Research Article

THERMODYNAMIC AND TRANSPORT PROPERTIES OF BINARY LIQUID MIXTURES OF SULFOLANE WITH SOME ORGANIC SOLVENTS AT 308.15 K

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ABSTRACT

Experimental data on density, viscosity and speed of sound have been studied for the binary mixtures of (sulfolane + Butanone), (sulfolane + n-Butyl amine), (sulfolane + n-Butyl acetate) at 308.15 K. The data of thermodynamic properties of the investigated liquids and their mixtures are required for the design of mixing, storage and process equipment. Furthermore, thermodynamic properties of binary mixtures containing components capable of undergoing specific interactions exhibit significant deviations from ideality not only arising from a difference in molecular size and shape but also due to structural changes. The results are fitted to a Redlich-Kister type polynomial equation to derive binary coefficients and standard deviations.

INTRODUCTION

Studies on thermodynamic properties are important in understanding the nature of molecular interactions in binary liquid mixtures. Properties of mixtures are useful for designing transport and process equipment in the chemical industry[1-2] and the theoretical interest in studying the structure of such solutions. 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 (thiolane-1,1-dioxide) is an important industrial solvent that has several advantageous physico-chemical properties and the ability to extract monocyclic aromatic hydrocarbons from petroleum products. Butanone is highly efficient solvent used to make high solid coatings with lower solvent content and lower solvent emissions. n-butylamine is used as raw material for manufacture of drugs such as chlorpromazine and tolbutamide. n-butyl acetate is used as plasticizer in polymer-processing industries in order to impart favorable thermoplastic behavior and also in the flavor and fragrance industries. The interactions between the carbonyl group of ketone, amine, ester and solvents with polar groups, such as sulfolane play a crucial role in the structural effects, molecular level and for practical applications. Mixtures of sulfolane with other solvents are also of particular interest. An understanding of the mixing behavior of sulfolane with butanone, n-butylamine and n-butyl acetate 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 butanone, n-butylamine and n-butyl acetate at 308.15K. This paper reports the systematic measurements of the properties of organic solvents [3-9]. The present study is undertaken to determine experimentally density and speed of sound of three pure liquid solvents, butanone, n-butylamine and n-butyl acetate and their binary mixtures with sulfolane at 308.15K at a pressure of 0.1MPa. With this data, the excess molar volume and deviation in isentropic compressibility of the mixtures were computed. The Redlich-Kister polynomial equation[10] was fitted to the results to derive the binary coefficients and estimate the standard deviation between experimental and calculated data.

Experimental

MATERIAL AND METHODS

Ethyl acetate (Sigma-Aldrich, USA), The high purity grade sulfolane (99 %) was furnished by Sigma-Aldrich chemicals (USA) and used without further purification. To minimize the

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contact of this deliquescent reagent with moist air, the product was kept in sealed bottles in a desiccator. The purity of the substances was checked by GLC. Densities and viscosities of pure substances and their comparison with literature values are listed in Table 1[11-16].

General 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 $0.01 \cdot 10^{-6}$ kg. The required properties of the mixture were measured on the same day. The uncertainty in mole fraction was estimated to be less than $\pm 1 \cdot 10^{-4}$.

Detection Method

Density of pure liquids and their mixtures were determined by using a $1 \cdot 10^{-5}$ m^3 double arm pycnometer[6]. The density values from triplicate replication at the measured temperatures were reproducible within $\pm 2 \cdot 10^{-2}$ kg·m^{-3}. The uncertainty in density values was found to be ± 0.04 kg·m^{-3}.

Speed of sound was determined by using an ultrasonic interferometer [model M-82, Mittal Enterprises, India], working at 2 MHz frequency. The detailed procedures for measuring speed of sound was discussed in our previous paper [3]. The temperature of the solution was controlled by circulating water at a desired temperature through the jacket of the double-walled cell. The speed of sound was measured with relative uncertainty of ± 0.3 %.

In all the property measurements, the temperature was controlled within ± 0.01 K using a constant temperature bath [INSREF model IRI – 016 C, India], and the temperature was monitored with a platinum resistance thermometer with an accuracy of ± 0.001 K and an uncertainty of ± 0.004 K.

Table 1 Experimental densities (ρ) and speeds of sound (u) of pure components at 308.15K

Component	$\rho \cdot 10^{-3}$ kg·m^{-3}		u m·s^{-1}	
	Expt	Lit	Expt	Lit
sulfolane	1.2639*	1.2640[11]	1588**	1588[12]
Butanone	0.8012*	0.8009[13]	1192	1192[14]
n-Butyl amine	0.72225	0.7239 [15]	1198.2	-------
n-Butyl acetate	0.8756*	0.8759[16]	1203*	1201[13]
*T=298.15K				
** T=303.15K				

Table 2 The Values of Density (ρ); Speed of Sound (u); Excess Molar Volume (V^E); Deviation in Isentropic Compressibility ($\Delta\kappa_s$) for the Binary Liquid Mixtures at 308.15 K

x_1	$\rho \cdot 10^{-3}$/kg·m^{-3}	u/m·s^{-1}	$V^E \cdot 10^6$/m^3·mol^{-1}	$\Delta\kappa_s \cdot 10^{11}$/m^2·N^{-1}
sulfolane (1) + 2-butanone (2)				
0.0000	0.7904	1158	0.000	0
0.0293	0.8062	1170	-0.174	-0.944
0.1391	0.8656	1215	-0.819	-5.1188
0.2575	0.9275	1266	-1.271	-7.7244
0.3803	0.9896	1319	-1.560	-8.9378
0.4834	1.0399	1366	-1.662	-9.4587
0.5854	1.0866	1413	-1.536	-9.2365
0.7119	1.1420	1465	-1.240	-8.1254
0.8428	1.1968	1517	-0.821	-6.0014
0.9756	1.2490	1568	-0.219	-0.7321
1.0000	1.2570	1576	0.0000	0.0000
Sulfolane (1) + n-butylamine (2)				
0.0000	0.7223	1198.2	0.0000	0.0000
0.0317	0.7434	1221.1	-0.6988	-3.6969

0.1455	0.8105	1252.2	-1.7472	-10.997
0.2586	0.8769	1283.7	-2.5038	-16.236
0.3670	0.9392	1317.3	-2.9554	-19.124
0.5080	1.0189	1374.9	-3.1158	-20.327
0.6454	1.0905	1437.7	-2.9031	-18.57
0.7534	1.1435	1481.5	-2.2898	-14.236
0.8603	1.1945	1526.5	-1.2166	-8.5632
0.9714	1.2442	1565.9	-0.1806	-1.4599
1.0000	1.2581	1575.5	0.0000	0.0000
sulfolane (1) + n-butyl acetate (2)				
0.0000	0.8671	1176	0.000	0.0000
0.0311	0.8769	1182	-0.068	-1.0209
0.1903	0.9286	1232	-0.624	-5.3097
0.3402	0.9809	1280	-1.040	-7.3265
0.4740	1.0309	1327	-1.291	-7.9696
0.5789	1.0727	1372	-1.396	-8.0236
0.6793	1.1144	1424	-1.336	-7.4545
0.7887	1.1621	1477	-1.131	-6.0321
0.8876	1.2071	1528	-0.750	-4.0125
0.9836	1.2501	1577	-0.098	-0.2568
1.0000	1.2570	1588	0.0000	0.0000

Table 3 The Binary Coefficients (A_i) and Standard Errors (σ) of Sulfolane (1)+Butanone, n-Butylamine and n-Butyl acetate (2) at 308.15 K.

| Function	A_0	A_1	A_2	A_3	A_4	σ
sulfolane (1) + 2-butanone (2)						
$V^E \cdot 10^6$/m^3·mol^{-1}	-6.56	1.07	1.83	-1.73	-3.5	0.022
$\Delta\kappa_s \cdot 10^{11}$/m^2·N^{-1}	-36.34	6.8	-3.2	-1.3	7.9	0.12
sulfolane (1) + n-Butylamine (2)						
$V^E \cdot 10^6$/m^3·mol^{-1}	-12.4478	-1.2945	4.4924	10.8785	-7.9880	0.1467
$\Delta\kappa_s \cdot 10^{11}$/m^2·N^{-1}	-52.7449	-8.1251	28.6612	71.0619	-84.8676	0.1020
sulfolane (1) + n-Butyl acetate (2)						
$V^E \cdot 10^6$/m^3·mol^{-1}	-5.1403	-0.9133	-0.4219	-0.9498	-2.1388	0.0088
$\Delta\kappa_s \cdot 10^{11}$/m^2·N^{-1}	-38.2010	2.6331	8.0557	6.1304	-17.3010	0.0935
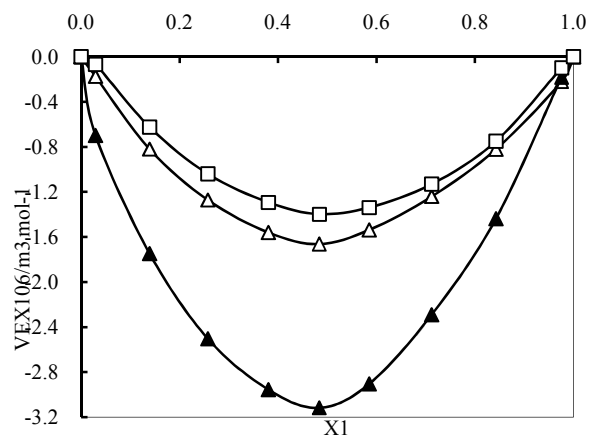
Figure 1 Plots of excess molar volume, V^E, of sulfolane (1) + Butanone, n-Butylamine and n-Butyl acetate (2) system as function of mole fraction at *T*=308.15 K; Δ, Butanone; ▲, n-Butylamine; □, n-Butyl acetate; the symbols represent experimental values.
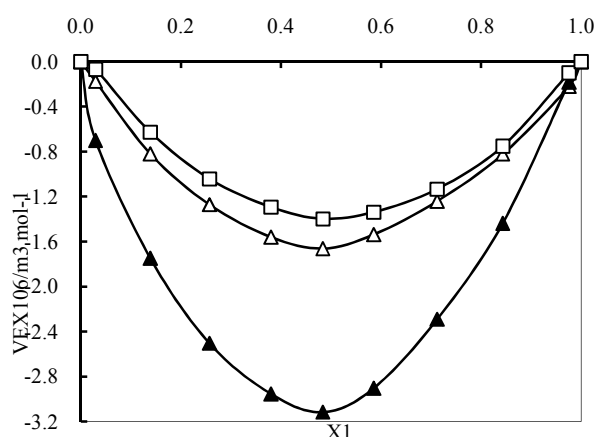
Figure 2 Plots of deviation in isentropic compressibility, $\Delta\kappa_s$, of sulfolane (1) + Butanone, n-Butylamine and n-Butyl acetate (2) system as function of volume fraction at T=308.15 K; Δ, Butanone; ▲, n-Butylamine; □, n-Butyl acetate; the symbols represent experimental values.

RESULTS AND DISCUSSION

Experimental values of density (ρ), speed of sound (u), excess molar volume (V^E), and deviation in isentropic compressibility ($\Delta\kappa_s$) for the binary mixtures of sulfolane with butanone, n-butyl amine and n-butyl acetate at T =308.15 K are given as a function of mole fraction in Table 2.

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

$$V^E = (x_1M_1 + x_2M_2) / \rho_m - (x_1M_1/ \rho_1 + x_2M_2/ \rho_2) \qquad (1)$$

where ρ_m is the density of the mixture; 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' is used to calculate the isentropic compressibility (κ_s) using the equation

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

The deviation from isentropic compressibility ($\Delta\kappa_s$) have been evaluated using the equation

$$\Delta\kappa_s = \kappa_s - (\Phi_1\kappa_{s1} + \Phi_2\kappa_{S2}) \qquad (3)$$

where κ_{s1}, κ_{s2} and κ_s are the isentropic compressibility of the pure components and observed isentropic compressibility of liquid mixture respectively. Φ_1 is the volume fraction of pure components and is calculated from the individual pure molar volumes, V_i, with the relation:

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

The excess properties ΔY were fitted by the method of non linear least squares to a Redlich-Kister type polynomial [10].

$$x_1x_2 \Sigma A_i(x_1 - x_2)^i \qquad (5)$$

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:

$$\sigma (\Delta Y) = [\Sigma (\Delta Y_{obs} - \Delta Y_{cal}) / (n - m)]^{\frac{1}{2}} \qquad (6)$$

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 ones 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-The variation of excess molar volume (V^E) values with the mole fraction (x_1) of sulfolane for butanone, n-butyl amine and n-butyl acetate at 308.15 K are plotted in Fig. 1. The excess molar volumes for all binary mixtures with sulfolane are negative. The observed V^E values are the resultant of physical and chemical forces and they may be broadly recognized as: (i) The breaking of liquid order on mixing with the second component; (ii) Non – specific physical interactions and unfavorable interactions between unlike molecules; (iii) Specific interactions appearing in the mixture between dissimilar molecules by hydrogen bond formation; and (iv) Specific interactions appearing in the mixture between solvent and co-solvent molecules by dipole-dipole.

The first two factors contribute for the expansion of volume and the latter two factors contribute to the reduction of the volume. From the V^E curves at 308.15 K shown in Fig. 1, it is clear that the volume reduction factors are dominant over the expansion factors in the present systems. The negative values of V^E vary in the following order: n-butyl amine < butanone < n-butyl acetate < 0.

As the amines are associated liquids through H-bonding, when sulfolane is mixed with n-butyl amine, dissociation of associated liquid structure takes place resulting in an expansion of volume of the mixture. But the observed negative excess molar volume shows that the volume reduction factor plays an important role between unlike molecules. This indicates the formation of hydrogen bond complexes. Thus, the observed large negative values of V^E indicate the predominance of formation of -S=O·····HN- bonds over the rupture of bonds present in pure sulfolane and n-butyl amine.

n-butyl amine is moderately polar solvent. Sulfolane is a dipolar aprotic solvent [17], because its high dipole moment (4.8 D) favours dipole-dipole interactions[17] in which negative end of the dipole has exposed. Hence, there will be dipole-dipole interactions between unlike molecules of the four systems, contributing to the reduction in the volume. From the above argument (Fig. 1) it is clear that the large specific interactions are present between the mixtures of sulfolane and n-butyl amine than sulfolane + butanone and sulfolane + n-butyl acetate.

Deviation in isentropic compressibility-The variation of $\Delta\kappa_s$ with composition of mixture (Φ_1 of sulfolane) is shown in Fig. 2. From the isotherms it is seen that $\Delta\kappa_s$ values are negative for all the systems studied. The algebric values of $\Delta\kappa_s$ for the three systems at equimolar compositions are in the order
n-butyl amine < butanone < n-butyl acetate < 0.

Sulfolane and n-butyl amine are highly polar in nature. The behaviour of mixtures can be explained in terms of (i) physical forces – dispersion (ii) chemical forces – dipole-dipole interactions and hydrogen boding formation. The former factor increases the intermolecular path lengths, as described by

Jacobson [18]. This in turn causes positive deviation in compressibility. On the other hand, the latter factor decreases the inter-molecular path lengths leading to a negative deviation in compressibility. The actual values depend upon the relative strengths of the two opposing effects. The observed negative values of $\Delta\kappa_s$ for these mixtures imply that the specific interactions dominate over the dispersive interactions between unlike molecules. Usually the behaviour of V^E and $\Delta\kappa_s$ are similar in nature. This tendency is also found in the present study, showing the same sign and same order as that of V^E.

CONCLUSIONS

The experimental values of density, viscosity and speed of sound for the binary mixtures of sulfolane with butanone, n-butylamine and n-butyl acetate at 308.15 K and different compositions are measured. From these data, the thermodynamic excess functions have been calculated and correlated using the Redlich-Kister polynomial equation. The sign and magnitude of these quantities have been discussed in terms of hydrogen bonding and dipole-dipole interactions between the mixing components. In the entire composition range excess molar volume, deviation in viscosity and deviation in isentropic compressibility are negative for all binary mixtures.

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