Indian Journal of Chemistry
Vol. 24A, January 1985, pp. 12-15

Isentropic Compressibilities & Excess Volumes of Binary Mixtures of Cyclohexanone with 1, 2-Dichloroethane, Benzene & Carbon Tetrachloride

X ROSARIO RAJKUMAR, N MATHIYALAGAN & K V RAMAN*
Department of Chemistry, St. Joseph's College, Tiruchirapalli 620002

Received 8 *June* 1984; *revised and accepted* 6 *August* 1984

Ultrasonic velocities and densities for the binary mixtures of cyclohexanone with 1, 2-dichloroethane, benzene and carbon tetrachloride have been measured at 303.15 K over the entire composition range. From the experimental results, isentropic compressibilities (K_s) and excess volumes of mixing (V^E) have been computed. The deviation in isentropic compressibilities from ideal behaviour (ΔK_s) and the V^E values are negative for cyclohexanone + benzene and cyclohexanone + carbon tetrachloride systems and positive for cyclohexanone + 1, 2-dichloroethane system at all compositions. The equimolar V^E values of these systems have been examined in terms of (i) Prigogine's refined version of average potential model and (ii) Flory's theory.

The title investigation has been undertaken to study the relative strengths of interactions present in binary systems of cyclohexanone + 1, 2-dichloroethane, + benzene and + carbon tetrachloride in terms of the deviation in isentropic compressibility from ideal behaviour (ΔK_s) and excess volume of mixing (V^E). Also, these systems were chosen to test the applicability of (i) Prigogine's refined version of average potential model and (ii) Flory's theory with reference to excess volumes.

Materials and Methods

All the chemicals (BDH) were further purified by the methods described by Weissberger[1] and Vogel[2]. Ultrasonic velocities (u) in liquids and liquid mixtures were measured at 2MHz using an ultrasonic interferometer (Mittal Enterprises, New Delhi) and the values are accurate within ±0.15%. The isentropic compressibilities (K_s) were calculated at 303.15 K from the relation (1)

$$K_s = 1/u^2\rho \qquad \text{... (1)}$$

where ρ is the density of the liquid or liquid mixture. Excess volumes of mixing were calculated from precision density values of pure liquids and liquid mixtures obtained by pyknometric method at 303.15 K. The density values are accurate to four decimal places and the excess volumes to two decimal places. The temperature of the thermostatic bath was controlled to ±0.01 K by means of a toluene regulator.

Results and Discussion

Isentropic compressibilities

Isentropic compressibilities of these three systems were determined over the entire volume fraction range at 303.15 K and hence the deviations in isentropic compressibilities (ΔK_s) based on volume fractions of the mixtures were computed from equation (2)[3]

$$\Delta K_s = K_s - \varphi_1 K_{s,1} - \varphi_2 K_{s,2} \qquad \text{... (2)}$$

where K_s, $K_{s,1}$ and $K_{s,2}$ are the isentropic compressibilities of the mixture, component-1 and component-2 respectively and φ_1 and φ_2 are respective volume fractions of components 1 and 2. The K_s values are accurate to ± 2 TPa^{-1}. The deviation of ΔK_s value from zero indicates the extent of deviation of the mixture from ideal behaviour. The values of u, ρ, K_s and ΔK_s are reported in Table 1. The ΔK_s values were fitted into Eq. (3)[4]

$$\frac{\Delta K_s}{\varphi_1 \varphi_2} = A + B(\varphi_1 - \varphi_2) + C(\varphi_1 - \varphi_2)^2 \qquad \text{... (3)}$$

The values of the parameters A, B and C of Eq. (3), determined by the method of least squares are given in Table 2 along with the standard deviations $\sigma(\Delta K_s)$.

Excess volumes of mixing

The experimental excess volumes at 303.15 K were fitted into the analytical equation of the type (4)

$$\frac{V^E}{x_1 x_2} = A + B(x_1 - x_2) + C(x_1 - x_2)^2 \qquad \text{... (4)}$$

where x_1 and x_2 are the mol fractions of components 1 and 2 respectively. The values of A, B and C of Eq. (4) were determined by the method of least squares and are recorded in Table 3 along with the standard deviations $\sigma(V^E)$. The V^E values are negative for cyclohexanone + benzene and cyclohexanone + carbon tetrachloride systems and positive for cyclohexanone + 1, 2-

dichloroethane system over the entire composition range.

The excess volumes at equimolar compositions were calculated using Prigogine's refined version of average potential model[5,6] (APM). The APM data for pure components are given in Table 4. The molar volume of the reference component, V_1 was calculated using the density values at 303.15K. V_1' and V_1'' were determined from the data given by Lange[7]. The parameters of APM namely δ, ρ (calculated using critical constants T_c and P_c) and θ are presented in Table 5. The critical constants for cyclohexanone were taken from the data given by Arvind *et al.*[8], and those for other components were obtained from the data given by Deshpande and Pandya[9] and Lange[7].

Several workers[10-12] have attempted to apply this theory to mixtures containing a polar component with a dipole moment of moderate magnitude and a non-polar component. In this work, the polar component is cyclohexanone ($\mu = 2.8$ D). The non-polar components are benzene and carbon tetrachloride and compara-

Table 1—Isentropic Compressibilities of Binary Systems Containing Cyclohexanone at 303.15 K

Volume fraction of (1), φ	Density (g cm^{-3})	u (m sec^{-1})	K_s (TPa^{-1})	ΔK_s (TPa^{-1})
	Carbon tetrachloride (1) + Cyclohexanone (2)			
0	0.9379	1388	553.4	0
0.1461	1.0385	1300	569.8	−15.9
0.2858	1.1280	1224	591.7	−25.0
0.4358	1.2225	1147	621.8	−28.1
0.5847	1.3197	1074	656.9	−26.0
0.7359	1.4050	1008	700.5	−16.4
0.8946	1.5075	944	744.4	−7.1
1.0000	1.5756	905	774.9	0
	Benzene (1) + Cyclohexanone (2)			
0	0.9379	1388	553.4	0
0.1334	0.9298	1374	569.7	−4.5
0.2728	0.9208	1363	584.6	−11.2
0.4184	0.9110	1347	605.0	−13.5
0.5633	0.9009	1331	626.6	−14.4
0.7198	0.8898	1309	655.9	−9.5
0.8882	0.8770	1288	687.3	−4.2
1.0000	0.8677	1275	708.9	0
	1, 2-Dichloroethane (1) + Cyclohexanone (2)			
0	0.9379	1388	553.4	0
0.1198	0.9730	1357	558.1	0.7
0.2462	1.0110	1324	564.3	2.7
0.3880	1.0545	1288	571.6	5.3
0.5301	1.0961	1256	578.3	7.3
0.6945	1.1455	1223	583.6	7.0
0.8694	1.1989	1193	586.1	3.7
1.0000	1.2388	1173	586.7	0

Table 2—Values of Parameters, A, B and C of Eq (3) and the Standard Deviations of Binary Systems Containing Cyclohexanone

Binary mixture of Cyclohexanone with	A (TPa^{-1})	B (TPa^{-1})	C (TPa^{-1})	$\sigma(\Delta K_s)$ (TPa^{-1})
Carbon tetrachloride	−109.8	35.5	13.6	0.8
Benzene	−57.7	0	30.1	0.9
1,2-Dichloroethane	28.1	18.0	−14.9	0.2

Table 3—Values of Parameters, A, B and C of Eq. (4) and the Standard Deviations of the Binary Systems at 303.15 K

Binary mixture of cyclohexanone with	A ($cm^3 mol^{-1}$)	B ($cm^3 mol^{-1}$)	C ($cm^3 mol^{-1}$)	$\sigma(V^E)$ ($cm^3 mol^{-1}$)
Carbon tetrachloride	−2.5815	0.0165	0.2529	0.009
Benzene	−0.9596	−0.2535	−0.2036	0.008
1, 2-Dichloroethane	0.2675	0.1066	0.1607	0.002

Table 4—APM Data for Pure Components

V (cm^3/mol)	V′ (cm^3/mol deg)	V″ (cm^3/mol deg^2)	T_c (K)	P_c (atm)
		Carbon tetrachloride		
97.01	0.1192	0.000396	556.20	44.98
		Benzene		
89.81	0.1104	0.000347	562.50	47.90
		1,2-Dichloroethane		
79.89	0.0915	0.000176	561.40	53.00
		Cyclohexanone		
—	—	—	629.15	38.00

Table 5—Values of APM Parameters Using Component (1) as the Reference Component

δ	ρ	$\theta = -\delta^2/8$	$\theta = +\delta/2$
Carbon tetrachloride (1)+Cyclohexanone (2)			
0.1312	0.1022	−0.002152	0.065600
Benzene (1)+Cyclohexanone (2)			
0.1185	0.1182	−0.001755	0.059250
1,2-Dichloroethane (1)+Cyclohexanone (2)			
0.1207	0.1606	−0.001821	0.060350

Table 6—Values of V^E Calculated by APM for Equimolar Mixtures

Binary mixture of Cyclohexanone with	V^E (cm^3 mol^{-1})		
	Calculated using		Experimental
	$\theta = -\delta^2/8$	$\theta = +\delta/2$	
Carbon tetrachloride	0.574	−0.538	−0.645
Benzene	0.645	−0.339	−0.240
1,2-Dichloroethane	1.013	0.197	0.067

Table 7—Parameters of Flory's Theory for Pure Components at 303.15 K

$\alpha \times 10^3$ (deg^{-1})	V_i (cm^3 mol^{-1})	$\tilde{V}_i$	V_i^* (cm^3 mol^{-1})	P_i^* (cal cm^{-3})	$\tilde{T}_i$
Cyclohexanone					
0.951	104.67	1.2410	84.39	153.20	0.0559
Carbon tetrachloride					
1.248	97.01	1.3005	74.62	134.18	0.0645
Benzene					
1.242	89.81	1.2990	69.12	149.00	0.0643
1, 2-Dichloroethane					
1.184	79.89	1.2881	62.02	166.90	0.0628

Table 8—V^E Calculated Using $\theta_2\chi_{12}$ Derived from Experimental H^E at 303.15 K

H^E (cal mol^{-1})	$\theta_2\chi_{12}$	V^E(cm^{3}mol^{-1}) of equimolar mixture	
		Calc	Expl
Carbon tetrachloride + Cyclohexanone			
−104.8	−2.5259	−0.520	−0.645
Benzene + Cyclohexanone			
−57.5	−1.3657	−0.244	−0.240
1,2-Dichloroethane + Cyclohexanone			
−165.4	−4.9029	−0.388	0.067

Table 9—H^E Calculated Using $\theta_2\chi_{12}$ Derived from Experimental Equimolar V^E at 303.15 K

Binary systems of Cyclohexanone with	$\theta_2\chi_{12}$	H^E(cal mol^{-1})*	
		Calc.	Expl
Carbon tetrachloride	−3.7224	−150.3	−104.8
Benzene	−1.3079	−50.5	−57.5
1,2-Dichloroethane	0.9984	26.7	−165.4

* Calculated at $x_1 = x_2 = 0.5$

tively less polar component is 1, 2-dichloroethane ($\mu = 2.06$ D). Generally the relation, $\theta = -\delta^2/8$ is used whenever dispersion forces are predominant. In cases where dispersion forces are not predominant, the relation, $\theta = +\delta/2$ can be used. This $\theta = +\delta/2$ value is applicable to systems, which are accompanied by contraction in volume and evolution of heat on mixing[6]. Here the agreement between experimental V^E values and theoretical V^E values using $\theta = +\delta/2$ is found to be better than the values calculated using $\theta = -\delta^2/8$ for all the three systems both in sign and magnitude (Table 6).

The measured equimolar excess volumes of these binary systems were also compared with the V^E values calculated using the theory developed by Flory and coworkers[13-17]. The parameter $\theta_2\chi_{12}$ in Flory's theory for V^E calculation was computed from the experimental heat of mixing (H^E) of equimolar mixtures[18,19]. Parameters in Flory's theory α_i, V_i, $\tilde{V}_i$, V_i^*, P_i^* and $\tilde{T}_i$ of pure components, namely, 1, 2-dichloroethane[20], cyclohexanone[21], carbon tetrachloride[22] and benzene[23] are presented in Table 7. The calculated values of V^E and H^E by Flory's theory, presented in Tables 8 and 9, show that Flory's theory gives comparable results of V^E and H^E values both in sign and magnitude for the systems carbon tetrachloride + cyclohexanone and benzene + cyclohexanone but fails in the case of 1, 2-dichloroethane + cyclohexanone which may be due to the fact that both the components are polar.

The negative V^E values of carbon tetrachloride + cyclohexanone system indicate the existence of

Table 10—Values of Δbp, ΔK_s at $\varphi_1=\varphi_2=0.5$ and Equimolar V^E

Component	Boiling point (K)	Δbp (2)-(1)	$\Delta K_s^{(a)}$ (TPa^{-1})	$V^{E(b)}$ ($cm^3\,mol^{-1}$)
Cyclohexanone (2)	428.80	—	—	—
Carbon tetrachloride (1)	349.90	78.90	−27.5	−0.645
Benzene (1)	353.25	75.55	−14.4	−0.240
1,2-Dichloroethane (1)	356.63	72.17	7.0	0.067

(a) At $\varphi_1=\varphi_2=0.5$; and (b) at $x_1=x_2=0.5$

specific interaction between unlike components since the difference in molar volumes of the two components is not very large. The specific interaction could be of charge transfer type. Carbon tetrachloride is known to act as an electron acceptor for a number of donors. In this case, the oxygen atom of the carbonyl group of cyclohexanone may act as electron donor[24,25]. This attractive interaction is also supported by the observed exothermic heat of mixing and negative values of ΔK_s. The negative values of V^E and ΔK_s and exothermic heat of mixing of benzene + cyclohexanone system indicate the presence of attractive interaction between unlike molecules. Benzene can be polarized[26] due to the proton accepting nature of cyclohexanone. Hence there may be dipole-induced dipole interaction. The small positive V^E values and exothermic heat of mixing of 1, 2-dichloroethane + cyclohexanone system indicate that there may be attractive interaction of the dipole-dipole type, similar to that observed by Bougard and Jadot[27] between some carbonyl compounds and 1,2-dichloropropane.

The difference in boiling points (Δbp) of unlike components of a binary system can be taken as a rough measure of the strength of interaction[28]. This is supported by the variation of Δbp with V^E (Table 10). Also it is to be noted from Table 10 that the change in V^E (equimolar) parallels the change in ΔK_s ($\varphi_1=\varphi_2=0.5$) in these systems.

Acknowledgement

We are thankful to Prof S J Arulraj, and Dr M V Prabhakara Rao, Department of Chemistry, Sri Venkateswara University College, Tirupati for their invaluable help.

References

1 Weissberger A, *Technique of organic chemistry*, Vol 7 (Interscience, New York), 1955.
2 Vogel A I, *A textbook of practical organic chemistry* (Longmans, London), 1975.
3 Rao M V P & Naidu P R, *J chem Thermodyn*, **6** (1974) 1195.
4 Choudary N V & Naidu P R, *Chem Scr*, **19** (1982) 89.
5 Prigogine I & Englert-Chwoles A, *J chem Phys*, **24** (1956) 518.
6 Prigogine I, *Molecular theory of solutions* (North-Holland, Amsterdam), 1957.
7 Dean J A, *Lange's handbook of chemistry* (McGraw-Hill, New York), 1973.
8 Arvind P K, Ghalib H A & Bruno J Z, *Chem Rev*, **68** (1968) 659.
9 Deshpande D D & Pandya M V, *Trans Faraday Soc*, **61** (1965) 1858.
10 Vij J N & Mahl B S, *Thermochim Acta*, **12** (1975) 155.
11 Anantaraman A V, Bhattacharyya S N & Palit S R, *Trans Faraday Soc*, **57** (1961) 41.
12 Naidu P R & Krishnan V R, *Trans Faraday Soc*, **61** (1965) 1347.
13 Flory P J, *J Am chem Soc*, **87** (1965) 1833.
14 Abe A & Flory P J, *J Am chem Soc*, **87** (1965) 1838.
15 Flory P J, Orwoll R A & Vrij A, *J Am chem Soc*, **86** (1964) 3507.
16 Flory P J & Abe A, *J Am chem Soc*, **86** (1964) 3563.
17 Orwoll R A& Flory P J, *J Am chem Soc*, **89** (1967) 6822.
18 Weissberger A, *Technique of organic chemistry*, Vol 1, Part I (Interscience, New York), 1959, 572.
19 Wilson J M, Newcombe R J, Denaro A R & Rickett R M W, *Experiments in physical chemistry* (Pergamon Press, London), 1962.
20 Wilhelm E, Schano R, Becker G, Findenegg G H & Kohler F, *Trans Faraday Soc*, **65** (1969) 1443.
21 Raman G K, *Physicochemical properties of liquid mixtures: Excess volumes and viscosities*, Ph D Thesis, Sri Venkateswara University, Tirupati, 1972.
22 Nigam R K & Singh P P, *Indian J Chem*, **7** (1969) 156.
23 Reddy K S, *A study in thermodynamic properties of solutions: Excess volumes and isentropic compressibilities*, Ph D Thesis, Sri Venkateswara University, Tirupati, 1977.
24 Jain D V S, Saini S B & Bajaj S K, *Indian J Chem*, **19A** (1980) 1007.
25 Naidu P R & Raman G K, *Indian J Chem*, **14A** (1976) 275.
26 Oswal S L & Bakore G V, *Indian J Chem*, **17A** (1979) 89.
27 Bougard J & Jadot R, *J chem Thermodyn*, **9** (1977) 491.
28 Fort R J & Moore W R, *Trans Faraday Soc*, **61** (1965) 2102.