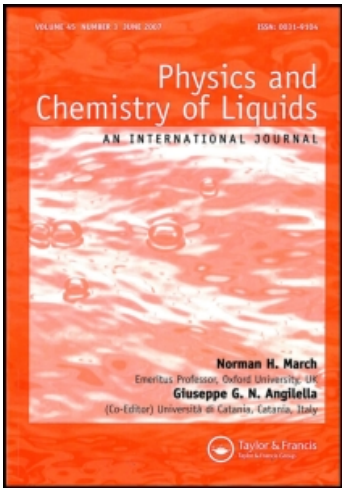

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Excess Isentropic Compressibilities of Binary Liquid Mixtures of Cyclohexanone with Alkanes, Benzene, Toluene and Tetrachloromethane at 298.15 K

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Isentropic compressibilities for binary liquid mixtures of cyclohexanone with *n*-hexane, *n*-heptane, 2,2,4-trimethylpentane, benzene, toluene and tetrachloromethane have been computed using measured density and sound velocity data at 298.15 K. Excess isentropic compressibilities exhibit an inversion in sign in the system cyclohexanone with toluene and in the remaining systems the excess property is negative over the entire range of composition studied. The results have been discussed in terms of the difference in molecular size and shape of the components, and specific interactions between unlike molecules.

Key Words: Free volume, density, molecular interaction.

INTRODUCTION

As part of our study on the measurement of excess thermodynamic properties of binary liquid mixtures[1–3] here we report the excess isentropic compressibilities for cyclohexanone with *n*-hexane, *n*-heptane, 2,2,4-trimethylpentane , benzene, toluene and tetrachloromethane at 298.15 K. The different type of molecular interactions involved in these mixtures have been examined as a function of composition. A survey of literature also reveals that the excess property for these systems have not been studied earlier.

EXPERIMENTAL

Ultrasonic velocities were measured using a single-crystal interferometer at a frequency of 1 MHz and the values were accurate to $\pm 0.1\,\%$. Density data for the pure components were measured using a bicapillary pyknometer, and for mixtures the data were obtained from excess volumes[4] by using the relation

$$\rho = \frac{x_1 M_1 + x_2 M_2}{x_1 V_1 + x_2 V_2 + V^E} \tag{1}$$

Density values obtained from both the methods were accurate to $\pm 0.05\ \mathrm{kgm}^{-3}$.

Cyclohexanone (BDH), benzene (BDH) and toluene (BDH) were purified by the methods described earlier[5,6]. Tetrachloromethane (BDH) was dried over fused calcium chloride for 2 days and fractionally distilled. Analar samples of *n*-hexane(BDH), *n*-heptane (BDH) and 2,2,4-trimethylpentane (SD's) were dried with sodium wire and fractionally distilled. The purity of the chemicals was checked by comparing the density and boiling point data with the literature values[7,8]. A comparison of the pure component properties was shown in Table 1.

RESULTS AND DISCUSSION

The isentropic compressibilities are calculated by indirect method using the ultrasonic velocity, u, and density, ρ, with the relation

$$K_S = 1/u^2\rho \tag{2}$$

The excess isentropic compressibilities are computed by using the equation

$$K_S^E = K_S^{\mathrm{mix}} - K_S^{\mathrm{ideal}} \tag{3}$$

where $K_S(\mathrm{ideal}) = (\phi_1 K_{S1} + \phi_2 K_{S2})$ and ϕ_1, ϕ_2 are volume fractions of components 1 and 2.

The values of densities and sound velocities, isentropic compressibilities and excess isentropic compressibilities are given in Table 2. Excess isentropic compressibilities versus mole fraction profiles are shown in Figure 1. The dependence of K_S^E on mole fraction has been represented by an empirical equation of the form

$$K_S^E = x_1 x_2 [a_0 + a_1(x_1 - x_2) + a_2(x_1 - x_2)^2] \tag{4}$$

Table 1 Boiling points and densities of the pure components at 298.15 K.

Component	Boiling point K		Density kg.m^{-3}	
	Present work	Literature	Present work	Literature
cyclohexanone	428.70	428.80	942.01	942.07
n-hexane	341.65	341.74	654.70	654.81
n-heptane	371.30	371.43	679.20	679.51
2,2,4-trimethylpentane	372.10	372.24	687.50	687.81
benzene	353.15	353.25	873.60	873.70
toluene	383.35	383.77	862.20	862.31
tetrachloromethane	349.60	349.75	1584.01	1584.39

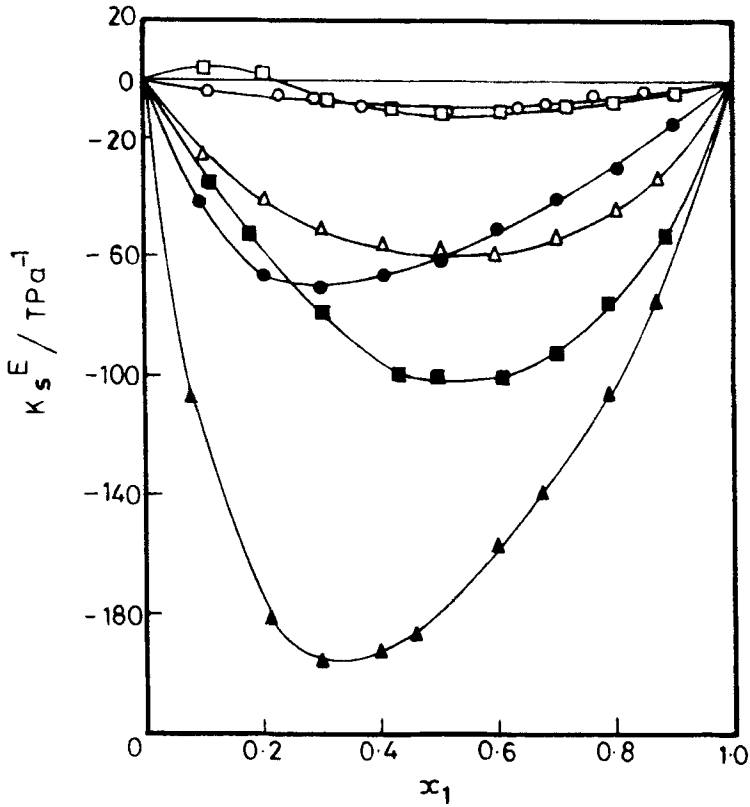

Figure 1 Excess Isentropic Compressibility versus mole faction graphs for cyclohexanone with *n*-hexane, ▲, *n*-heptane, △, 2,2,4-trimethylpentane, ■, benzene, ○, toluene, □, and tetrachloromethane, ●, at 298.15 K.

Table 2 Mole fraction of cyclohexanone, x_1, density ρ, sound velocity, u, isentropic compressibility, K_S and excess isentropic compressibility, K_S^E at 298.15 K

x_1	ρ / kg·m^{-3}	u / mS^{-1}	K_S / TPa^{-1}	K_S^E / TPa^{-1}	x_1	ρ / kg·m^{-3}	u / mS^{-1}	K_S / TPa^{-1}	K_S^E / TPa^{-1}
				Cyclohexanone + *n*-hexane					
0.0000	654.70	1030	1439	0	0.6023	814.11	1252	783	−155
0.0863	675.05	1080	1268	.107	0.6701	834.54	1278	733	−140
0.2109	705.96	1136	1096	−182	0.7991	874.87	1338	638	−104
0.3038	730.13	1166	1006	−197	0.8720	898.57	1373	590	−74
0.4007	756.34	1192	930	−191	1.0000	942.01	1426	522	0
0.4630	773.73	1212	879	−187					
				Cyclohexanone + *n*-heptane					
0.0000	679.20	1138	1136	0	0.5928	812.86	1268	765	−60
0.1125	700.39	1160	1061	−25	0.7027	844.05	1302	698	−52
0.2097	720.25	1178	999	−40	0.8091	876.58	1344	633	−44
0.3055	741.23	1198	940	−51	0.8686	895.92	1369	595	−35
0.4144	766.81	1218	878	−53	1.0000	942.01	1426	522	0
0.5033	789.09	1242	821	−58					
				Cyclohexanone + 2,2,4-trimethylpentane					
0.0000	687.50	1089	1226	0	0.6149	817.94	1257	773	−100
0.1270	709.20	1116	1132	−35	0.7054	843.51	1292	710	−93
0.1885	720.01	1130	1087	−50	0.7982	871.87	1328	650	−74
0.3071	744.25	1162	994	−78	0.8836	900.06	1372	590	−54
0.4354	772.67	1200	898	−98	1.0000	942.01	1426	522	0
0.5171	792.43	1223	843	−100					

Cyclohexanone + benzene

0.0000	873.60	1318	658	0	0.5301	915.03	1386	568	−12.0
0.1219	884.41	1334	635	−4.4	0.6452	922.21	1396	556	−9.5
0.2329	893.60	1346	617	−5.4	0.6876	924.73	1400	551	−8.7
0.2984	898.71	1354	606	−6.6	0.7775	929.89	1408	542	−6.6
0.3789	904.69	1366	592	−9.3	0.8575	934.31	1414	535	−3.8
0.5166	914.15	1380	572	−10.2	1.0000	942.01	1426	522	0

Cyclohexanone + toluene

0.0000	862.20	1326	659	0	0.6049	913.87	1390	566	−10.8
0.1059	871.90	1332	646	1.0	0.7171	922.22	1400	553	−8.4
0.2177	881.93	1342	629	−0.6	0.7943	927.76	1408	543	−7.2
0.3103	890.00	1356	611	−6.6	0.9041	935.43	1417	532	−3.1
0.4166	898.94	1370	592	−10.4	1.0000	942.01	1426	522	0
0.5047	906.07	1380	579	−11.5					

Cyclohexanone + tetrachloromethane

0.0000	1584.01	886	804	0	0.6004	1194.95	1202	579	−50.8
0.0951	1522.31	946	734	−41.5	0.7013	1130.48	1254	562	−45.0
0.2086	1448.45	1012	674	−67.9	0.8072	1063.24	1314	544	−28.6
0.3074	1384.18	1060	642	−70.2	0.9023	1003.26	1370	531	−16.8
0.4109	1317.05	1108	618	−64.9	1.0000	942.01	1426	522	0
0.5072	1254.85	1155	597	−59.0					

Table 3 Least squares parameters and standard deviation for excess isentropic compressibility

Cyclohexanone +	A_0	A_1	A_2	$\sigma(K_S^E)$
		(TPa^{-1})		
n-hexane	−712.1	395.2	−469.1	1.8
n-heptane	−234.2	−36.1	−85.9	1.3
2,2,4-trimethylpentane	−400.3	−117.9	−27.3	2.3
benzene	−41.12	−0.10	12.28	1.1
toluene	−44.62	−29.4	53.5	1.0
tetrachloromethane	−238.9	183.3	−154.5	1.3

The parameters a_0, a_1 and a_2 are obtained by the method of least squares and are given in Table 3 along with the standard deviation $\sigma(K_S^E)$.

Excess isentropic compressibilities are negative for all the systems over the entire range of composition except in the system cyclohexanone with toluene. In this system a slight positive K_S^E values are observed at lower mole fraction of cyclohexanone. The algebraic values of K_S^E fall in the order.

Toluene ≈ benzene > *n*-heptane ≈ tetrachloromethane > 2,2,4-trimethylpentane > *n*-hexane.

The small negative values of K_S^E in the systems cyclohexanone wth benzene, toluene and tetrachloromethane may be explained mostly in terms of the specific interactions. The interactions of the type $n - \pi$ in systems containing benzene and toluene and $n - \sigma$ in the mixtures having tetrachloromethane dominate over the other effects such as the mutual loss of dipolar association in the pure components. As a result the free volume in mixtures decreases and the deviation in isentropic compressibility is negative. Unexpectedly large negative K_S^E values observed in the systems containing cyclohexanone with alkanes may be explained on the basis of interstitial accommodation of the components and as a consequence the reduction of free volume in these mixtures. The contribution of the above effect may be greater over the counter effect such as the loss of polar-polar association in cyclohexanone, which contribute to increase in free volume. The values of excess thermodynamic properties, excess viscosities and excess free volumes obtained for equimolar mixtures are presented in Table 4 for comparison. Excess free volumes calculated on the basis of Flory theory[4,9] and

Table 4 Excess volume, V^E, excess isentropic compressibility, K_S^E, excess enthalpy, H^E, excess free volume, $V^E(f \cdot V)$, and excess viscosity, $\Delta \ln \eta$, at 298.15 K

System	$V^{E\,(a)}$ / $cm^3\ mol^{-1}$	K_E^S / TPa^{-1}	$H^{E\,(a)}$ / $J \cdot mol^{-1}$	$V^E(f \cdot V)_{(a)}$ / $cm^3\ mol^{-1}$	$\Delta \ln \eta^{(b)}$
cyclohexanone + *n*-hexane	−0.395	−178.0	980.7	−0.302	−0.190
cyclohexanone + *n*-heptane	−0.051	−58.5	1212.5	−0.197	−0.196
cyclohexanone + 2,2,4-trimethylpentane	−0.452	−100.1	1132.2	−0.163	−0.158
cyclohexanone + benzene	−0.275	−10.3	−280.9	−0.121	−0.082
cyclohexanone + toluene	−0.232	−11.1	−168.8	−0.043	−0.107
cyclohexanone + tetrachloromethane	−0.642	−59.7	−543.6	−0.131	0.047

[a] from Ref. 4.
[b] from Ref. 10.

experimental excess volumes are in parallel with the observed K_S^E values and giving reasonable support to the above explanation.

References

1. K. P. C. Rao and K. S. Reddy, *Phys. Chem. Liqs.*, **15**, 147, 1985.
2. K. P. C. Rao and K. S. Reddy, *Thermochim. Acta*, **91**, 321, 1985.
3. K. S. Reddy, *J. Chem. Eng. Data*, **31**, 238–240, 1986.
4. K. P. C. Rao and K. S. Reddy, *Fluid Phase Equilibria* (communicated).
5. K. P. C. Rao and K. S. Reddy, *Fluid Phase Equilibria* (in press).
6. T. Jayalakshmi, and K. S. Reddy, *Can. J. Chem.*, **63**, 2824, 1985.
7. J. Timmermans, *Physico-chemical constants of pure organic compounds*, Elsevier (Amsterdan, 1950, 1965), Vol I and II.
8. J. A. Riddick, and W. S. Bunger, *Organic Solvents in Techniques of Chemistry*, 3rd ed. Vol. II. Wiley Interscience (New York, 1970).
9. B. Riedl, and G. Delmas, *Can. J. Chem.*, **61**, 876 (1983).
10. K. P. C. Rao and K. S. Reddy, *Can. J. Chem. Eng. Data* (communicated).