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

Vadlamoodi C. Kumar and Puligundla R. Naidu*

Department of Chemistry, University College, S.V. University, Tirupati 517502, India

New experimental results for excess volume and deviation in isentropic compressibility are reported for three binary mixtures. The mixtures include 1,3-dichlorobenzene as the common component and three isoalcohols as noncommon components. The isoalcohols are 2-propanol, 2-methyl-1-propanol, and 3-methyl-1-butanol. Both excess volume and deviation in isentropic compressibility are negative over the whole range of composition. Further, a comparison between the data for isoalcohols and the corresponding 1-alcohols shows that branching of alcohols leads to an increase in the excess volume and a decrease in the deviation in isentropic compressibility.

Introduction

Excess volumes and isentropic compressibilities for binary mixtures of 1,3-dichlorobenzene with 1-butanol and 1-pentanol are reported in the literature (*1*, *2*). Both the excess volume and deviation in isentropic compressibility exhibit inversion in sign. We report here new experimental excess volumes and deviations in isentropic compressibilities for mixtures of 1,3-dichlorobenzene with 2-propanol, 2-methyl-1-propanol, and 3-methyl-1-butanol. The mixtures were chosen to study the effect of branching of an alcohol on the two properties. The results have been compared with those of the three corresponding 1-alcohols.

Experimental Section

Excess volumes were measured directly by using the dialatometer described by Rao and Naidu (*3*). 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. The excess volumes were accurate to ±0.003 cm^3 mol^{-1}.

Isentropic compressibilities were computed from measured sound speed data and densities evaluated from excess volumes. The ultrasonic sound speed was measured with a single-crystal interferometer at 4-MHz frequency, and the data were accurate to ±0.15%. All the measurements were made at constant temperature employing a thermostat that could be maintained to ±0.01 K. The density was computed from the measured excess volume using the relation

$$\rho_{1,2} = \frac{x_1M_1 + x_2M_2}{V^\circ + V^E} \qquad (1)$$

where M, $\rho_{1,2}$, V°, and x represent the molecular weight, density, and molar volume of the ideal mixture and the mole fraction of the mixture, respectively.

Purification of Materials. All the materials were purified by the methods described by Riddick and Bunger (*4*). 1,3-Dichlorobenzene (Sisco Chemicals) was washed successfully with 10% sodium hydroxide solution and then with water until the washings were neutral, dried, and fractionated. All alcohols were dried by refluxing with calcium oxide and finally distilled using a fractionating column.

* To whom correspondence should be addressed.

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

component	ρ/(g·cm^{-3}) lit. (*5*)	ρ/(g·cm^{-3}) present study
1,3-dichlorobenzene	1.277 18	1.277 15
1-propanol	0.796 00	0.796 02
2-propanol	0.776 90	0.776 85
2-methyl-1-propanol	0.794 37	0.794 35
3-methyl-1-butanol	0.801 79	0.801 78

Table II. Excess Volumes (V_m^E) for 1,3-Dichlorobenzene (1) with Alkanols (2) at 303.15 K

x_1	V_m^E/(cm^3·mol^{-1})	x_1	V_m^E/(cm^3·mol^{-1})	x_1	V_m^E/(cm^3·mol^{-1})
1,3-Dichlorobenzene (1) + 1-Propanol (2)					
0.1091	−0.128	0.4476	−0.152	0.7279	0.004
0.1859	−0.184	0.5922	−0.077	0.7788	0.032
0.3051	−0.199	0.6413	−0.046	0.8257	0.038
1,3-Dichlorobenzene (1) + 2-Propanol (2)					
0.1163	−0.118	0.4887	−0.027	0.7846	0.111
0.2308	−0.138	0.6078	0.047	0.8568	0.105
0.3684	−0.093	0.7065	0.092		
1,3-Dichlorobenzene (1) + 2-Methyl-1-propanol (2)					
0.0934	−0.076	0.4195	−0.026	0.7387	0.099
0.1806	−0.097	0.5085	0.015	0.8516	0.089
0.3146	−0.073	0.6423	0.071		
1,3-Dichlorobenzene (1) + 3-Methyl-1-butanol (2)					
0.1242	−0.080	0.4368	−0.028	0.6865	0.067
0.2343	−0.090	0.5181	0.008	0.7655	0.081
0.2965	−0.077	0.5942	0.035	0.8616	0.082

The purity of the sample was checked by comparing the measured densities of the compounds with those reported in the literature (*4*, *5*). 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.

Results and Discussion

Experimental results for the excess volumes of the mixtures of 1,3-dichlorobenzene with 1-propanol, 2-propanol, 2-methyl-1-propanol, and 3-methyl-1-butanol are included in Table II. The results are also graphically presented in Figure 1. Experimental V^E data have been reduced using the polynomial

$$V^E/x_1x_2 = [a_0 + a_1(x_1 - x_2) + a_2(x_1 - x_2)^2] \qquad (2)$$

where x_1 and x_2 denote the mole fractions of components 1 and 2 and a_0, a_1, and a_2 are constants. The values of the

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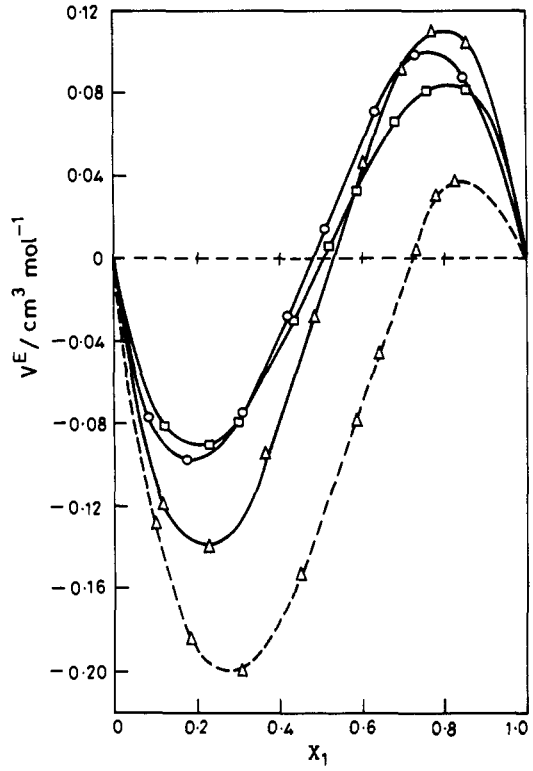

Figure 1. Excess volume V^E for 1,3-dichlorobenzene (1) + 1-propanol (2) (Δ- - -Δ), 1,3-dichlorobenzene (1) + 2-propanol (2) (Δ—Δ), 1,3-dichlorobenzene (1) + 2-methyl-1-propanol (2) (O—O), and 1,3-dichlorobenzene (1) + 3-methyl-1-butanol (2) (□—□).

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

system	a_0/ (cm^3·mol^{-1})	a_1/ (cm^3·mol^{-1})	a_2/ (cm^3·mol^{-1})	$\sigma(V^E)$/ (cm^3·mol^{-1})
1,3-dichlorobenzene (1) + 1-propanol (2)	−0.5200	1.1407	0.1283	0.004
1,3-dichlorobenzene (1) + 2-propanol (2)	−0.0705	1.3207	−0.0694	0.004
1,3-dichlorobenzene (1) + 2-methyl-1-propanol (2)	0.0519	1.0256	−0.1534	0.003
1,3-dichlorobenzene (1) + 3-methyl-1-butanol (2)	−0.0119	0.9281	−0.0091	0.005

constants obtained by the least-squares method are given in Table III along with the standard deviations $\sigma(V^E)$.

Experimental sound speed (u) data and densities (ρ) computed from measured excess volume data are presented in columns 3 and 2 of Table IV. Isentropic compressibility K_s and the deviation in isentropic compressibility ΔK_s are calculated using the equations

$$K_s = u^{-2}\rho^{-1} \tag{3}$$

$$\Delta K_s = K_s - \phi_1 K_{s_1} - \phi_2 K_{s_2} \tag{4}$$

$$\phi_1 = \frac{x_1 V_1^\circ}{x_1 V_1^\circ + x_2 V_2^\circ} \tag{5}$$

and

$$\phi_2 = 1 - \phi_1$$

where K_s, K_{s_1}, and K_{s_2} represent isentropic compressibilities of a mixture and the pure components 1 and 2, respectively. ϕ_1 and ϕ_2 denote 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 graphically represented along with those

Table IV. Volume Fractions (ϕ_1), Densities (ρ), Sound Velocities (u), Isentropic Compressibilities (K_s), and Deviations in the Isentropic Compressibilities (ΔK_s) of 1,3-Dichlorobenzene (1) with Alkanols (2) at 303.15 K

ϕ_1	ρ/(g·cm^{-3})	u/(m·s^{-1})	K_s/TPa^{-1}	ΔK_s/TPa^{-1}
	1,3-Dichlorobenzene (1) + 1-Propanol (2)			
0.0000	0.796 02	1219	845	
0.1573	0.873 11	1211	781	−11
0.2582	0.922 31	1206	745	−13
0.4010	0.991 19	1204	696	−14
0.5526	1.063 64	1206	646	−13
0.6888	1.128 32	1211	604	−9
0.7316	1.148 53	1215	590	−8
0.8031	1.182 36	1220	568	−6
0.8784	1.218 20	1226	546	−3
1.0000	1.277 15	1241	508	
	1,3-Dichlorobenzene (1) + 2-Propanol (2)			
0.0000	0.776 85	1138	994	
0.1637	0.860 01	1146	885	−29
0.3086	0.932 76	1159	798	−46
0.4646	1.010 32	1176	716	−52
0.5871	1.070 89	1186	664	−45
0.6975	1.125 28	1196	621	−34
0.7817	1.166 91	1205	590	−24
0.8442	1.197 97	1214	566	−18
0.8990	1.225 45	1223	546	−11
1.0000	1.277 15	1241	508	
	1,3-Dichlorobenzene (1) + 2-Methyl-1-propanol (2)			
0.0000	0.794 35	1173	915	
0.1128	0.849 46	1180	845	−24
0.2138	0.898 45	1182	797	−31
0.3615	0.969 59	1188	731	−37
0.4713	1.022 15	1193	687	−36
0.5607	1.064 89	1198	654	−33
0.6890	1.126 23	1204	613	−22
0.7764	1.168 50	1212	583	−16
0.8762	1.216 42	1221	551	−7
1.0000	1.277 15	1241	508	
	1,3-Dichlorobenzene (1) + 3-Methyl-1-butanol (2)			
0.0000	0.801 78	1214	846	
0.1293	0.863 86	1219	779	−23
0.2426	0.917 86	1217	736	−28
0.3062	0.947 97	1216	713	−30
0.4481	1.015 05	1215	667	−28
0.5295	1.053 43	1216	642	−25
0.6052	1.089 14	1215	622	−19
0.6963	1.132 10	1216	597	−14
0.7746	1.169 17	1221	574	−10
0.8670	1.213 05	1227	548	−5
1.0000	1.277 15	1241	508	

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

system	b_0/ TPa^{-1}	b_1/ TPa^{-1}	b_2/ TPa^{-1}	$\sigma(\Delta K_s)$/ TPa^{-1}
1,3-dichlorobenzene (1) + 1-propanol (2)	−53.9	33.9	−5.3	1
1,3-dichlorobenzene (1) + 2-propanol (2)	−198.0	59.6	52.1	1
1,3-dichlorobenzene (1) + 2-methyl-1-propanol (2)	−143.0	102.0	5.0	2
1,3-dichlorobenzene (1) + 3-methyl-1-butanol (2)	−100.0	102.0	−38.3	1

for mixtures of 1,3-dichlorobenzene with 1-propanol, 1-butanol, and 1-pentanol in Figure 2.

These results have been fitted into an empirical equation of the form

$$\Delta K_s/\phi_1\phi_2 = [b_0 + b_1(\phi_1 - \phi_2) + b_2(\phi_1 - \phi_2)^2] \tag{6}$$

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

The data in Table II and the curves in Figure 1 show that V^E exhibits inversion in sign in the mixtures of 1,3-dichlo-

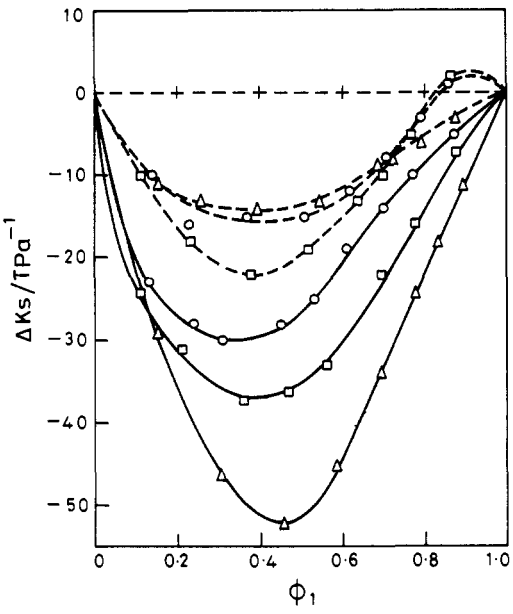

Figure 2. Deviation in the isentropic compressibility ΔK_s for 1,3-dichlorobenzene (1) + 2-propanol (2) (△—△), 1,3-dichlorobenzene (1) + 2-methyl-1-propanol (2) (□—□), 1,3-dichlorobenzene (1) + 3-methyl-1-butanol (2) (○—○), 1,3-dichlorobenzene (1) + 1-propanol (2) (△- - -△), 1,3-dichlorobenzene (1) + 1-butanol (2) (□- - -□), and 1,3-dichlorobenzene (1) + 1-pentanol (2) (○- - -○).

robenzene with three isoalcohols. However, the algebric values of V^E for the three mixtures are greater than those for the mixtures containing 1-alkanols. This indicates that structural effects become weak in mixtures containing the former alcohols. The structural effects include the interstitial accommodation of molecules of dichlorobenzene in the hydrogen-bonding aggregates of the 2-propanol and a weak hydrogen bond interaction between the halogen function in the dichlorobenzene and the hydroxyl function in 2-propanols.

The deviation in isentropic compressibility is negative over the entire range of composition, as indicated by curves in Figure 2 and the data included in Table IV. Here ΔK_s is algebrically smaller than that observed for mixtures containing the corresponding 1-alcohols. The trend shows that ΔK_s is determined by factors different from those that determine excess volume. The sign and magnitude of V^E depend upon the opposing structure-breaking and structure-making effects. The sign and magnitude of ΔK_s would depend on the entropy factor to a considerable degree.

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