−0.71	−0.6	−2.1	0.011
$\Delta\kappa_s \cdot 10^{11}$/ $m^2 \cdot N^{-1}$	303.15	−32.81	3.8	−11.1	5.5	15.7	0.17
	308.15	−38.20	2.63	8.1	6.1	−17.3	0.094
	313.15	−42.80	−1	5.7	12.9	−16.5	0.10

speed of sound for the binary mixtures of sulfolane + ethyl acetate, + *n*-propyl acetate, and + *n*-butyl acetate at $T = (303.15$ to $313.15)$ K are reported. The results are correlated using the Redlich−Kister polynomial equation.

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