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Speeds of sound, isentropic compressibilities, viscosities and excess molar volumes of cyclohexanol + cyclohexane at 303.15 K

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Abstract

Isentropic compressibilities κ_S, excess isentropic compressibilities κ_S^E, excess molar volumes V^E, viscosity deviations $\Delta\eta$ and excess Gibbs energy of activation ΔG^{*E} of viscous flow have been determined from measurements of speeds of sound u, densities ρ and viscosities η of cyclohexanol + cyclohexane binary mixture at 303.15 K and over the whole mole fraction range. The values of κ_S^E and $\Delta\eta$ are negative over the entire range of composition but the V^E plot is sigmoid with very small magnitude of V^E. The experimental speeds of sound in terms of collision factor theory and free length theory and the excess molar volumes in terms of associated solution theory with a Flory equation of state contribution described by Treszczanowicz and Benson [Fluid Phase Equilib. 23 (1985) 117] and Heintz [Ber. Bunsen-Ges. Phys. Chem. 89 (1985) 172] have been analyzed.

Keywords: Associated solution model; Excess molar volume; Isentropic compressibility; Speeds of sound; Viscosity

1. Introduction

In the previous papers from our laboratory, the speeds of sound, isentropic compressibilities and excess molar volumes for binary mixtures of 1-alkanols and 2-alkanols with cyclohexane and methylcyclohexane [1,2] have been reported. The excess properties were dependent on size and type of alkanol. In this paper, we extend our studies on cyclohexanol+cyclohexane mixture at 303.15 K. An attempt has also been made to analyze V^E in terms of associated solution theory with a Flory equation of state contribution [3,4] and speed of sound in terms of collision factor theory and free length theory [5,6].

2. Experimental

The speeds of sound in pure liquids and in binary mixtures were measured with multi-frequency ultrasonic interferometer supplied by Mittal Enterprise, New Delhi. In the present work, a steel cell fitted with a quartz crystal of 2 MHz frequency was employed. A water circulating thermostat with an accuracy of ±0.02 K supplied by Gemini Scientific Instruments, Madras, was used for controlling the temperature for the speed of sound measurements. The viscosity η was measured with a modified suspended-level Ubbelohde viscometer [7] employing water-thermostat bath, with ±0.02 K accuracy. The viscometer was designed so as to reduce surface tension effects to negligible values [8]. The viscometer has been calibrated so as to determine the two constants C and B in the equation $\eta/\rho = Ct - B/t$, obtained by measuring the flow time t with pure water, benzene, toluene and cyclohexane [9–11]. The flow time of a definite volume of liquid through the capillary was measured with an accurate stopwatch with a precision of ±0.1 s. The densities were measured with an Anton–Paar vibrating tube digital densimeter (Model DMA 60/602) with a thermostated bath controlled to ±0.01 K. The details of the apparatus and procedure have been described in previous publications [12–14].

Mixtures were prepared by mixing known masses of pure liquids in narrow-mouth ground glass stoppered bottles. All the mass measurements were performed on an electronic balance (Mettler AE163, Switzerland) accurate to 0.01 mg. The possible error in the mole fraction is estimated to be less

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Table 1
Pure component properties at 303.15 K

Liquids	ρ (kg m^{-3})	u (m s^{-1})	η (mPa s)	α (kK^{-1})	C_P (J mol^{-1} K^{-1})
Cyclohexane	769.12 769.04 [15] 769.15 [16] 769.18 [17]	1230 1229.1 [16]	0.821 0.820 [9]	1.233 [16]	158.1 [16]
Cyclohexanol	941.52 941.52 [9]	1443 1444 [18]	41.078 41.067 [9]	0.810 [18]	210 [18]

than 1×10^{-4}. The values of u, η and ρ were reproducible to within ± 1.0 m s^{-1}, ± 0.002 mPa s and ± 0.01 kg m^{-3}, respectively. The isentropic compressibilities determined from the relation $\kappa_S = 1/u^2\rho$ are believed to be reliable to within 0.15%.

Cyclohexane (Ranbaxy, AR) was dried over molecular sieves 4 Å and fractionally distilled over Na. Cyclohexanol (Sarabhai Chem.) was used as received after drying over molecular sieves 4 Å. The purity of both the liquid samples was checked by gas liquid chromatography analysis at Gujarat Insecticide Ltd., Ankleshwar. The estimated purities were better than 99.5 mol% for cyclohexanol and 99.9 mol% for cyclohexane. Furthermore, in Table 1 the experimental densities, speeds of sound, and viscosities are compared with the literature values [15–18]. The agreement between the two sets of data is good.

3. Results

The densities ρ, speeds of sound u, isentropic compressibilities κ_S, Rao's molar sound functions R, viscosities η, excess molar volumes V^E, excess isentropic compressibilities κ_S^E, excess Rao's molar sound functions R^E, viscosity deviations $\Delta\eta$, and excess Gibbs energy of activation of flow ΔG^{*E} for cyclohexanol + cyclohexane at 303.15 K have been reported in Table 2, where x_A is the mole fraction of cyclohexanol.

The Rao's molar sound functions R [19] were obtained from the following relation:

$$R = u^{1/3}\frac{\sum x_i M_i}{\rho} \tag{1}$$

The values of R are expected to be uncertain by 0.3%. Excess molar volumes V^E of binary mixture were calculated from ρ of pure liquids and binary mixtures with following expression:

$$V^E = \frac{\sum x_i M_i}{\rho} - \sum \frac{x_i M_i}{\rho_i} \tag{2}$$

Excess isentropic compressibilities κ_S^E were calculated from the relation recommended by Benson and Kiyohara [20] and Douheret et al. [21]:

$$\kappa_S^E = \kappa_S - \sum \phi_i \left\{ \frac{\kappa_{S,i}^o + TV_i^o(\alpha_i^o)^2}{C_{P,i}^o} \right\} - T\frac{\sum x_i V_i^o \left(\sum \phi_i \alpha_i^o\right)^2}{\sum x_i C_{P,i}^o} \tag{3}$$

Excess Rao's molar sound functions R^E were obtained from

$$R^E = R - \sum x_i R_i \tag{4}$$

in which V_i^o, α_i^o, and $C_{P,i}^o$ are, respectively, the molar volume, isobaric thermal expansion coefficient and molar isobaric heat capacity of pure component i and $\phi_i =$

Table 2
Densities, speeds of sound, isentropic compressibilities, Rao's molar sound functions, viscosities, excess molar volumes, excess isentropic compressibilities, excess Rao's molar sound functions, viscosity deviations, and excess Gibbs energies of activation of flow for cyclohexanol + cyclohexane at 303.15 K

x_A	ρ (kg m^{-3})	u (m s^{-1})	κ_S (TPa^{-1})	10^6 R (m$^{10/3}$ s$^{-1/3}$ mol^{-1})	η (mPa s)	10^9 V^E (m^3 mol^{-1})	κ_S^E (TPa^{-1})	10^6 R^E (m$^{10/3}$ s$^{-1/3}$ mol^{-1})	$\Delta\eta$ (mPa s)	ΔG^{*E} (J mol^{-1})
0.0988	785.40	1244	823	1174	1.801	45.1	−13	−1	−2.997	1006
0.1912	800.96	1259	788	1176	3.186	51.2	−23	−2	−5.332	1533
0.2963	818.90	1278	748	1178	5.255	38.9	−32	−3	−7.494	1758
0.3962	836.20	1298	710	1181	7.778	8.3	−38	−4	−8.993	1760
0.4916	852.84	1319	674	1183	10.808	−23.3	−41	−4	−9.803	1648
0.5950	870.90	1342	638	1187	14.778	−46.7	−39	−4	−9.996	1416
0.6873	887.08	1364	606	1190	19.085	−63.0	−36	−3	−9.405	1150
0.7945	905.80	1390	571	1194	25.175	−60.2	−27	−2	−7.630	791
0.9098	925.89	1419	536	1198	33.309	−37.4	−13	−1	−4.138	360

x_A: the mole fraction of cyclohexanol.

Table 3
Coefficients A_i of Eq. (7) and standard deviations σ for cyclohexanol + cyclohexane

Property	A_1	A_2	A_3	A_4	A_5	σ
u (m s^{-1})	1230	125	151	−92	29	0.3
κ_S (TPa^{-1})	858	−362	−105	181	−63	0.6
η (mPa s)	0.821	7.252	27.531	−9.376	14.839	0.021
10^6R (m$^{10/3}$ s$^{-1/3}$ mol^{-1})	1172	16	11	3		0.3

$x_iV_i/\sum x_jV_j$ is the volume fraction of i in the mixture, stated in terms of the unmixed components. The values of α^o and C_P^o used for these calculations are listed in Table 1. The estimated accuracy in the values of V^E and κ_S^E is 5×10^{-9} mol^{-1} and 2.0 TPa^{-1}, respectively.

The viscosity deviations from a linear dependence on mole fraction were calculated from

$$\Delta\eta = \eta - \sum x_i\eta_i \tag{5}$$

where η and η_i represent the viscosities of the mixture and of the pure component i. On the basis of the theory of absolute reaction rates [22], the excess Gibbs energy of activation ΔG^{*E} of viscous flow may be calculated from

$$\frac{\Delta G^{*E}}{RT} = \ln\left(\frac{\eta V}{\eta_B V_B}\right) - x_A \ln\left(\frac{\eta_A V_A}{\eta_B V_B}\right) \tag{6}$$

where V is the molar volume of the mixture and V_i is the molar volume of the pure component i. $\Delta\eta$ and ΔG^{*E} data are included in Table 2. The estimated uncertainty of ΔG^{*E} is about 15 J mol^{-1}.

For compact and smooth representation, the values of u, κ_S, R, and η were fitted to a polynomial equation of the form:

$$Y = \sum_{i=1}^{m} A_i x_A^{i-1} \tag{7}$$

where $Y = u$, κ_S, R, and η.

The values of V^E, κ_S^E, R^E, $\Delta\eta$ and ΔG^{*E} for the mixture were smoothed to a Redlich–Kister [23] polynomial regression of the type:

$$\psi^E = x_A(1 - x_A)\sum_{i=1}^{m} B_i(1 - 2x_A)^{i-1} \tag{8}$$

where $\psi^E = V^E$, κ_S^E, R^E, $\Delta\eta$, and ΔG^{*E}.

The values of coefficients A_i of Eq. (7) and B_i of Eq. (8) and the corresponding standard deviations σ obtained by the method of least squares, assigning equal weights to each point are given in Tables 3 and 4.

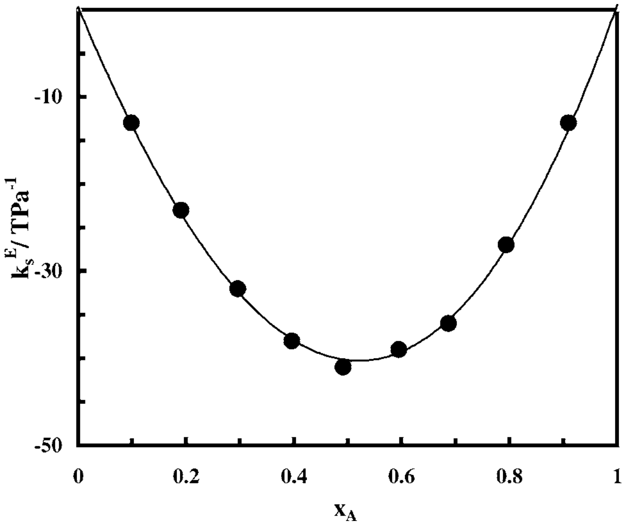

Fig. 1. Excess isentropic compressibilities for cyclohexanol + cyclohexane at 303.15 K. (●): experimental points; (—): calculated with Eq. (8).

4. Discussion

The dependence of κ_S^E, R^E, V^E, $\Delta\eta$ and ΔG^{*E} on composition is shown in Figs. 1–5. The values of κ_S^E and R^E for cyclohexanol + cyclohexane are negative over the entire range of composition. The V^E curve (Fig. 3) is sigmoid with very small magnitude of V^E. The maximum V^E is 51×10^{-9} m^3 mol^{-1} at $x_1 = 0.191$ while minimum V^E is -63×10^{-9} m^3 mol^{-1} at $x_1 = 0.687$. The inversion of sign from small positive to small negative values occurs around at 0.43 mol fraction of cyclohexanol. V^E for this mixture have been measured at 298.15 K [24], 303.15 K [25,26], 313.15 K [18] and 323.15 K [18]. The agreement between our values and those reported by Jones et al. [24], Rajgopal and Subrahmanyam [18] is reasonable but the values of Diaz-Peña and Haya [25] and Rastogi and Varma [26] are of higher magnitude than our values. Sigmoid-shaped

Table 4
Coefficients B_i of Eq. (8) and standard deviations σ for cyclohexanol + cyclohexane

Property	B_1	B_2	B_3	B_4	σ
$V^E \times 10^9$ (m^3 mol^{-1})	−94.9	590.4	190.1		1.65
κ_S^E (TPa^{-1})	−163	10	17		0.5
$\Delta\eta$ (mPa s)	−39.43	10.080	−3.784	0.315	0.013
ΔG^{*E} (J mol^{-1})	6510	3781	2123	821	7.1
$R^E \times 10^6$ (m$^{10/3}$ s$^{-1/3}$ mol^{-1})	−15				0.1

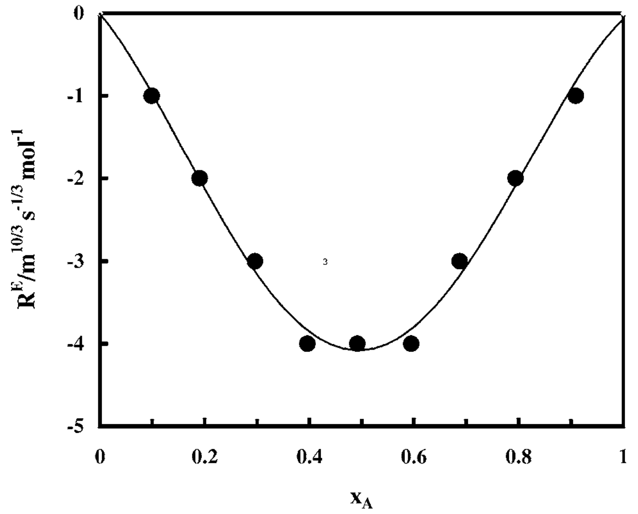

Fig. 2. Excess Rao's molar sound functions for cyclohexanol+cyclohexane at 303.15 K. (●): experimental points; (—): calculated with Eq. (8).

V^E curves have also been observed for mixtures of cycloalkanol + cycloalkane [24,27], alkanol + alkane [28] and alkanol + tetrachloromethane [29]. It has been suggested that this shape results from two opposing effects. The behavior in the cyclohexane rich region may be attributed to the break down of the hydrogen-bonded structure of cyclohexanol, resulting into positive V^E while the behavior in the alkanol-rich region may be attributed to the accommodation of cyclohexane interstitially in the H-bonded structure of cyclohexanol. The present equimolar values of κ_S^E at 303.15 K are lower by 14 TPa^{-1} with the calculated and interpolated values of κ_S^E from speed of sound and excess molar volume data at 298.15 and 313.15 K [18].

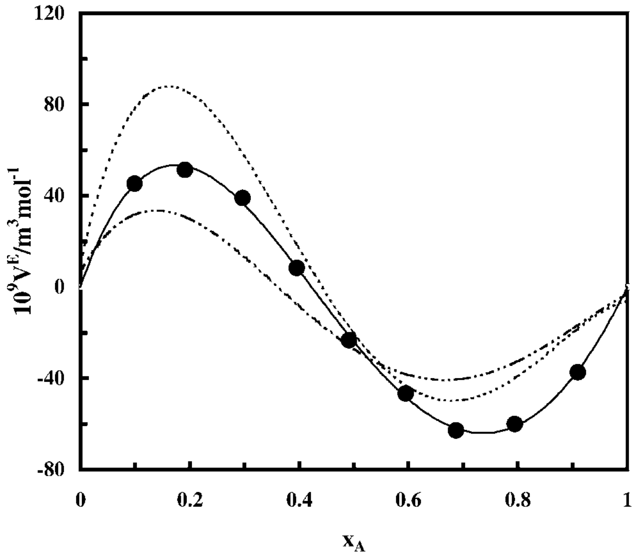

Fig. 3. Excess molar volumes for cyclohexanol+cyclohexane at 303.15 K. (●): experimental points; (—): calculated with Eq. (8); (- - -): AST model; (- - · · · -): ERAS model.

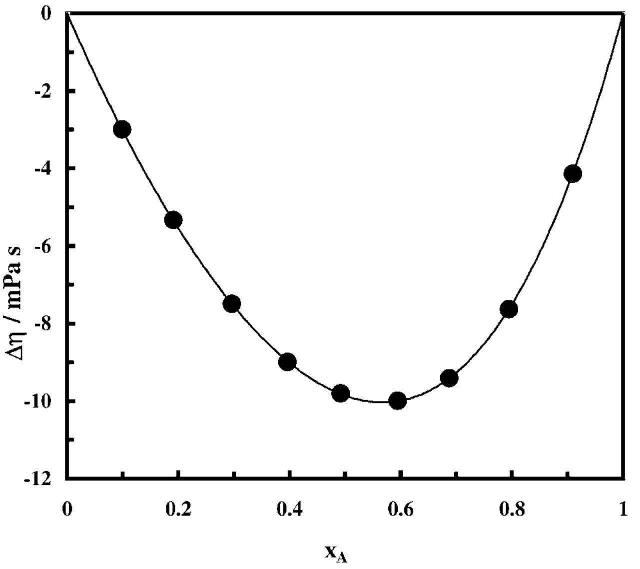

Fig. 4. Viscosity deviations in cyclohexanol + cyclohexane at 303.15 K. (●): experimental points; (—): calculated with Eq. (8).

Figs. 4 and 5 show that the values of viscosity deviations $\Delta\eta$ are very large and negative and ΔG^{*E} are very large and positive over the entire range of composition. The viscosity of cyclohexanol at 303.15 K is almost 50 times larger than the second component. This is due to the strong H-bonding in cyclohexanol and flat molecular shape. When the cyclohexane molecules are added, the H-bonds in cyclohexanol are broken, resulting into the loss of cohesive energy. Thus, the unlike interactions are weak compared to the like interactions, which ultimately result into the decrease in the viscosity of mixtures. As the molar volumes of cyclohexanol (106.38×10^{-6} m^3 mol^{-1}) and cyclohexane

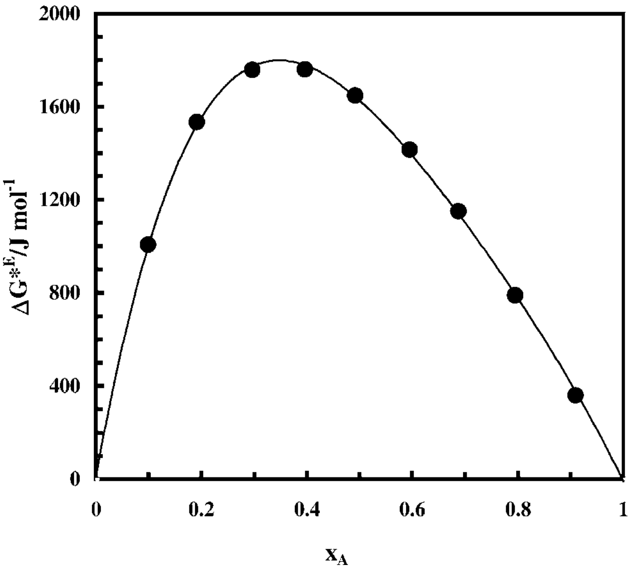

Fig. 5. Excess Gibbs energies of activation of viscous flow for cyclohexanol + cyclohexane at 303.15 K. (●): experimental points; (—): calculated with Eq. (8).

($109.43 \times 10^{-6}\,\mathrm{m^3\,mol^{-1}}$) are similar, such large deviations in case of this system are attributable to large difference in the viscosities, i.e. cohesive energies of the two participating components.

Apart from expressing η as a polynomial fit, we have also correlated viscosity data employing two-parameter McAllister [30] and three-parameter Auslaender [31] equations. The two-parameter McAllister equation based on the Eyring's theory of absolute reaction rates [23] and three-body interaction model is

$$\ln \nu = x_{\mathrm{A}}^3 \ln \nu_{\mathrm{A}} + 3x_{\mathrm{A}}^2 x_{\mathrm{B}} \ln Z_{\mathrm{AB}} + 3x_{\mathrm{A}} x_{\mathrm{B}}^2 \ln Z_{\mathrm{BA}} + x_{\mathrm{B}}^3 \ln \nu_{\mathrm{B}} - \ln\left(\frac{x_{\mathrm{A}} + x_{\mathrm{B}} M_{\mathrm{B}}}{M_{\mathrm{A}}}\right) + 3x_{\mathrm{A}}^2 x_{\mathrm{B}} \ln\left(\frac{2}{3} + \frac{M_{\mathrm{B}}}{3M_{\mathrm{A}}}\right) + 3x_{\mathrm{A}} x_{\mathrm{B}}^2 \ln\left(\frac{1}{3} + \frac{2M_{\mathrm{B}}}{3M_{\mathrm{A}}}\right) + x_{\mathrm{B}}^3 \ln\left(\frac{M_{\mathrm{B}}}{M_{\mathrm{A}}}\right) \qquad (9)$$

where Z_{AB} and Z_{BA} are the interaction parameters and M_{i} and ν_i are the molecular mass and kinematic viscosity of pure component i. The less complicated three-parameter Auslaender equation [28] has the form:

$$x_{\mathrm{A}}(x_{\mathrm{A}} + B_{\mathrm{AB}} x_{\mathrm{B}})(\eta - \eta_{\mathrm{A}}) + A_{\mathrm{BA}} x_{\mathrm{B}}(B_{\mathrm{BA}} x_{\mathrm{A}} + x_{\mathrm{B}})(\eta - \eta_{\mathrm{B}}) = 0 \qquad (10)$$

where B_{AB}, A_{BA} and B_{BA} are the parameters representing binary AB interactions. The values of Z_{AB} and Z_{BA} for Eq. (9) are 4.047 and 1.501 and the values of A_{BA}, B_{AB}, and B_{BA} for Eq. (10) are 1.466, 0.266 and 1.142, respectively. The values of standard deviations σ are 3.23% for two-parameter equation (9); 0.31% for the three-parameter equation (10). Thus, for this system, the three-parameter Auslaender equation (10) correlates viscosity data very well.

5. Application of theories

5.1. *Speed of sound in terms of CFT and FLT*

The speeds of sound u from the Schaaffs' collision factor theory (CFT) [5], and the Jacobson's intermolecular free length theory (FLT) [6] have also been estimated for cyclohexanol + cyclohexane binary mixture as carried out for 1-alkanol + cyclohexane, 2-alkanol + cyclohexane and 1-alkanol + methylcyclohexane mixtures in our previous study [2]. Pertinent relations of the CFT and the FLT can be found elsewhere [32,33].

The theoretical speeds of sound u for the binary mixture over the entire range of composition are compared with experimental results in Table 5. The values of the standard percentage deviation dev% are also included in this table. Table 5 reveals that the values of dev% for CFT are in the range from −0.4 to −1.1% while the corresponding values of dev% for the FLT are from 0 to −0.3%. The overall standard percentage deviations for the whole mixture are 0.9 and 0.2% for the CFT and the FLT, respectively. Thus, the estimation of speeds of sound in the mixtures by both theories is reasonably well, however, the prediction by the FLT is somewhat better than that by the CFT formulation.

Table 5
Comparison of speed of sound estimated from the CFT and FLT with those observed experimentally for cyclohexanol + cyclohexane

x_{A}	$u_{\mathrm{expt.}}$ ($\mathrm{m\,s^{-1}}$)	σ (%) = 0.9		σ (%) = 0.2	
		u_{CFT} ($\mathrm{m\,s^{-1}}$)	dev%	u_{FLT} ($\mathrm{m\,s^{-1}}$)	dev%
0.1	1244	1250	−0.5	1244	0.0
0.2	1261	1271	−0.8	1261	0.0
0.3	1279	1292	−1.0	1280	−0.1
0.4	1299	1314	−1.1	1301	−0.2
0.5	1320	1335	−1.1	1323	−0.2
0.6	1343	1357	−1.0	1346	−0.3
0.7	1367	1379	−0.9	1370	−0.3
0.8	1391	1400	−0.7	1394	−0.2
0.9	1416	1422	−0.4	1419	−0.2

5.2. *Excess molar volumes in terms of associated solution theories with Flory equation of state contribution*

The descriptions of the volumetric properties of associated mixtures using association model and equation of state contribution were described at the same time by Treszczanowicz and Benson [3] and by Heintz [4]. Both models apply the Flory equation of state theory [34], but differ in model of association contributions as well as in the method of approximation of hypothetical monomer of self-associated component. Both the models are quite successful in describing volumetric properties of alkanol + alkane mixtures [2,27,35–39]. In the present study, an attempt has been made to estimate molar excess volume of cyclohexanol + cyclohexane and compared with the experimental results. We shall abbreviate association theory due Treszczanowicz and Benson [3] as the AST model while extended real associated solution model due to Heintz [4] as the ERAS model.

5.2.1. *The AST model*

The AST model equations [3] describing excess molar volume are expressed as the sum of a chemical term described by an athermal associated model with a Mecke–Kempter mode of continuous association of the alkanol, and a physical contribution given by the Flory equation of state theory:

$$V^{\mathrm{E}} = \Delta v_{\mathrm{H}} x_{\mathrm{A}} \left[\frac{\ln(1 + K^{\Phi})}{K^{\Phi}} - \frac{\ln(1 + K^{\Phi}\Phi_A)}{K^{\Phi}\Phi_A}\right] + V^{*}\left[\tilde{v} - (\Phi_A \tilde{v}_{\mathrm{A}} + \Phi_A \tilde{v}_{\mathrm{B}})\right] \qquad (11)$$

where $K^{\Phi} = \exp(1 - \Delta h_{\mathrm{H}}/RT + \Delta S_{\mathrm{H}}/R)/r_{\mathrm{A}}$ is the association constant for a homologous alkanol with $r_{\mathrm{A}} = V_{\mathrm{A}}^{*}/17.12$ number of segments; $\Delta h_{\mathrm{H}} = -24.4\,\mathrm{kJ\,mol^{-1}}$, $\Delta S_{\mathrm{H}} = -32.01\,\mathrm{J\,K^{-1}\,mol^{-1}}$, $\Delta v_{\mathrm{H}} = -10\,\mathrm{cm^3\,mol^{-1}}$ are the standard enthalpy, entropy, volume, respectively, for

Table 6
Properties of pure components for the AST and the ERAS models

Liquid	K	V_M (cm^3 mol^{-1})	V^* (cm^3 mol^{-1})	P^* (J cm^{-3})	S (Å^{-1})	Δh_H (Kj mol^{-1})	Δv_H (cm^3 mol^{-1})	ΔS_H (J mol^{-1} K^{-1})
Cyclohexane[a]		109.43	84.33	534.1	1.32	0	0	0
Cyclohexanol[b]	150	106.38	87.89	588.5	1.33	−24.4	−10	−32.01
Cyclohexanol[c]	150	106.38	88.27	552.2	1.33	−17	−2.6	–

[a] Same for both AST and ERAS models.
[b] For AST model.
[c] For ERAS model.

H-bond formation [27]; x_i and $\Phi_i = V_i^* x_i / V^*$ are the molar and segment fractions of the ith component; $\tilde{v}$ and $\tilde{v}_i$ are the reduced volumes of the mixture and pure liquid i, respectively; $V^* = V_A^* x_A + V_B^* x_B$ is the characteristic temperature of the mixture given by

$$T^* = \frac{\sum_{i=A}^{B} \phi_i P_i^* - \Phi_A \theta_B X_{AB}}{\sum_{i=A}^{B} \Phi_i P_i^* / T_i^*} \tag{12}$$

where $\theta_B = \Phi_B / \Phi_A r_{BA}^{1/3} + \Phi_B$ is the site fraction of component 2, where $r_{BA} = V_B^*/V_A^*$; V_i^*, T_i^*, P_i^* are the characteristic volume, temperature and pressure of the ith pure component, respectively. The Flory interchange interaction parameter $X_{AB} = 21.3$ J cm^{-3} for cyclohexanol + cyclohexane was taken from literature [27]. More details and derivation of the model are given in [3,40].

5.2.2. The ERAS model

The expression for the excess molar volume V^E of the ERAS model is given by [4,37,38]

$$\begin{aligned} V^E_{ERAS} &= x_A \tilde{v}_M \Delta v_H K_A (\phi_{1A} - \phi_{1A}^o) \\ &\quad + (x_A V_A^* + x_B V_B^*)(\tilde{v}_M - \phi_A \tilde{v}_A - \phi_B \tilde{v}_B) \end{aligned} \tag{13}$$

The first term in Eq. (13) represents the chemical contribution while the second term the physical contribution to excess molar volume. $\Phi_A = 1 - \Phi_B$ is the stoichiometric hard core volume fraction of component A. $\theta_B = 1 - \theta_A = S_B \Phi_B / S_B \Phi_B + S_A \Phi_A$ is the surface fraction of component B, where S_A and S_B are the surface to volume ratio of component A and B. ϕ_{1A} and ϕ_{1A}^o are the volume fraction of the monomerous cyclohexanol species in the mixture and in the pure cyclohexanol, respectively. ϕ_{1A} is the function of K_A and Φ_A. ϕ_{1A} becomes identical with ϕ_{1A}^o for $\Phi_A = 1$. K_A is the equilibrium constant of chain self-association of cyclohexanol. Δv_H is the corresponding hydrogen-bonding volume.

The values of various parameters for the pure components required in the application of AST model and ERAS model are listed in Table 6. In Table 7, we have reported the values of Flory interchange interaction parameter X_{AB}, due to both the AST and the ERAS models and compared the experimental values of V^E with the results of AST and ERAS models over the entire range of compositions. The physical and chemical contributions evaluated from both the theories are also included in Table 7.

Table 7
Comparison of experimental equimolar excess molar volume V^E (in 10^{-9} m^3 mol^{-1}) for cyclohexanol + cyclohexane at 303.15 K and the values obtained using the AST and the ERAS models along with Flory interaction parameter X_{AB} (J cm^{-3})

x_A	Experiment	AST model ($X_{AB} = 21.3$)			ERAS model ($X_{AB} = 15.72$)		
	$V^E_{Expt.}$	$V^E_{chem.}$	$V^E_{phy.}$	V^E_{AST}	$V^E_{chem.}$	$V^E_{phy.}$	V^E_{ERAS}
0.1	44.9	130	−29	101	48	0	48
0.2	52.5	138	−58	80	57	−34	23
0.3	36.1	131	−84	47	57	−50	8
0.4	7.6	118	−105	13	54	−63	−9
0.5	−23.3	102	−117	−15	48	−72	−24
0.6	−48.6	84	−119	−35	40	−74	−34
0.7	−62.2	64	−109	−44	31	−70	−38
0.8	−59.8	44	−87	−43	22	−56	−35
0.9	−39.2	22	−51	−29	11	−34	−22

Fig. 3 shows comparison between the experimental, the AST, and the ERAS models values of excess molar volumes for cyclohexanol + cyclohexane. It may be noted that both the models are able to predict sigmoid curve for the excess molar volumes. However, the predictions of the ERAS model are more close to the experimental data than those of the AST model.

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