J. Chem. Eng. Data 1993, 38, 619–621

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

Bojja Sreenivasulu and Puligundla R. Naidu*

Department of Chemistry, Sri Venkateswara University College, Tirupati 517502, A.P., India

Excess volumes and isentropic compressibilities of binary mixtures of *p*-xylene with 2-propanol, 2-methyl-1-propanol, and 3-methyl-1-butanol have been measured at 303.15 K. The excess volume exhibits positive deviation over the whole range of composition in the three mixtures, and the deviation in isentropic compressibility exhibits inversion in sign in the three mixtures. The results have been compared with those reported in the literature for binary mixtures of *p*-chlorotoluene with the same alcohols (*1*).

Introduction

We report new experimental results for excess volumes and isentropic compressibilities of three binary mixtures. The mixtures included *p*-xylene as a common component and three isoalcohols as noncommon components. The three isoalcohols were 2-propanol, 2-methyl-1-propanol, and 3-methyl-1-butanol. The study was undertaken to examine the effect of replacement of *p*-chlorotoluene by *p*-xylene 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 each 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. The excess volumes were accurate to ±0.003 $cm^3\ mol^{-1}$. Isentropic compressibilities were computed from the measured sound speed, and the density was derived from the excess volume.

The ultrasonic sound speed was measured with a single crystal interferometer at 4 MHz, and the results were accurate to ±0.15%. All the measurements were made at constant temperature using a thermostat that could be maintained to ±0.01 K.

Purification of Materials. *p*-Xylene was purified by the method described by Vogel (*3*). *p*-Xylene was washed with concentrated sulfuric acid until the acid developed no more color, then with water, dilute sodium hydroxide, and finally with two portions of water. The sample was dried over anhydrous calcium chloride. The sample was refluxed with metallic sodium and finally fractioned over sodium. The isoalcohols were dried over fused calcium oxide and then fractionated 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 (*4*). 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 are given in Table I.

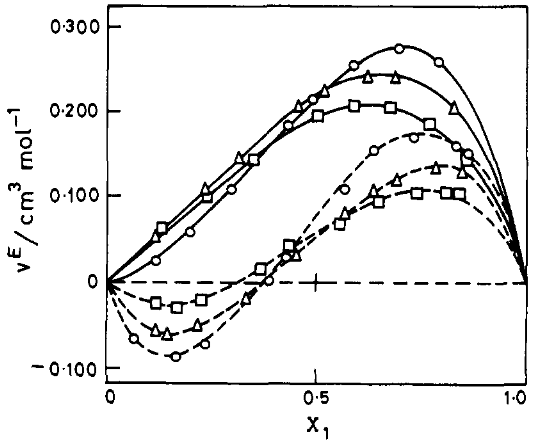

Figure 1. V^E plotted against the mole fraction (x_1) of (—) *p*-xylene with 2-propanol (○), 2-methyl-1-propanol (△), and 3-methyl-1-butanol (□) and of (- - -) *p*-chlorotoluene (1) with 2-propanol (○), 2-methyl-1-propanol (△), and 3-methyl-1-butanol (□) at 303.15 K.

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

component	ρ/(g cm^{-3}) lit. (*4*)	ρ/(g cm^{-3}) present study
p-xylene	0.852 30	0.852 34
2-propanol	0.776 90	0.776 85
2-methyl-1-propanol	0.794 37	0.794 34
3-methyl-1-butanol	0.801 79	0.801 82

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

x_1	$V^E/(cm^3\ mol^{-1})$	x_1	$V^E/(cm^3\ mol^{-1})$	x_1	$V^E/(cm^3\ mol^{-1})$
		p-Xylene (1) + 2-Propanol (2)			
0.1151	0.026	0.4291	0.185	0.7038	0.275
0.2039	0.062	0.4894	0.213	0.7924	0.262
0.2966	0.112	0.5922	0.254		
		p-Xylene (1) + 2-Methyl-1-propanol (2)			
0.1202	0.057	0.4633	0.205	0.6919	0.240
0.2430	0.108	0.5185	0.227	0.8294	0.205
0.3196	0.146	0.6232	0.240		
		p-Xylene (1) + 3-Methyl-1-butanol (2)			
0.1302	0.060	0.4950	0.193	0.7727	0.188
0.2372	0.103	0.5884	0.205	0.8577	0.147
0.3450	0.146	0.6727	0.205		

Results and Discussion

Excess volumes of mixtures of *p*-xylene (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 isoalcohols. The V^E results were fitted, by the least-squares

---

* To whom correspondence should be addressed.

0021-9568/93/1738-0619$04.00/0

Table III. Standard Deviations $\sigma(V^E)$ and Values of the Constants from the Redlich and Kister Equation (eq 1) and the H³M Equation (eq 2)

	eq 1				eq 2			
	a_0	a_1	a_2	$\sigma(V^E)$	V_0	V_1	V_2	$\sigma(V^E)$
p-xylene + 2-propanol	0.8785	1.0127	0.2885	0.005	0.7859	1.5812	−0.8281	0.003
p-xylene + 2-methyl-1-propanol	0.8592	0.6596	0.3127	0.005	0.7560	1.2051	−0.3732	0.004
p-xylene + 3-methyl-1-butanol	0.7627	0.4617	0.2002	0.002	0.6990	0.8119	−0.2924	0.002

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

ϕ_1	$\rho/(\mathrm{g\ cm^{-3}})$	$u/(\mathrm{m\ s^{-1}})$	$k_s/\mathrm{TPa^{-1}}$	$\Delta k_s/\mathrm{TPa^{-1}}$
	p-Xylene (1) + 2-Propanol (2)			
0.0000	0.776 85	1126	1015	
0.1732	0.789 67	1151	956	−5
0.2920	0.798 32	1168	918	−6
0.4044	0.806 39	1183	886	−3
0.5475	0.816 64	1203	846	2
0.6068	0.820 92	1209	833	7
0.7004	0.827 73	1224	806	10
0.7928	0.834 62	1241	778	10
0.8601	0.839 86	1256	755	8
1.0000	0.852 34	1292	703	
	p-Xylene (1) + 2-Methyl-1-propanol (2)			
0.0000	0.794 34	1172	916	
0.1542	0.802 81	1190	880	−3
0.3000	0.810 87	1206	848	−4
0.3854	0.815 54	1212	835	1
0.5354	0.823 83	1223	812	10
0.5897	0.826 83	1228	802	12
0.6883	0.832 49	1240	781	12
0.7499	0.836 09	1247	769	13
0.8665	0.843 15	1264	742	11
1.0000	0.852 34	1292	703	
	p-Xylene (1) + 3-Methyl-1-butanol (2)			
0.0000	0.801 82	1220	838	
0.1450	0.808 71	1233	813	−5
0.2605	0.814 24	1235	805	2
0.3737	0.819 66	1239	795	7
0.5262	0.827 04	1245	780	13
0.6183	0.831 62	1250	770	15
0.6996	0.835 73	1256	758	14
0.7939	0.840 62	1265	743	12
0.8723	0.844 87	1273	730	10
1.0000	0.852 34	1292	703	

method, to the polynomial proposed by Redlich and Kister (*5*):

$$V^E/(\mathrm{cm^3\ mol^{-1}}) = x_1x_2[a_0 + a_1(x_1 - x_2) + a_2(x_1 - x_2)^2] \quad (1)$$

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 V^E results were also fitted to the H³M equation recently proposed by Hwang et al. (*6*):

$$V^E/(\mathrm{cm^3\ mol^{-1}}) = x_1x_2(V_0 + V_1x_1^3 + V_2x_2^3) \quad (2)$$

where x_1 and x_2 represent mole fractions of components 1 and 2, and V_0, V_1, and V_2 are constants. The values of the two sets of the constants are given in Table III along with standard deviations $\sigma(V^E)$. The standard deviation values given in Table III indicate that the H³M equation gives a better fit of the experimental data.

Experimental sound speed (u) data and density (ρ) data computed from measured excess volume data are presented in columns 3 and 2, respectively, of Table IV. The isentropic compressibility k_s and deviation in isentropic compressibility Δk_s are calculated using the equations

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

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

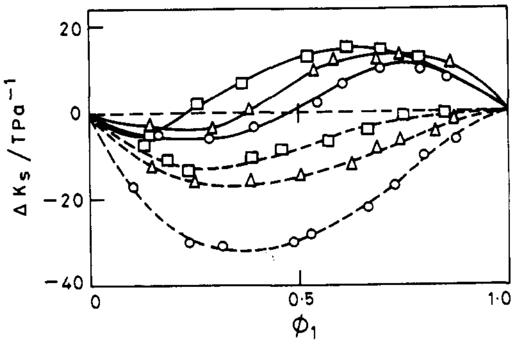

Figure 2. Δk_s plotted against the volume fraction (ϕ_1) of (—) *p*-xylene with 2-propanol (○), 2-methyl-1-propanol (△), and 3-methyl-1-butanol (□) and of (- - -) *p*-chlorotoluene (1) with 2-propanol (○), 2-methyl-1-propanol (△), and 3-methyl-1-butanol (□) at 303.15 K.

Table V. Standard Deviations $\sigma(\Delta k_s)$ and Values of the Constants Obtained by the Redlich and Kister Equation (eq 6)

system	b_0	b_1	b_2	$\sigma(\Delta k_s)/\mathrm{TPa^{-1}}$
p-xylene + 2-propanol	5.7	80.3	17.2	1
p-xylene + 2-methyl-1-propanol	26.2	86.9	9.5	2
p-xylene + 3-methyl-1-butanol	49.0	79.4	−48.4	1

$$\phi_1 = \frac{x_1V_1^\circ}{x_1V_1^\circ + x_2V_2^\circ} \quad (5)$$

where k_s, $k_{s,1}$, and $k_{s,2}$ represent isentropic compressibilities of a mixture and 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 included in columns 4 and 5 of Table IV. The results are shown in Figure 2 along with those for mixtures of *p*-chlorotoluene with the three isoalcohols.

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 $\sigma(\Delta k_s)$.

The results in Table II and the curves in Figure 1 show that the excess volume is positive over the whole range of composition in the three mixtures. The V^E values at higher mole fractions fall in the order 2-propanol > 2-methyl-1-propanol > 3-methyl-1-butanol.

However, V^E exhibits inversion in sign in the mixtures of *p*-chlorotoluene with the three isoalcohols (*1*). This shows that replacement of *p*-chlorotoluene by *p*-xylene promotes a structure-breaking effect. The structure-breaking effect may be ascribed to the loss of dipolar association of the components and the breakup of H bonds in alcohol aggregates.

The deviation in isentropic compressibility, the difference between the value of the function for the real mixture and that for the ideal mixture, included in Table IV and in Figure 2 shows that replacement of *p*-chlorotoluene (1) by *p*-xylene leads to an increase in the algebraic value of the deviation. This supports the contention that mixing of components results in a structure-breaking effect. This effect leads to an increase in free spaces, a decrease in the sound speed, and a consequent increase in the algebraic value of the deviation in isentropic compressibility.

Literature Cited

(1) Sreenivasulu, B.; Kumar, V. C.; Naidu, P. R. *J. Chem. Eng. Data.* **1992**, *37*, 47.
(2) Rao, M. V. P.; Naidu, P. R. *Can. J. Chem.* **1974**, *52*, 788–90.
(3) Vogel, A. I. *A Text Book of Practical Organic Chemistry*, 4th ed.; Longman: ELBS, 1978.
(4) Timmermans, J. *Physico-Chemical Constants of Pure Organic Compounds*; Elsevier: Amsterdam, 1950.
(5) Redlich, O.; Kister, A. T. *Ind. Eng. Chem.* **1948**, *40*, 135.
(6) Hwang, C. A.; Holste, J. C.; Hall, K. R.; Mansoori, G. A. *Fluid Phase Equilib.* **1991**, *62*, 173.

Received for review December 9, 1992. Revised May 4, 1993. Accepted June 8, 1993.[⊗]

[⊗] Abstract published in *Advance ACS Abstracts*, August 15, 1993.