

Thermodynamics of binary liquid mixtures of cyclopentane with 2-propanol, 1-butanol and 2-butanol at different temperatures

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Abstract Densities and speeds of sound of the cyclopentane with 2-propanol, 1-butanol and 2-butanol are measured over the whole composition range at different temperatures in the range 288.15–308.15 K and atmospheric pressure using Anton Paar DSA 5000 densimeter. The experimental densities and speeds of sound have been used to calculate excess molar volumes, excess molar isentropic compressibilities and excess intermolecular free length. The partial molar volumes and apparent molar volumes at infinite dilution have also been calculated. The mixing quantities like $(\partial V_m^E/\partial T)_P$ and $(\partial H_m^E/\partial P)_T$ have been calculated at $T = 298.15$ K and these values are compared with the values calculated from Flory's theory at equimolar composition.

Keywords Partial molar volume · Excess molar isentropic compressibility · Flory's theory · Cyclopentane · *n*-Alkanols

Introduction

Non-ideal behaviour of binary liquid mixtures of cyclopentane with alkanols is of particular interest due to their simple structure and the self-association of alkanol

through hydrogen bonding of the hydroxyl group, the extent and strength of which changes in the mixture. Excess thermodynamic properties are crucial for the chemical process design [1] as well as for progress in the thermodynamic theories and modelling of the liquid state. Excess compressibilities and excess molar volumes give important information about intermolecular forces determining the properties of the mixtures. Studies on the cyclopentane + *n*-alkanols mixtures due to their simple structure components are of particular interest. Moreover, *n*-alkanol molecules are self-associating; it is of interest to see how they behave in the presence of cyclopentane molecules, i.e. the extent to which hydrogen bonding and self-association of *n*-alkanol molecules changes in mixture.

In continuation to our work on thermodynamic studies of binary liquid mixtures [2–4], in the present study, we report the experimental densities, ρ , and speeds of sound, u over the whole composition range at temperatures of 288.15, 298.15, and 308.15 K. From these experimental densities and speeds of sound, excess molar volume V_m^E , isentropic compressibility, κ_S , excess molar isentropic compressibility, $K_{S,m}^E$, and excess intermolecular free length, L_f^E have been calculated for each of the binary liquid mixtures at all the temperatures. The results of V_m^E , $K_{S,m}^E$, and L_f^E have been correlated with Redlich–Kister polynomial. Also, the partial molar volumes, $\bar{V}_{m,i}$, apparent molar volumes, $\bar{V}_{\phi,i}^0$ and their limiting values $\bar{V}_{m,i}^0$, $\bar{V}_{\phi,i}^0$, at infinite dilution have been calculated. An attempt has also been made to interpret the results by deriving the different mixing properties like $(\partial V_m^E/\partial T)_P$, $(\partial H_m^E/\partial P)_T$, and α^E at $T = 298.15$ K. By using the Flory's theory, the above thermodynamic mixing functions have been calculated and compared with experimental results.

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Experimental

Materials

Cyclopentane, 2-propanol and 1-butanol were obtained from S.D. Fine Chemicals, India. 2-Butanol was obtained from Merck specialities Pvt Ltd, India. All the solvents, prior to experimental measurements were stored in dark bottles over 0.4 nm molecular sieves to reduce water content and were partially degassed with vacuum under nitrogen pressure. The estimated purities as per gas chromatographic analysis were better than 99.5 mol% for all liquid samples. Further, the purities of liquids were checked by comparing densities and speeds of sound of pure solvents at all studied temperatures, with their corresponding literature values [5–23]. The experimental and literature values are reported in Table 1.

Apparatus and procedure

The densities and speeds of sound of the pure liquids and their mixtures were measured using an Anton Paar DSA 5000 densimeter. As the densities and speeds of sound are extremely sensitive to temperature, so it was controlled to ± 0.01 K by built-in solid state thermostat. Before each series of measurements, the apparatus was calibrated with double distilled and degassed water, *n*-hexane, *n*-heptane, *n*-octane, cyclohexane and benzene. The sensitivity of the instrument corresponds to a precision in density and speeds of sound of 1×10^{-6} g cm⁻³ and 1×10^{-2} m s⁻¹. The reproducibility of density and speeds of sound estimates was found to be within $\pm 5 \times 10^{-6}$ g cm⁻³ and $\pm 5 \times 10^{-2}$ m s⁻¹, respectively.

The mole fraction of each mixture was obtained with an accuracy of 1×10^{-4} from the measured apparent masses

Table 1 Experimental densities value $\rho \times 10^3/\text{kg m}^{-3}$, speeds of sound values, $u/\text{m s}^{-1}$, and their literature values along with isobaric thermal expansivities α_p/kK^{-1} , molar isobaric heat capacities $C_{p,m}/\text{J K}^{-1} \text{mol}^{-1}$, and the product $K_{S,m}/\text{mm}^3 \text{mol}^{-1} \text{MPa}^{-1}$ of the molar volume and isentropic compressibility of pure liquid components at several temperatures

Component	<i>T</i> /K	$\rho \times 10^{-3}/\text{kg m}^{-3}$		α_p/kK^{-1}	$C_{p,m}/\text{J K}^{-1} \text{mol}^{-1}$	$u/\text{m s}^{-1}$		$K_{S,m}/\text{mm}^3 \text{mol}^{-1} \text{MPa}^{-1}$
		This work	Literature			This work	Literature	
Cyclopentane	288.15	0.746658		1.337	123.02 ^a	1252.74		80.161
	298.15	0.736751	0.73947 [5]	1.355	130.62 ^a	1199.98	1206.6 [5]	89.730
			0.73969 [6]				1206 [7]	
308.15	0.726687	0.72942 [5]	1.374	138.12 ^a	1148.51		100.685	
Propan-2-ol	288.15	0.789404		1.076	147.58 ^a	1175.65		69.273
	298.15	0.781053	0.78105 [8]	1.087	155.8 [12]	1140.40	1140.1 [10]	75.747
			0.78126 [9]				1141 [13]	
			0.7812 [10]				1139 [14]	
			0.78130 [11]					
308.15	0.772422	0.77243 [8]	1.099	164.01 [12]	1104.95	1104.04 [17]	82.499	
		0.772559 [15]						
Butan-1-ol	288.15	0.815405	0.8133 [17]	0.949	170.59 ^a	1278.02	1274 [17]	68.254
	298.15	0.807718	0.80849 [8]	0.958	177.10 ^a	1243.89	1240.5 [14]	73.429
			0.80575 [14]				1239.8 [17]	
308.15	0.799916	0.80067 [8]	0.968	183.61 ^a	1210.16	1206.2 [17]	79.101	
		0.79808 [17]						
		0.79825 [18]						
Butan-2-ol	288.15	0.810869	0.8104 [17]	1.029	188.67 ^a	1248.00	1248 [17]	72.380
	298.15	0.802690	0.8022 [17]	1.039	196.9 [21]	1212.11	1212 [14]	78.302
			0.802634 [19]				1212.1 [17]	
			0.8026 [20]					
	308.15	0.794180	0.80241 [9]	1.051	205.13 ^a	1176.10	1175.8 [17]	84.962
		0.79390 [22]				1175 [23]		
		0.7937 [17]						
		0.79372 [18]						

^a Calculated from group additivity

of the components. All the mass measurements were performed on an electrical balance with a precision of ±0.01 mg. All masses were corrected for buoyancy. All molar quantities were based on the IUPAC table of atomic weights [24].

Results and discussion

Excess molar volumes and excess molar isentropic compressibilities

Experimental densities, ρ, and speeds of sound, u for binary mixtures of cyclopentane (1) + propan-2-ol (2), +butan-1-ol (2) and butan-2-ol (2) at T = 288.15, 298.15 and 308.15 K and atmospheric pressure are listed in Table 2. Excess molar volumes were calculated from our measured densities according to the following equation:

$$V_m^E = (x_1M_1 + x_2M_2)/\rho - x_1M_1/\rho_1 - x_2M_2/\rho_2, \tag{1}$$

where x₁ and x₂ are mole fractions, M₁ and M₂ are molar masses and ρ₁ and ρ₂ are the densities of pure components 1 and 2, respectively. ρ is the density of the binary mixtures.

Isentropic compressibilities κ_S were obtained from the relation

$$\kappa_S = (\rho u^2)^{-1} = V_m (Mu^2)^{-1}, \tag{2}$$

where ρ is the density of the mixture.

Products K_{S,m} of the molar volume and the isentropic compressibility were calculated from:

$$K_{S,m} = -(\partial V/\partial P)_S = V\kappa_S = \sum x_i M_i / (\rho u)^2 \tag{3}$$

The corresponding excess molar quantities K_{S,m}^E were calculated from the relation [25–27]

$$K_{S,m}^E = K_{S,m} - K_{S,m}^{id} \tag{4}$$

where [25, 26]

$$K_{S,m}^{id} = \sum x_i \left[K_{S,i}^{*} - TA_{P,i}^* \left\{ \left(\frac{\sum x_i A_{P,i}^* / \sum x_i C_{P,i}^*}{\sum x_i C_{P,i}^*} \right) - \left(\frac{A_{P,i}^*}{C_{P,i}^*} \right) \right\} \right], \tag{5}$$

where x_i are the mole fraction of component i in the mixture, respectively. A_{P,i}^{*} is the product of molar volume V_i^{*} and the isobaric expansivity α_{P,i}^{*}, C_{P,i}^{*} is the isobaric molar heat capacity, and K_{S,i}^{*} are the properties of the pure liquid component i, respectively.

The excess intermolecular length has also been calculated with the help of following relation:

$$L_f^E = L_f - L_f^{id}, \tag{6}$$

where L_f [= K/(u ρ^{1/2})] is intermolecular free length and K is a temperature-dependent constant (=93.875 + 0.375 × 10⁻⁸ T).

Table 2 Densities values, ρ × 10³/kg m⁻³, and speeds of sound values, u/m s⁻¹, for binary mixtures as a function of mole fraction, x₁ of cyclopentane at several temperatures

x ₁	ρ × 10 ³ /kg m ⁻³			u/m s ⁻¹		
	T/K			T/K		
	288.15	298.15	308.15	288.15	298.15	308.15
<i>Cyclopentane (1) + Propan-2-ol (2)</i>						
0.1253	0.781928	0.773116	0.764005	1172.72	1134.78	1096.65
0.2135	0.776985	0.767897	0.758476	1173.28	1133.06	1092.75
0.3251	0.771371	0.761958	0.752214	1175.71	1133.49	1091.43
0.4019	0.767578	0.757951	0.748014	1178.23	1134.67	1091.25
0.4583	0.764741	0.754985	0.744913	1180.60	1135.31	1090.23
0.5399	0.761147	0.75125	0.741044	1185.15	1138.80	1092.63
0.6205	0.757834	0.74772	0.737542	1190.32	1141.83	1094.68
0.7612	0.752475	0.742388	0.732045	1204.31	1154.86	1106.14
0.8653	0.749249	0.739155	0.728802	1219.05	1168.16	1118.22
0.9301	0.747677	0.737596	0.727268	1230.81	1179.39	1128.96
<i>Cyclopentane (1) + butan-1-ol (2)</i>						
0.0632	0.810909	0.80307	0.795096	1270.95	1235.76	1200.84
0.1054	0.807898	0.799935	0.791835	1266.79	1230.78	1195.10
0.2098	0.800459	0.792218	0.783701	1256.51	1218.32	1180.69
0.312	0.793189	0.784642	0.775833	1248.32	1208.21	1168.52
0.4143	0.785801	0.776968	0.767958	1240.76	1198.51	1156.97
0.4368	0.784159	0.775285	0.766182	1223.62	1182.05	1140.78
0.6129	0.771805	0.762463	0.75285	1231.25	1185.17	1139.99
0.7102	0.764978	0.75543	0.745675	1229.36	1181.81	1135.01
0.8097	0.758146	0.74841	0.738464	1230.91	1181.37	1132.89
0.9046	0.752327	0.742292	0.732335	1235.77	1185.12	1135.28
<i>Cyclopentane (1) + butan-2-ol (2)</i>						
0.0633	0.806606	0.798208	0.789473	1241.95	1204.77	1167.38
0.1054	0.803484	0.794939	0.786234	1227.16	1186.40	1145.62
0.2132	0.796207	0.787316	0.778076	1228.84	1188.55	1148.26
0.3188	0.788783	0.77957	0.77003	1221.18	1178.84	1136.74
0.4169	0.782026	0.772564	0.762797	1215.73	1171.66	1128.02
0.5135	0.774911	0.765248	0.755325	1211.75	1166.27	1121.42
0.6135	0.768126	0.758336	0.748298	1210.57	1163.84	1118.00
0.7099	0.762189	0.75231	0.742178	1212.44	1164.66	1117.79
0.8082	0.75669	0.746752	0.736509	1220.99	1169.04	1120.90
0.9029	0.751443	0.741439	0.731132	1229.69	1179.09	1129.29

The values of V_m^E, K_{S,m}^E and L_f^E graphically represented in Figs. 1, 2 and 3.

The measured speeds of sound u were fitted for each mixture with a polynomial expression given by

$$u = \sum_{i=1}^k A_i x_1^{i-1} \tag{7}$$

by the method of least squares with each point weighted equally. The coefficients A_i and standard deviations σ are summarized in Table 3.

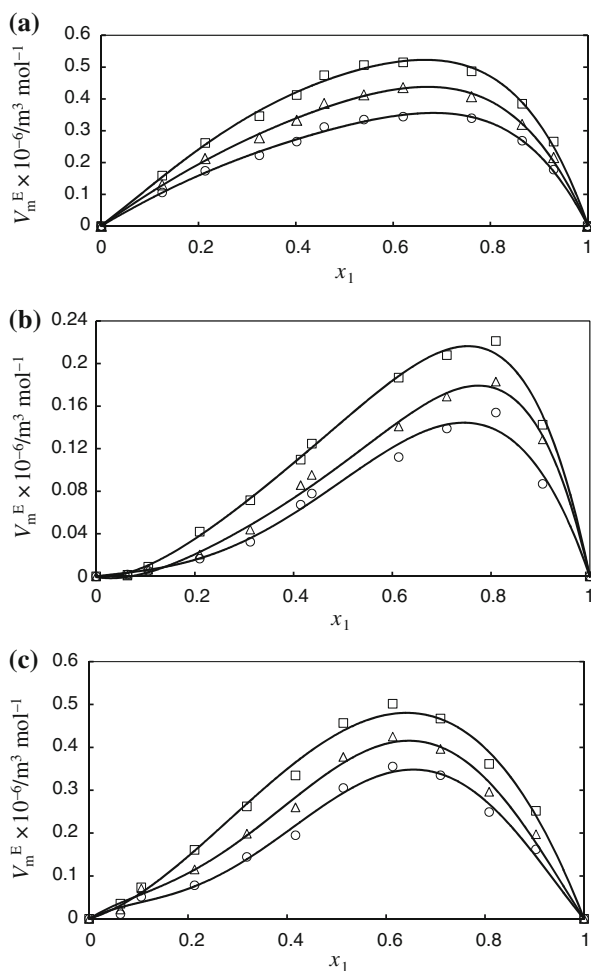


Fig. 1 Excess molar isentropic compressibility V_m^E for cyclopentane (1) + 2-propanol (2) (circle) + 1-butanol (2) (triangle); + 2-butanol (2) (square) at **a** 298.15 K, **b** 308.15 K and **c** 318.15 K. Smooth lines have been drawn from polynomial fitting

The values of V_m^E , $K_{S,m}^E$ and L_f^E were fitted with a polynomial expression

$$F(x) = x_1 x_2 \sum_{i=1}^k A_i (x_1 - x_2)^i, \quad (8)$$

where A_i is the polynomial coefficients and k is the polynomial degree. Values of coefficients A_i and standard deviations σ are summarized in Table 4.

Partial molar volumes and apparent molar volumes

The partial molar volumes $\bar{V}_{m,1}$ and $\bar{V}_{m,2}$ in these mixtures were evaluated [28, 29] over the complete composition range by using Eqs. 9 and 10:

$$\bar{V}_{m,1} = V_m^E + V_{m,1}^* + x_2 (\delta V_m^E / \delta x_2)_{\rho, T} \quad (9)$$

and

$$\bar{V}_{m,2} = V_m^E + V_{m,2}^* + (1 - x_2) (\delta V_m^E / \delta x_2)_{\rho, T} \quad (10)$$

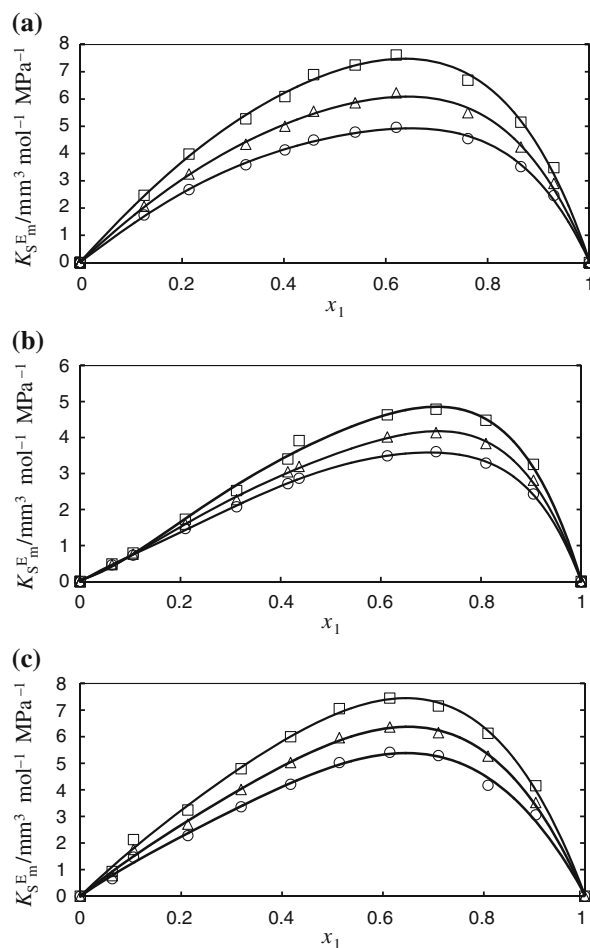


Fig. 2 Excess molar isentropic compressibility $K_{S,m}^E$ for cyclopentane (1) + 2-propanol (2) (circle) + 1-butanol (2) (triangle); + 2-butanol (2) (square) at **a** 298.15 K, **b** 308.15 K and **c** 318.15 K. Smooth lines have been drawn from polynomial fitting

The derivatives of Eqs. 9 and 10 were obtained by differentiation of V_m^E from Eq. 8. It leads to the following equations for the partial molar volumes of the solute cyclopentane (1) ($\bar{V}_{m,1}$) and the co-solvent alkanol (2) ($\bar{V}_{m,2}$):

$$\bar{V}_{m,1} = V_{m,1}^* + \left[(1 - x_1)^2 \sum_{i=1}^k A_i (2x_1 - 1)^{i-1} + x_1 (1 - x_1)^2 \sum_{i=1}^k 2(i-1) A_i (2x_1 - 1)^{i-2} \right] \quad (11)$$

and

$$\bar{V}_{m,2} = V_{m,2}^* + \left[(1 - x_2)^2 \sum_{i=1}^k A_i (1 - 2x_2)^{i-1} + x_2 (1 - x_2)^2 \sum_{i=1}^k (-2)(i-1) A_i (1 - 2x_2)^{i-2} \right] \quad (12)$$

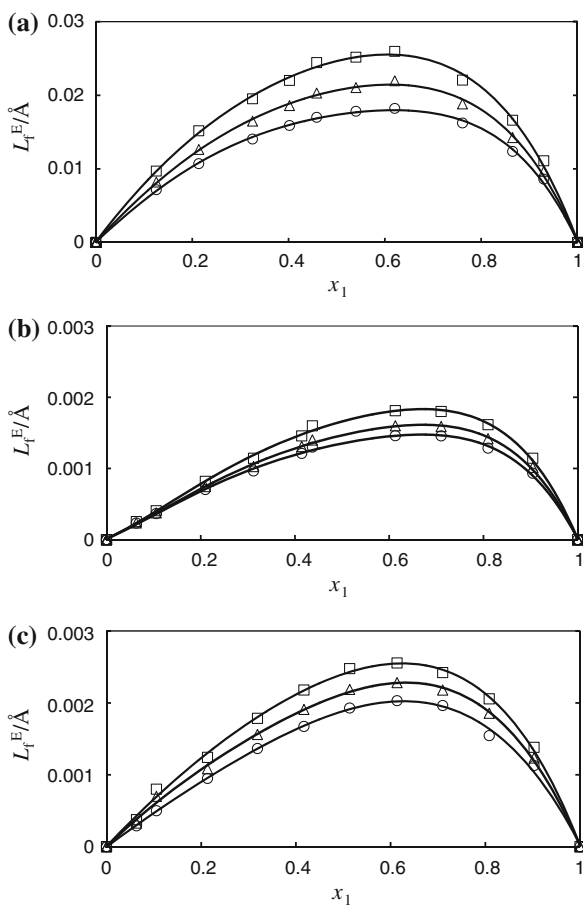


Fig. 3 Excess intermolecular free length L_r^E for cyclopentane (1) + 2-propanol (2) (circle) + 1-butanol (2) (triangle); + 2-butanol (2) (square) at **a** 298.15 K, **b** 308.15 K and **c** 318.15 K. Smooth lines have been drawn from polynomial fitting

Table 3 Coefficients A_i and standard deviations σ for least-squares representation by Eq. 7 for speeds of sound $u/\text{m s}^{-1}$ for binary mixtures at several temperatures and atmospheric pressure

T/K	A_1	A_2	A_3	A_4	A_5	$\sigma (u)$
<i>Cyclopentane (1) + Propan-2-ol (2)</i>						
288.15	1174.32	-27.00	128.19	-133.23	104.16	0.16
298.15	1135.36	-5.07	-32.39	95.19		0.65
308.15	1100.09	-29.14	-25.53	96.84		0.79
<i>Cyclopentane (1) + Butan-1-ol (2)</i>						
288.15	1278.23	-110.92	14.54	62.31		2.41
298.15	1243.73	-124.15	0.5	71.92		1.52
308.15	1210.08	-143.37	-0.85	75.06		1.64
<i>Cyclopentane (1) + Butan-2-ol (2)</i>						
288.15	1246.84	-83.98	-24.86	107.88		0.95
298.15	1209.33	-97.99	-29.84	111.67		1.54
308.15	1172.23	-119.56	-9.82	98.79		2.51

We are interested to focus on the partial molar volumes of cyclopentane at infinite dilution ($x_1 = 0$) in alkanol and the partial molar volume of alkanol at infinite dilution ($x_2 = 0$)

in cyclopentane. Therefore, putting $x_2 = 1$ (corresponding to $x_1 = 0$) in Eq. 10 leads to

$$\bar{V}_{m,1}^0 = V_{m,1}^* + \sum_{i=1} A_i (-1)^{i-1} \quad (13)$$

Similarly, putting $x_2 = 0$ in Eq. 11 leads to

$$\bar{V}_{m,2}^0 = V_{m,2}^* + \sum_{i=1} A_i \quad (14)$$

In Eqs 13 and 14, the $\bar{V}_{m,1}^0$ and $\bar{V}_{m,2}^0$ represent the partial molar volume of cyclopentane at infinite dilution in alkanol and the partial molar volume of the alkanol at infinite dilution in cyclopentane, respectively. All of these partial molar volumes at infinite dilution are evaluated by using the Redlich–Kister coefficients of Eq. 8. Instead of using the Redlich–Kister coefficients, we have also used another approach, which may be more convenient and accurate, by calculating apparent molar volumes in order to evaluate the partial molar volumes at infinite dilution. The apparent molar volumes $V_{\phi,1}$ and $V_{\phi,2}$ of the solute component cyclopentane in co-solvent and of the co-solvent alkanol in the solute can be expressed as

$$V_{\phi,1} = (V_m - n_2 V_{m,2}^*)/n_1 \quad (15)$$

and

$$V_{\phi,2} = (V_m - n_1 V_{m,1}^*)/n_2 \quad (16)$$

where V_m is the volume of the mixture containing one mole of (cyclopentane + n -alkanol). It can be written as

$$V_m = V_m^E + x_1 V_{m,1}^* + x_2 V_{m,2}^* \quad (17)$$

Combination of Eqs. 14, 16 and 15, 16 leads to

$$V_{\phi,1} = V_{m,1}^* + (V_m^E/x_1) \quad (18)$$

and

$$V_{\phi,2} = V_{m,2}^* + (V_m^E/x_2) \quad (19)$$

Equations 18 and 19 allow easy calculation of the apparent molar volumes of each component from the experimental excess molar volumes and corresponding mole fractions. Simple graphical extrapolation of $V_{\phi,1}$ to $x_1 = 0$ ($x_2 = 1$) and of $V_{\phi,2}$ to $x_2 = 0$ ($x_1 = 1$) gives value of $V_{\phi,1}^0$ and $V_{\phi,2}^0$ at infinite dilution. These are also the desired partial molar volumes at infinite dilution, represented by $\bar{V}_{m,1}^0$ and $\bar{V}_{m,2}^0$ same as before. The values of partial molar volumes and apparent molar volumes and their values at infinite dilution are reported in Tables 5 and 6, respectively.

The Flory's model

The Flory model [30, 31] has been commonly employed to analyze the molar volume of the mixture and the excess molar volume parting from the equation of the state in function of the reduced variables:

Table 4 Parameters A_i and standard deviations $\sigma[F(x)]$ for least squares representation by Eq. 8 for binary mixtures at several temperatures and atmospheric pressure

$F(x)$	T/K	A_1	A_2	A_3	A_4	A_5	σ
<i>Cyclopentane (1) + Propan-2-ol (2)</i>							
$V^E \times 10^{-6}/\text{m}^3 \text{ mol}^{-1}$	288.15	1.2746	0.7650	0.3499	0.2494	0.6860	0.0115
	298.15	1.5927	0.9419	0.2019	0.2028	1.0435	0.0139
	308.15	1.9482	0.9840	0.0675	0.5171	1.5408	0.0139
$K_{S,m}^E/\text{mm}^3 \text{ mol}^{-1} \text{ MPa}^{-1}$	288.15	18.732	07.671	2.814	4.571	11.447	0.082
	298.15	23.081	10.340	2.351	3.287	13.286	0.155
	308.15	28.444	12.856	1.168	3.400	17.25	0.202
$L_f^E/\text{\AA}$	288.15	0.0703	0.0211	0.0095	0.0153	0.0417	0.0003
	298.15	0.0838	0.0277	0.0061	0.0101	0.0466	0.0005
	308.15	0.0999	0.0326	0.0037	0.0073	0.0550	0.0007
<i>Cyclopentane (1) + Butan-1-ol (2)</i>							
$V^E \times 10^{-6}/\text{m}^3 \text{ mol}^{-1}$	288.15	0.3614	0.6459	0.3427	–	–	0.0110
	298.15	0.4363	0.6662	0.5151	0.4058	–	0.0078
	308.15	0.5844	0.7919	0.5188	0.3503	–	0.0085
$K_{S,m}^E/\text{mm}^3 \text{ mol}^{-1} \text{ MPa}^{-1}$	288.15	14.894	9.405	0.442	–	–	0.791
	298.15	16.693	11.624	0.989	–	–	0.840
	308.15	18.824	14.243	1.689	–	–	0.908
$L_f^E/\text{\AA}$	288.15	0.0063	0.0020	0.0002	–	–	0.0003
	298.15	0.0068	0.0037	–0.0002	–	–	0.0003
	308.15	0.0076	0.0041	0.0001	–	–	0.0003
<i>Cyclopentane (1) + Butan-2-ol (2)</i>							
$V^E \times 10^{-6}/\text{m}^3 \text{ mol}^{-1}$	288.15	1.1358	1.4518	–0.1502	–1.0483	–	0.0218
	298.15	1.4148	1.5033	–0.1582	–0.9651	–	0.0239
	308.15	1.7209	1.3166	–0.0588	–	–	0.0241
$K_{S,m}^E/\text{mm}^3 \text{ mol}^{-1} \text{ MPa}^{-1}$	288.15	17.624	5.425	7.015	–	–	1.211
	298.15	22.513	12.406	12.881	–	–	0.695
	308.15	26.510	13.564	15.997	–	–	0.9125
$L_f^E/\text{\AA}$	288.15	0.0074	0.0032	0.0032	–	–	0.0002
	298.15	0.0084	0.0051	0.0045	–0.0043	–	0.0003
	308.15	0.0094	0.0038	0.0054	–	–	0.0003

$$\tilde{P}\tilde{v}/\tilde{T} = [\tilde{v}^{1/3}/(\tilde{v}^{1/3} - 1)] - 1/(\tilde{v}T) \quad (20)$$

where

$$V^* = V/\tilde{v} = V[(1 + \alpha T)/(1 + (4/3)\alpha T)]^3 \quad (21)$$

$$P^* = P/\tilde{P} = [(\alpha T\tilde{v}^2)/\kappa T] \quad (22)$$

$$T^* = T/\tilde{T} = \tilde{v}^{4/3}/(\tilde{v}^{1/3} - 1) \quad (23)$$

Theoretical values of dV_m^E/dT [32] were calculated from the Flory theory using

$$T(dV_m^E/dT) = \left[\sum_{i=1}^2 x_i V_i^* [T(d\tilde{v}/dT)] - \left(\sum_{i=1}^2 x_i V_i^* [T(d\tilde{v}/dT)] \right) i \right] \quad (24)$$

where

$$T(d\tilde{v}/dT) = \tilde{v}(1 - \tilde{v}^{-1/3})/[(4/3)\tilde{v}^{-1/3} - 1] \quad (25)$$

In the present study, the value of the reduced volume for the liquids and their mixture \tilde{v} was determined from α values of the mixtures using the Eq. 21.

The excess function $(\partial V_m^E/\partial T)_P$ was computed by analytical differentiation of Eq. 7 at 298.15 K for each mixture. From $(\partial V_m^E/\partial T)_P$ and V_m^E of this work we also have obtained $(\partial H^E/\partial P)_T$ at zero pressure according to the equation:

$$(\partial H^E/\partial P)_T = V_m^E - T(\partial V_m^E/\partial T)_P \quad (26)$$

Values for $(\partial V_m^E/\partial T)_P$, and $(\partial H^E/\partial P)_T$, for equimolar mixtures are reported in Table 7.

It is observed from Fig. 1 that the excess molar volumes for all the mixtures at $T = 288.15, 298.15$ and 308.15 K are

Table 5 Values of $\bar{V}_{m,1} \times 10^{-6}/\text{m}^3 \text{ mol}^{-1}$, $\bar{V}_{m,2} \times 10^{-6}/\text{m}^3 \text{ mol}^{-1}$, $V_{\phi,1} \times 10^{-6}/\text{m}^3 \text{ mol}^{-1}$, and $V_{\phi,2} \times 10^{-6}/\text{m}^3 \text{ mol}^{-1}$ for binary mixtures at several temperatures

x_1	$\bar{V}_{m,1} \times 10^{-6}/\text{m}^3 \text{ mol}^{-1}$			$\bar{V}_{m,2} \times 10^{-6}/\text{m}^3 \text{ mol}^{-1}$			$V_{\phi,1} \times 10^{-6}/\text{m}^3 \text{ mol}^{-1}$			$V_{\phi,2} \times 10^{-6}/\text{m}^3 \text{ mol}^{-1}$		
	T/K			T/K			T/K			T/K		
	288.15	298.15	308.15	288.15	298.15	308.15	288.15	298.15	308.15	288.15	298.15	308.15
<i>Cyclopentane (1) + 2-propanol (2)</i>												
0.1253	94.6084	95.9985	97.5125	75.4462	76.1475	76.7440	94.7755	96.2314	97.7823	76.2492	77.0907	77.9838
0.2135	94.5611	95.9666	97.4927	75.5007	76.2322	76.9260	94.7475	96.1895	97.7374	76.3498	77.2122	78.1344
0.3251	94.5556	95.9903	97.5030	75.7561	76.5345	77.3720	94.6164	96.0483	97.5762	76.4583	77.3533	78.3143
0.4019	94.5206	95.9464	97.4198	75.9651	76.7718	77.6697	94.5924	96.0220	97.5389	76.5726	77.4981	78.4916
0.4583	94.4782	95.8839	97.3239	76.1280	76.9573	77.8816	94.6119	96.0356	97.5472	76.7042	77.6536	78.6773
0.5399	94.4034	95.7721	97.1720	76.3858	77.2580	78.2080	94.5516	95.9587	97.4501	76.8563	77.8387	78.9021
0.6205	94.3265	95.6620	97.0429	76.6810	77.6113	78.5941	94.4855	95.8961	97.3425	77.0347	78.0889	79.1590
0.7612	94.1867	95.4891	96.8693	77.3434	78.4072	79.5225	94.3771	95.7290	97.1523	77.5499	78.6453	79.8413
0.8653	94.0593	95.3450	96.7086	78.0262	79.2119	80.5415	94.2414	95.5641	96.9573	78.1215	79.3149	80.6594
0.9301	94.9777	95.2506	96.5883	78.6016	79.8932	81.4477	94.1224	95.4263	96.7984	78.6733	80.0237	81.6059
<i>Cyclopentane (1) + 1-butanol (2)</i>												
0.0632	93.9882	95.2510	96.6377	90.6984	91.3903	92.2766	93.9596	95.2058	96.5347	90.9050	91.7689	92.6647
0.1054	94.0005	95.3233	96.7067	90.6074	91.2543	92.1320	93.9804	95.2535	96.5989	90.9089	91.7751	92.6734
0.2098	94.0597	95.4096	96.7992	90.5098	91.1813	92.0403	94.0107	95.2924	96.7122	90.9242	91.7941	92.7163
0.3120	94.1246	95.4402	96.8367	90.5481	91.3124	92.1677	94.0353	95.3357	96.7417	90.9503	91.8321	92.7672
0.4143	94.1708	95.4589	96.8543	90.6771	91.5195	92.3913	94.0935	95.4018	96.7773	91.0180	91.9147	92.8505
0.4368	94.1766	95.4626	96.8563	90.7144	91.5688	92.4470	94.1094	95.4131	96.7980	91.0414	91.9376	92.8846
0.6129	94.1568	95.4637	96.8298	91.0792	91.9826	92.9359	94.1140	95.4246	96.8173	91.1926	92.1322	93.1458
0.7102	94.1007	95.4219	96.7681	91.3218	92.2649	93.2684	94.1268	95.4328	96.8054	91.3827	92.3517	93.3810
0.8097	94.0262	95.3400	96.6694	91.5988	92.6453	93.6973	94.1213	95.4208	96.7856	91.7123	92.7303	93.8251
0.9046	93.9610	95.2464	96.5667	91.8992	93.1377	94.2281	94.0270	95.3371	96.6699	91.8129	93.1183	94.1559
<i>Cyclopentane (1) + 2-butanol (2)</i>												
0.0633	94.2516	95.6945	97.1319	91.4802	92.3749	93.0634	94.0985	95.5375	97.0718	91.4229	92.3662	93.3703
0.1054	94.2149	95.6700	97.2663	91.4227	92.3080	92.9372	94.4188	95.8693	97.2089	91.4690	92.4225	93.4145
0.2132	94.3660	95.8105	97.4635	91.1544	92.0482	92.7924	94.2979	95.7355	97.2672	91.5109	92.4895	93.5370
0.3188	94.5677	95.9763	97.4882	90.9947	91.9189	92.8739	94.3837	95.8180	97.3347	91.6234	92.6347	93.7173
0.4169	94.6365	96.0092	97.4016	91.0794	92.0376	93.1193	94.3986	95.8184	97.3144	91.7458	92.7889	93.9058
0.5135	94.5595	95.9019	97.2475	91.3866	92.3800	93.4926	94.5251	95.9302	97.4019	92.0385	93.1194	94.2712
0.6135	94.3709	95.6819	97.0502	91.8571	92.8916	93.9871	94.5104	95.8878	97.3305	92.3311	93.4431	94.6308
0.7099	94.1614	95.4614	96.8544	92.3354	93.4201	94.5375	94.4028	95.7529	97.1705	92.5660	93.7091	94.9426
0.8082	93.9990	95.2827	96.6788	92.7155	93.8672	95.1411	94.2391	95.5614	96.9598	92.7093	93.8884	95.2173
0.9029	93.9326	95.3030	96.5592	92.8794	94.1148	95.7308	94.1104	95.4132	96.7913	93.0789	94.3749	95.9247

positive over the whole composition range. The excess molar volumes decrease with the increase in chain length of the primary and secondary alcohols. This supports our earlier results reported for cyclopentane + 1-alkanol systems [2]. The magnitude of V_m^E value increases as we move from propan-1-ol [2] to propan-2-ol and butan-1-ol to butan-2-ol. For the systems, cyclopentane with primary and secondary alcohols, the excess molar volume increase with decrease in the chain length of alcohol, this increase suggest that dipole–dipole interactions are weak in lower alcohol owing to decrease in their polarizability [33] with decreased chain length.

It is observed from Table 2 that u increases with increase in the concentration of cyclopentane in cyclopentane (1) + propan-2-ol (2) systems while for other two binary mixtures viz. cyclopentane (1) + butan-1-ol (2) and cyclopentane (1) + butan-2-ol (2) u decreases. The increase in u with x_1 indicate significant interaction between molecules. It is observed from Tables 3, 4 and Figs. 2, 3 that $K_{S,m}^E$ and L_f^E shows positive deviations for all mixtures over the whole composition range at all temperatures. For the same value of x_1 the absolute values of $K_{S,m}^E$ and L_f^E for mixtures decrease with decrease in chain length of primary and

Table 6 Values of $V_1^* \times 10^{-6}/\text{m}^3 \text{ mol}^{-1}$, $\bar{V}_{m,1}^0 \times 10^{-6}/\text{m}^3 \text{ mol}^{-1}$, $\bar{V}_{\phi,1}^0 \times 10^{-6}/\text{m}^3 \text{ mol}^{-1}$, $V_2^* \times 10^{-6}/\text{m}^3 \text{ mol}^{-1}$, $\bar{V}_{m,2}^0 \times 10^{-6}/\text{m}^3 \text{ mol}^{-1}$ and $\bar{V}_{\phi,2}^0 \times 10^{-6}/\text{m}^3 \text{ mol}^{-1}$ for binary mixtures at several temperatures

T/K	$V_1^* \times 10^{-6}/\text{m}^3 \text{ mol}^{-1}$	$\bar{V}_{m,1}^0 \times 10^{-6}/\text{m}^3 \text{ mol}^{-1}$	$\bar{V}_{\phi,1}^0 \times 10^{-6}/\text{m}^3 \text{ mol}^{-1}$	$V_2^* \times 10^{-6}/\text{m}^3 \text{ mol}^{-1}$	$\bar{V}_{m,2}^0 \times 10^{-6}/\text{m}^3 \text{ mol}^{-1}$	$\bar{V}_{\phi,2}^0 \times 10^{-6}/\text{m}^3 \text{ mol}^{-1}$
<i>Cyclopentane (1) + 2-propanol (2)</i>						
288.15	93.9310	94.6489	94.8398	76.1282	78.8390	78.8123
298.15	95.1947	96.0873	96.3074	76.9422	79.6810	79.6905
308.15	96.1253	97.6644	97.8814	77.8019	81.1501	81.1422
<i>Cyclopentane (1) + 1-butanol (2)</i>						
288.15	93.9310	93.9340	93.9510	90.9030	90.9030	91.7674
298.15	95.1947	95.0731	95.2000	91.7682	93.3225	93.2223
308.15	96.1253	96.4752	97.1707	92.6632	94.4586	94.3210
<i>Cyclopentane (1) + 2-butanol (2)</i>						
288.15	93.9310	94.5145	94.1885	91.4115	92.3822	92.2778
298.15	95.1947	96.3388	95.0153	92.3430	94.6618	94.5882
308.15	96.1253	96.85911	97.6999	93.3325	96.1794	96.1572.

Table 7 Equimolar values of the excess functions at $T = 298.15 \text{ K}$

$(\partial V_m^E/\partial T)_P \times 10^3/\text{m}^3 \text{ mol}^{-1} \text{ K}^{-1}$		$(\delta H^E/\delta P)_T/\text{m}^3 \text{ mol}^{-1}$	
Experimental	Flory Model	Experimental	Flory Model
<i>Cyclopentane (1) + 2-propanol (2)</i>			
0.0084	0.0115	-2.1063	-3.0305
<i>Cyclopentane (1) + 1-butanol (2)</i>			
0.0028	0.0035	-0.7257	-0.9344
<i>Cyclopentane (1) + 2-butanol (2)</i>			
0.0073	0.0107	-1.8228	-2.8365

secondary alcohols. The magnitude of $K_{S,m}^E$ and L_f^E increases with increase in temperature for all systems studied at all three temperatures. The deviations in these functions from rectilinear dependence on mole fraction indicate the extent of interaction between unlike molecules. For the same values of x_1 , the absolute values of $K_{S,m}^E$ and L_f^E for the mixtures fall in the order: butan-1-ol < propan-2-ol < butan-2-ol, which means that values increase with the increase in chain length of secondary alcohol and on changing the position of hydroxyl group, i.e. on branching. Further, the values increase with the increase on temperature for the all the mixtures studied. Positive values of $K_{S,m}^E$ mean that the mixture is more compressible than the corresponding ideal mixture and, likewise, L_f^E is positive, suggesting weaker interactions among the molecules which is in accordance with the positive values of excess molar volumes.

From Table 6, it is observed that partial molar volumes of cyclopentane at infinite dilution $\bar{V}_{m,1}^0$ in alkanols are greater than the corresponding V_1^* values of pure cyclopentane. Thus, the difference in values ($\bar{V}_{m,1}^0 - V_1^*$) are

positive, suggesting the expansion in volume of the mixture on mixing which may be attributed to the non-specific interactions between cyclopentane and alkanol molecules. It is also observed that all of the $\bar{V}_{m,2}^0$, i.e. partial molar volumes of alkanols in cyclopentane are greater than corresponding molar volumes V_2^* of n -alkanol which may suggest that alkanol molecules are not able to fit into the empty spaces in cyclopentane which results in positive excess molar volumes. Apparent molar volumes at infinite dilution $\bar{V}_{\phi,1}^0$ for cyclopentane in alkanol are higher than corresponding molar volume V_1^* of pure cyclopentane. This suggests the idea that apparent molar volume of cyclopentane is actually the molar volume of cyclopentane and additional volume that arises from the rupture of interaction between the mixture components. The difference between $\bar{V}_{\phi,1}^0$ and V_1^* increases as we from primary alkanol to secondary alkanol and with decrease in chain length of alkanol which constrained the structure formation in these mixtures and increases the excess molar volumes. This observation and positive values of V_m^E for these mixtures suggest that structure breaking effect between like molecules exceeds the structure formation between unlike molecules. Dispersion interactions between cyclopentane and alkanol increases with decrease in chain length of alkanol, i.e. from 1-butanol to 1-propanol. Repulsive interactions are relatively strong in cyclopentane + 2-propanol as observed from V_m^E data. Further, the difference between $\bar{V}_{\phi,2}^0$ and V_2^* are smaller in the case of 1-butanol as compared to 2-butanol which indicates more expansion means more positive V_m^E for cyclopentane + 2-butanol mixture.

It is observed from Table 7 that the values obtained for $(\partial V_m^E/\partial T)_P$ are positive for all the systems and are in

agreement with the values of V_m^E at $T = 298.15$ K. The values of $(\partial H^E/\partial P)_T$ are negative at equimolar concentration, for all cyclopentane + alkanol systems. The values of $(\partial V_m^E/\partial T)_P$ and $(\partial H^E/\partial P)_T$ have similar variation with the n -alkanol but with opposite sign. The values obtained from Flory's theory are greater than the experimental values. The difference between theoretical and experimental values is higher in case of cyclopentane + 2-butanol systems. The values of $(\partial V_m^E/\partial T)_P$ decrease with increase in the chain length, i.e. from 2-propanol to 2-butanol and with branching, i.e. from 1-butanol to 2-butanol. The mixing quantities $(\partial V_m^E/\partial T)_P$ and $(\partial H^E/\partial P)_T$ are an indicator of nonrandomness or order in the solution [34–36]. $(\partial V_m^E/\partial T)_P$ values are positive for all the cyclopentane + alkanol systems so it is expected that destruction of order during mixing is not important as positive contribution of $(\partial V_m^E/\partial T)_P$ implies the nonrandomness or order in the solution. Randomness in solution implies a negative contribution to $(\partial V_m^E/\partial T)_P$. An analysis of the results shows that out of three systems, cyclopentane + 2-propanol has more positive values of $(\partial V_m^E/\partial T)_P$ which implies that it has very less tendency to break the order or to create the randomness in the solution on mixing.

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