3. Results and Discussion

The measured values of surface tension and the computed values of the excess surface tension for binary mixtures of glycerol and organic cosolvents are reported in Table I. Plots of the surface tension versus mole fraction of cosolvents, shown in Figure 1, indicate that the surface tension of all the binary mixtures investigated here decreases with an increase of the cosolvent mole fraction.

The excess surface tension, σ^E, may be defined as

$$\sigma^E = \sigma - (\sigma_1 X_1 + \sigma_2 X_2) \qquad (1)$$

where σ is the surface tension of the mixture and σ_1 and σ_2 are surface tensions of the two components of mole fractions X_1 and X_2, respectively.

The values of σ^E for various mole fractions of cosolvents are shown in Table I and graphically shown in Figure 2. All these mixtures, except DMSO, show minima in σ^E values below a 0.3 mole fraction of the cosolvent. The minimum in the DMSO/ glycerol mixture is observed at a 0.75 mole fraction of DMSO. Positive excess mixing is also observed in methanol and DMF mixtures near 0.9 mole fractions of the cosolvents.

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Excess Volumes and Isentropic Compressibilities of Mixtures of p-Chlorotoluene + 2-Propanol, + 2-Methyl-1-propanol, and + 3-Methyl-1-butanol at 303.15 K

Bojja Sreenivasulu, Vadlamudi C. Kumar, and Puligundla R. Naidu*

Department of Chemistry, University College, Sri Venkateswara University, Tirupati 517 502, India

Excess volumes and isentropic compressibilities of binary mixtures of p-chlorotoluene with 2-propanol, 2-methyl-1-propanol, and 3-methyl-1-butanol have been measured at 303.15 K. The excess volume exhibits inversion in sign in the three mixtures. The results have been compared with those of the three corresponding 1-alkanols. V^E is more positive for the 1-alkanols group. Deviation in isentropic compressibility, the difference between the value of the function for the real mixture and that for the ideal mixture, is negative over the whole range of composition in the three mixtures.

Introduction

We report measurements of excess volumes and isentropic compressibilities for three binary mixtures. The mixtures are p-chlorotoluene + 2-propanol, + 2-methyl-1-propanol, and + 3-methyl-1-butanol. The results have been compared with those reported in the literature (*1*) for mixtures of p-chlorotoluene with the corresponding 1-alkanols. The comparison was made to determine the effect of the change in environment of the OH function on the two properties.

Experimental Section

Excess volumes were measured directly using the dilatometer described by Rao and Naidu (*2*). The mixing cell contained two bulbs of different capacities which were connected through a U tube with mercury to separate the two components. One end of the bulb was fitted with a capillary (1-mm i.d.), and the other end of the second bulb was fitted with a ground-glass stopper.

Table I. Densities (ρ) of Pure Components at 303.15 K

| | $\rho/(\text{g cm}^{-3})$ | | |
component	lit. (*5*)	present study	accuracy
2-propanol	0.776 90	0.776 85	±0.000 05
2-methyl-1-propanol	0.794 37	0.794 34	±0.000 03
3-methyl-1-butanol	0.801 79	0.801 82	±0.000 03

The excess volumes were accurate to ±0.003 cm^3 mol^{-1}. Isentropic compressibilities were computed from measured sound speed data and densities calculated from the excess volumes.

The ultrasonic sound speed was measured with a single-crystal interferometer at 4 MHz, and the results were accurate to $\pm0.15\%$. All the measurements were made at constant temperature employing a thermostat that could be maintained to ±0.01 K.

Purification of Materials

All the materials were purified by the methods described by Riddick and Bunger (*3*) and Vogel (*4*). p-Chlorotoluene (E. Merck) was washed successively with 30 cm^3 of (10% by mass) sodium hydroxide solution and an equal amount of concentrated sulfuric acid and water. It is dried with anhydrous calcium chloride, decanted, and distilled. All alcohols were dried by refluxing with fused calcium oxide and finally distilled using a fractionating column.

The purity of the samples was checked by comparing the measured densities of the compounds with those reported in the literature (*5*, *6*). Densities were determined with a bicapillary type pycnometer, which offered an accuracy of 2 parts in 10^5. The measured densities and those reported in the literature (*5*) are given in Table I. The density for p-chlorotoluene was available at 298.15 K in the literature (*6*). The

Table II. Excess Volumes (V^E) for the Binary Mixtures of p-Chlorotoluene (1) with the Isoalcohols (2) at 303.15 K

x_1	$V^E/$ (cm³ mol⁻¹)	x_1	$V^E/$ (cm³ mol⁻¹)	x_1	$V^E/$ (cm³ mol⁻¹)
	p-Chlorotoluene (1) + 2-Propanol (2)				
0.0749	−0.064	0.4271	0.028	0.8251	0.159
0.1670	−0.084	0.5656	0.111	0.8565	0.152
0.2370	−0.070	0.6420	0.156		
0.3875	0.006	0.7252	0.168		
	p-Chlorotoluene (1) + 2-Methyl-1-propanol (2)				
0.1285	−0.053	0.4500	0.030	0.7948	0.134
0.1523	−0.057	0.5659	0.078	0.8521	0.128
0.2170	−0.050	0.6384	0.103		
0.3378	−0.020	0.7022	0.121		
	p-Chlorotoluene (1) + 3-Methyl-1-butanol (2)				
0.1194	−0.025	0.4422	0.040	0.8072	0.104
0.1745	−0.028	0.5632	0.071	0.8438	0.103
0.2328	−0.020	0.6489	0.094		
0.3692	0.013	0.7429	0.105		
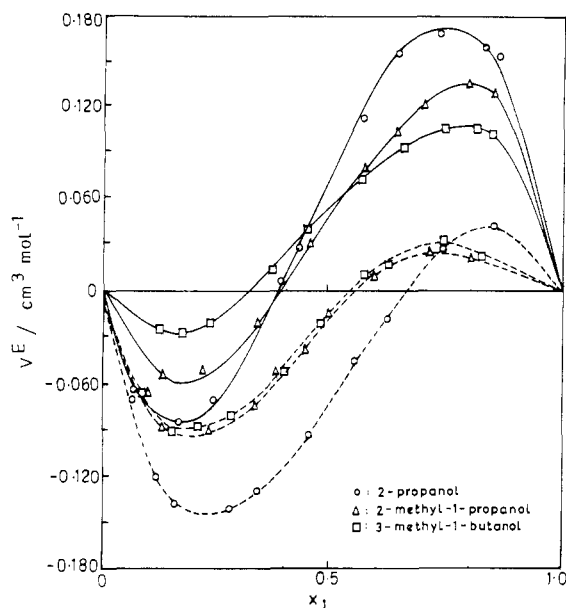
Figure 1. V^E plotted against mole fraction (x_1) of p-chlorotoluene at 303.15 K (—) for p-chlorotoluene (1) + (O) 2-propanol (2), (△) 2-methyl-1-propanol (2), and (□) 3-methyl-1-butanol (2) and (- -) for p-chlorotoluene (1) + (O) 1-propanol (2), (△) 1-butanol (2), and (□) 1-pentanol (2).

value agreed with that determined in the present investigation within the experimental error.

Results and Discussion

Excess volumes of mixtures of p-chlorotoluene (1) with 2-propanol (2), 2-methyl-1-propanol (2), and 3-methyl-1-butanol (2) are given in Table II. The results are also shown in Figure 1 along with those for p-chlorotoluene and the corresponding 1-alkanols. The V^E results were fitted by least-squares method to the polynomial

$$V^E = x_1 x_2 [a_0 + a_1(x_1 - x_2) + a_2(x_1 - x_2)^2] \quad (1)$$

where x_1 and x_2 denote mole fractions of the components 1 and 2 and a_0, a_1, and a_2 are constants. The values of the constants are given in Table III, along with standard deviations $\sigma(V^E)$.

Speed of sound (u) results and densities (ρ) are presented in Table IV. The density of the mixture was calculated using the relation

$$\rho = \frac{x_1 M_1 + x_2 M_2}{x_1 V_1^\circ + x_2 V_2^\circ + V^E} \quad (2)$$

Table III. Standard Deviations $\sigma(V^E)$ and Values of Constants in Equation 1

	a_0	a_1	a_2	$\sigma(V^E)/$ (cm³ mol⁻¹)
p-chlorotoluene + 2-propanol	0.3080	1.3182	−0.1091	0.005
p-chlorotoluene + 2-methyl-1-propanol	0.1887	0.9936	0.1693	0.006
p-chlorotoluene + 3-methyl-1-butanol	0.2123	0.6856	0.1283	0.004

Table IV. Volume Fractions (ϕ_1), Densities (ρ), Sound Velocities (u), Isentropic Compressibilities (k_s), and Deviations in Isentropic Compressibility (Δk_s) of p-Chlorotoluene with Isoalcohols at 303.15 K

ϕ_1	$\rho/$(g cm⁻³)	$u/$(m s⁻¹)	$k_s/$(T Pa⁻¹)	$\Delta k_s/$(T Pa⁻¹)
	p-Chlorotoluene + 2-Propanol			
0.0000	0.776 85	1139	992	
0.1110	0.808 99	1153	930	−17
0.2362	0.844 71	1169	866	−30
0.3240	0.869 45	1178	829	−31
0.4940	0.916 91	1198	760	−30
0.5349	0.928 32	1202	746	−28
0.6677	0.965 18	1218	698	−22
0.7345	0.983 74	1227	675	−17
0.8028	1.003 03	1235	654	−10
0.8792	1.024 80	1249	626	−7
1.0000	1.060 52	1271	584	
	p-Chlorotoluene + 2-Methyl-1-propanol			
0.0000	0.794 34	1175	912	
0.1587	0.837 04	1187	848	−12
0.2617	0.864 45	1194	811	−15
0.3949	0.899 61	1205	766	−16
0.5114	0.930 21	1214	729	−15
0.6251	0.960 06	1224	695	−12
0.6931	0.977 93	1230	676	−9
0.7510	0.993 18	1286	659	−7
0.8321	1.014 64	1247	634	−5
0.8805	1.027 59	1252	621	−2
1.0000	1.060 52	1271	584	
	p-Chlorotoluene + 3-Methyl-1-butanol			
0.0000	0.801 82	1220	838	
0.1283	0.835 21	1225	798	−8
0.1867	0.850 34	1228	780	−11
0.2478	0.866 10	1231	762	−13
0.3886	0.902 26	1234	728	−11
0.4626	0.921 20	1236	711	−9
0.5833	0.952 18	1240	683	−7
0.6674	0.973 74	1244	664	−4
0.7583	0.997 15	1248	644	−1
0.8543	1.022 01	1256	620	−1
1.0000	1.060 52	1271	584	

Table V. Standard Deviations $\sigma(\Delta K_s)$ and Values of Constants in Equation 6

system	b_0	b_1	b_2	$\sigma(\Delta k_s)/$ (T Pa⁻¹)
p-chlorotoluene + 2-propanol	−119.4	74.5	1.7	1
p-chlorotoluene + 2-methyl-1-propanol	−60.5	43.2	5.2	1
p-chlorotoluene + 3-methyl-1-butanol	−35.0	50.6	−8.8	1

where M_i and V_i are the molar mass and molar volume of component i.

The isentropic compressibility k_s and deviation in isentropic compressibility Δk_s are calculated using the equations

$$k_s = u^{-2} \rho^{-1} \quad (3)$$

$$\Delta k_s = k_s - \phi_1 k_{s,1} - \phi_2 k_{s,2} \quad (4)$$

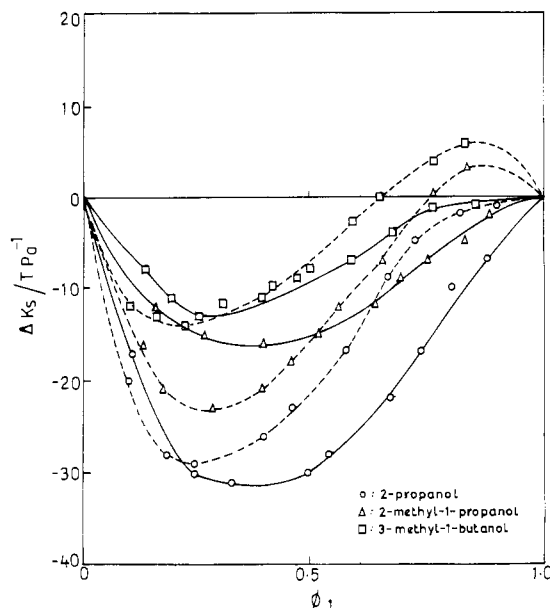$$\phi_1 = \frac{x_1 V_1^\circ}{x_1 V_1^\circ + x_2 V_2^\circ} \quad (5)$$

Figure 2. Δk_s plotted against volume fraction (ϕ_1) of p-chlorotoluene at 303.15 K (—) for p-chlorotoluene (1) + (O) 2-propanol (2), ($\triangle$) 2-methyl-1-propanol (2), and ($\square$) 3-methyl-1-butanol (2) and (--) for p-chlorotoluene (1) + (O) 1-propanol (2), ($\triangle$) 1-butanol (2), and ($\square$) 1-pentanol (2).

k_s, $k_{s,1}$, and $k_{s,2}$ are the isentropic compressibilities of a mixture and the pure components 1 and 2, respectively. ϕ_1 and ϕ_2 are the volume fractions of the components. The values of k_s and Δk_s are also given in Table IV. The results are shown in Figure 2 along with those for mixtures of p-chlorotoluene with 1-propanol, 1-butanol, and 1-pentanol.

The isothermal compressibility results also have been fitted into an empirical equation of the form

$$\Delta k_s = \phi_1 \phi_2 [b_0 + b_1(\phi_1 - \phi_2) + b_2(\phi_1 - \phi_2)^2] \quad (6)$$

The values of the constants b_0, b_1, and b_2 are included in Table V, along with the standard deviations $\sigma(\Delta k_s)$.

Excess volume data included in Table II show that the excess function exhibits a sign inversion for the three mixtures. However, positive values of V^E dominate over a large range of concentration of p-chlorotoluene. Figure 1 indicates that the replacement of 1-alcohols by isoalcohols leads to an increase in algebraic value of V^E.

Results included in the Table IV indicate that Δk_s is negative over the whole range of composition. Figure 2 shows that the replacement of 1-alcohols by isoalcohols does not lead to a significant change in this property.

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Solubility and Diffusivity Data for the Absorption of COS, CO2, and N2O in Amine Solutions

Rob J. Littel,* Geert F. Versteeg, and Wim P. M. van Swaaij

Department of Chemical Engineering, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands

Absorption data for COS and N_2O in aqueous solutions of N-methyldiethanolamine (MDEA), ethylene glycol, and sulfolane (tetrahydrothiophene 1,1-dioxide) at 298 K and solubility data for COS in water at temperatures ranging from 298 to 338 K are presented. Also density, viscosity, N_2O solubility, and N_2O diffusivity data are reported for a wide range of aqueous alkanolamine solutions, aqueous mixtures of alkanolamines, and solutions of MDEA in water/ethanol. It is shown that an analogy between COS and N_2O with respect to gas solubility in aqueous solutions of ethylene glycol and sulfolane holds up to about 25 mass %. This seems to justify, for engineering purposes, the application of this analogy for the estimation of COS solubilities in diluted aqueous amine solutions. Direct verification of a COS–N_2O analogy was provided by absorption of N_2O and COS into aqueous MDEA solutions in a laminar film reactor.

1. Introduction

Alkanolamine processes are one of the most frequently applied processes for the removal of acid components like H_2S,

COS, and CO_2 from industrial and natural gases. Diethanolamine (DEA), diisopropanolamine (DIPA), and N-methyldiethanolamine (MDEA) are industrially well-known alkanolamines for gas-treating purposes (1). Apart from mass-transfer and kinetic data, physical data like gas diffusivity and solubility are also required for an adequate design of gas-treating plants. These data are also necessary in the deduction of chemical reaction kinetics from absorption experiments. However, due to chemical reactions, these physical constants can usually not be measured in a direct way.

For CO_2 the analogy with N_2O is widely applied to estimate the solubility and diffusivity in aqueous alkanolamine solutions. N_2O is similar to CO_2 with regard to configuration, molecular volume, and electronic structure but does not react with alkanolamines. The CO_2–N_2O analogy states that the ratio of the solubilities of CO_2 and N_2O in water is the same as the ratio of the solubilities of both gases in the alkanolamine solution:

$$(m_{CO_2}/m_{N_2O})_{am.\ soln} = (m_{CO_2}/m_{N_2O})_{H_2O} \quad (1)$$

Laddha et al. (2) showed that the CO_2–N_2O analogy holds for various aqueous solutions of alcohols. Haimour and Sandall (3) studied the absorption of CO_2 and N_2O into aqueous MDEA solutions at various temperatures in a laminar liquid jet. Due