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Isentropic Compressibilities of Binary Mixtures of Methylcyclohexane with Substituted Benzenes and Cyclohexanone

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Ultrasonic sound velocities for four binary liquid systems of methylcyclohexane with substituted benzenes and cyclohexanone have been determined at 303.15 K. The substituted benzenes include chlorobenzene, nitrobenzene and benzonitrile. Further, isentropic compressibilities (K_s) and deviation in isentropic compressibilities (ΔK_s) have been computed from the sound velocity and density data derived from excess volumes. The results show that ΔK_s are negative over the entire range of composition for all the binary systems studied. The observed values of ΔK_s have been discussed in terms of existence of specific interactions between the components of various mixtures.

INTRODUCTION

Like excess volumes, the isentropic compressibilities also throw light on the nature and degree of molecular interactions in the binary mixtures. Hence, we measured sound velocities and isentropic compressibilities of methylcyclohexane with chlorobenzene, nitrobenzene, benzonitrile and cyclohexanone at 303.15 K and reported here.

EXPERIMENTAL

Methylcyclohexane (BDH) was purified by the standard method described by Rao and Naidu[1]. Chlorobenzene (E. Merk, India), benzonitrile (Riedel) and nitrobenzene (BDH) were purified by the standard methods described by Reddy *et al*[2]. Cyclohexanone (BDH) was dried over anhydrous sodium sulphate for two days and then fractionally distilled. The purities of the chemicals were checked by comparing the measured densities of the components with those reported in literature[3,4]. Densities of the pure liquids were measured with a bicapillary pyknometer described by Rao[5], which gave an accuracy of 2 parts in 10^5. The measured densities and the literature data are presented in Table 1. Mixture densities were computed from the measured excess volume data. Ultrasonic sound velocities were measured with a single-crystal interferometer at a frequency of 1 MHz. and were accurate to $\pm$ 0.075%. All the measurements were made at a constant temperature employing a themostat that could be maintained to $\pm$ 0.01 K.

TABLE 1

DENSITIES OF PURE LIQUIDS AT 303.15 K

Components	Density g cm^{-3}	
	Exp.	Lit.
Methylcyclohexane	0.76025	0.76030
Chlorobenzene	1.09546	1.09550
Cyclohexanone	0.93757	0.93761
Benzonitrile	0.99622	0.99628
Nitrobenzene	1.19337	0.19341

RESULTS AND DISCUSSION

Isentropic compressibilities (K_S) were calculated from the measured ultrasonic velocities and precise density values at 303.15 K using the relation

$$K \equiv U^{-2}\rho^{-1} \tag{1}$$

where U and ρ denote sound velocity and density respectively. The deviation in isentropic compressibility (ΔK_S) was calculated from the equation

$$\Delta K_S = K_S - \phi_1 K_{S_1} - \phi_2 K_{S_2} \tag{2}$$

where K_S, K_{S_1} and K_{S_2} are the isentropic compressibilities of the mixture and the pure components respectively. ϕ_1 and ϕ_2 are volume fractions of the components. The experimental data for the density, sound velocity, isentropic compressibility and deviation in isentropic compressibility are included in Table 2 and are graphically represented in Fig. 1. The ΔK_S values may be fitted to an empirical equation of the form

$$\Delta K_S = \phi_1\phi_2[b_0 + b_1(\phi_1 - \delta_2) + b_2(\phi_1 - \phi_2)^2] \tag{3}$$

The values of b_0, b_1 and b_2 computed by the method of least square and are given in Table 3 along with standard deviation $\sigma(\Delta K_S)$.

The results included in Table 2 show that the ΔK_S values are negative over the entire volume fraction range in all the four binary systems. The ΔK_S values may be attributed to:

(i) aliphatic-aromatic interactions between the components,
(ii) loss of dipolar association in the substituted benzenes and cyclohexanone by the addition of methylcyclohexane and
(iii) specific interactions between unlike components.

The second factor contributes to an increase in free lengths described

TABLE 2

VOLUME FRACTION (ϕ_1) OF METHYLCYCLOHEXANE, DENSITY (ρ), SOUND VELOCITY (U), ISENTROPIC COMPRESSIBILITY (K_s) AND DEVIATION IN ISENTROPIC COMPRESSIBILITY (ΔK_s) FOR THE BELOW SYSTEMS AT 303.15 K

ϕ_1	σ/g cm^{-3}	U/m S^{-1}	$K_s/T\rho a^{-1}$	$\Delta K_s/T\rho a^{-1}$
Methylcyclohexane + Chlorobenzene				
0.0000	1.09546	1251	583	–
0.1868	1.03236	1234	636	−11
0.3553	0.97551	1222	687	−17
0.5040	0.92547	1211	737	−18
0.6785	0.86687	1201	800	−14
0.8060	0.82431	1196	848	−10
0.9548	0.77505	1194	905	−04
1.0000	0.76025	1193	924	–
Methylcyclohexane + Cyclohexanone				
0.0000	0.93757	1391	551	–
0.1851	0.90483	1350	606	−14
0.3284	0.87926	1317	656	−18
0.5064	0.84741	1281	719	−21
0.6603	0.81984	1251	779	−18
0.7893	0.79684	1227	834	−11
8.9207	0.77389	1204	891	−03
1.0000	0.76025	1193	924	–
Methylcyclohexane + Benzonitrile				
0.0000	0.99622	1402	511	–
0.1833	0.95318	1364	564	−23
0.3567	0.91225	1326	624	−34
0.5035	0.87726	1291	684	−35
0.6620	0.83949	1256	755	−29
0.7879	0.80950	1231	815	−21
0.9211	0.77840	1207	882	−09
1.0000	0.76025	1193	924	–
Methylcyclohexane + Nitrobenzene				
0.0000	1.19337	1441	404	–
0.1860	0.11295	1388	466	−35
0.3581	1.03840	1339	537	−53
0.5189	0·96847	1295	616	−58
0.6545	0.90934	1259	694	−50
0.8011	0.84564	1229	783	−38
0.9249	0.79236	1207	866	−19
1.0000	0.76025	1193	924	–

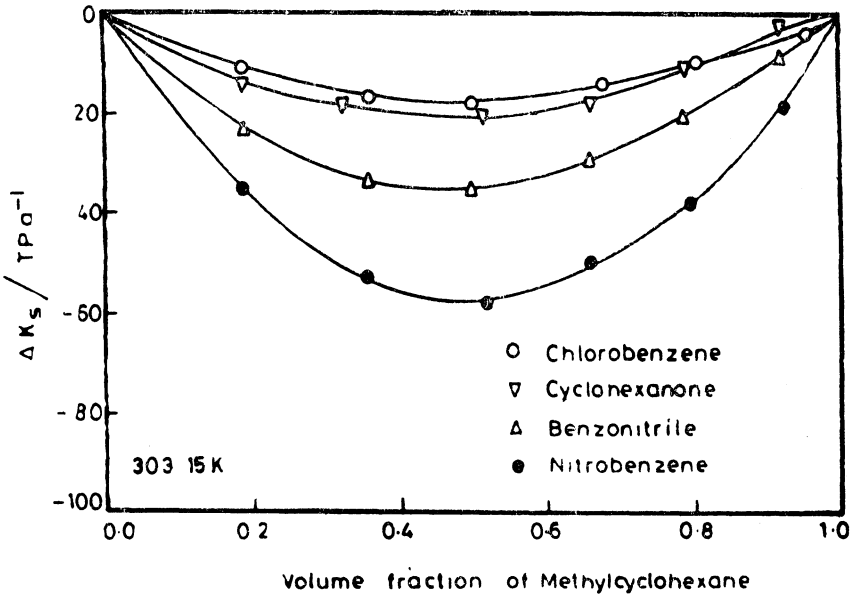

Fig. 1

by Jacobson[6]. The effect would contribute to positive deviation in isentropic compressibilities. On the other hand the effect due to specific

TABLE 3

VALUES OF PARAMETERS IN EQUATION 3 AND THE STANDARD DEVIATION $\sigma(\Delta K_S)$ AT 303.15 K

System	b_0	b_1	b_2	$\sigma(\Delta K_S)/T\rho a^{-1}$
Methylcyclohexane + Chlorobenzene	−65.60	2.02	−26.48	1.7
Methylcyclohexane + Cyclohexanone	−85.77	22.51	30.81	1.4
Methylcyclohexane + Benzonitrile	−138.94	22.99	−3.90	0.5
Methylcyclohexane + Nitrobenzene	−223.04	−9.69	−48.51	2.2

interactions between unlike components would contribute to decrease in interspaces in mixtures than in pure components, consequently sound velocities are high and isentropic compressibilities are less in mixtures

than in pure components. As a result of this effect ΔK_S are to be negative. The actual value and sign of the deviation would depend upon the relative strengths of the two opposing effects. The experimental values of ΔK_S which are negative indicates that the later effect is dominant.

The graphical representation of ΔK_S versus volume fraction for methylcyclohexane with substituted benzenes and cyclohexanone shows that the curves are symmetrical in all systems. The algebraic values of ΔK_S for all the binary systems with methylcyclohexane fall in the following order:

chlorobenzene > cyclohexanone > benzonitrile > nitrobenzene

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