Excess parameters for binary mixtures of alkyl benzoates with 2-propanol at different temperatures

S. Sreehari Sastry · Shaik Babu · T. Vishwam · Ha Sie Tiong

Abstract Density (ρ), viscosity (η), and speed of sound (U) values for the binary mixture systems of methyl benzoate + 2-propanol and ethyl benzoate + 2-propanol including those of pure liquids were measured over the entire mole fraction range at five different temperatures (303.15, 308.15, 313.15, 318.15, and 323.15) K. From these experimentally determined values, various thermo-acoustic parameters such as excess isentropic compressibility $\left(K_s^E\right)$, excess molar volume (V^E) and excess free length $\left(L_f^E\right)$, excess Gibb's free energy (ΔG^{*E}), and excess enthalpy (H^E) have been calculated. The excess functions have been fitted to the Redlich–Kister type polynomial equation. The deviations for excess thermo-acoustic parameters have been explained on the basis of the intermolecular interactions present in these binary mixtures. The theoretical values of speed of sound in the mixtures have been evaluated using various theories and have been compared with experimentally determined speed of sound values in order to check the applicability of such theories to the liquid mixture systems under study. Viscosity data have been used to test the applicability of standard viscosity models of Grunberg–Nissan, Hind–Mc Laughlin, Katti–Chaudhary, Heric and Brewer, Frenkel, Tamura and Kurata at various temperatures for the binary liquid systems under study.

Introduction

Volumetric, viscometric, and speed of sound investigations of liquids and liquid mixtures are of considerable importance and they play a relevant role in understanding the intermolecular interactions occurring among the component molecules besides finding extensive applications in several industrial and technological processes [1, 2]. Extensive studies have been done to understand these kinds of interactions on different types of binary and ternary mixtures. Several researchers [3–8] have measured the density, viscosity, and speed of sound for a wide range of binary mixtures containing alcohols as one of the components, and these properties were interpreted in terms of specific or nonspecific interactions. The objective of the present study is to understand the influence of non associative molecule on the associative molecule. Alcohols are strongly associated in solution because of dipole–dipole interaction and hydrogen bonding. They are of great importance for their relevant role in chemistry, biology, and studies on hydrogen bonding in liquid mixtures. Alcohols are widely used as solvents. The molecules with –OH group form associative liquids due to hydrogen

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bonding. The effect shown by the molecules with other functional groups on these molecules plays a relevant role in understanding the behavior of hydrogen bonding. On the other hand alkyl benzoates are non-associated in solution, good hydrogen bonding acceptors. They are widely used in perfumery and pesticides. Also, hydrocarbons are among the most important chemicals used in hydrocarbon processing industries. The investigations regarding the molecular association in liquid mixtures having aromatic group as one of the components is of particular interest, since aromatic group is highly non-polar and can associate with any other group having some degree of polar attractions. Even though considerable work has been reported on alcohols as one of the component in binary and ternary mixtures, the data on binary mixtures of alcohols with alkylbenzoates with temperature variation are scanty. In order to get a better understanding of the nature of molecular interactions based on the temperature dependent ultrasonic studies, the authors have made an attempt to study the thermodynamic and acoustic properties of binary mixtures involving alcohol and alkyl benzoates. So, in our present study we have selected methyl benzoate and ethyl benzoate as non-associative liquids and 2-propanol as associative liquid. In continuation of our earlier reported work on molecular interactions of liquid mixtures [9–12] using excess thermodynamic and acoustic properties, the present study gives further investigations on molecular interactions in the commercially important liquid mixtures of methyl benzoate/ethyl benzoate with 2-propanol over the entire composition range. Here, we report the results of speed of sound, density, and viscosity for the binary liquid mixtures of (methyl benzoate + 2-propanol), (ethyl benzoate + 2-propanol) at temperatures of (303.15, 308.15, 313.15, 318.15, and 323.15) K.

Thermodynamic and transport properties [13, 14] of liquid mixtures provide important information with which to speculate the molecular liquid structure. These properties have been widely used to study the intermolecular interactions between various species present in the liquid mixtures. The study of thermodynamic properties of multicomponent liquid mixtures and data on the analysis in terms of various models are important for industrial and pharmaceutical applications [15]. The excess thermodynamic functions [16] are sensitively dependent not only on the differences in intermolecular forces, but also on the differences in the size of the molecules. Excess functions are thermodynamic properties in excess compared to those of an ideal solution at the same temperature, pressure, and composition. The variation of these properties with temperatures and composition for mixtures containing polar molecules and hydrogen bonded components may be complex due to a decrease or an increase in hydrogen bonding interaction due to mixing, depending upon the

nature of the liquids whether they are polar or non-polar, the signs and magnitudes of these excess values can throw light on the strength of interactions. So, from the experimentally determined values of speed of sound density and viscosity, various thermo-acoustic parameters like excess isentropic compressibility $\left(K_s^E\right)$, excess molar volume (V^E), excess free length $\left(L_f^E\right)$, excess Gibb's free energy (ΔG^{*E}), and excess enthalpy (H^E) have been calculated. The results of excess values were fitted to the Redlich and Kister [17] polynomial equation. The intermolecular interactions have been estimated in the light of these excess parameters. In the present study, theoretical speed of sound and viscosity values has been evaluated using several empirical relations in the liquid mixtures considering methyl benzoate/ethyl benzoate as one component and 2-propanol as the other component at $T = (303.15, 308.15, 313.15, 318.15,$ and $323.15)$ K. This kind of evaluation of theoretical speed of sound values proves to be useful to verify the applicability of various postulates of these theories of liquid mixtures and to arrive at some useful inferences regarding the strength of molecular interactions between component liquids in some cases.

Experimental

Materials

The chemicals used in the present study are methyl benzoate, ethyl benzoate, and 2-propanol which are of AR grade obtained from Merck Co. Inc., Germany, with purities of greater than 99 %. All the chemicals were further purified by standard methods [18] and only middle fractions were collected. The density and speed of sound were experimentally determined at a temperature of 303.15 K and compared with the literature [19–25]. Comparison of experimental densities (ρ), viscosity (η), and speed of sound (U) of pure liquids with the literature values are given in Table 1.

Methods

All binary mixtures were prepared gravimetrically in airtight bottles, and adequate precautions have been taken to minimize evaporation losses. Before use, the chemicals were stored over 0.4 nm molecular sieves approximately for 72 h to remove water content and then degassed. The mass measurements were performed on a digital electronic balance (Mettler Toledo AB 135, Switzerland) with an uncertainty of $\pm 10^{-8}$ kg. The binary mixtures were prepared just before use. The uncertainty in mole fraction was estimated to be less than ± 0.0001.

Table 1 Comparison of experimental densities (ρ), viscosities (η), and speed of sound (U) of pure liquids with the literature values along with isobaric thermal expansion coefficient and molar isobaric heat capacity values at $T/\text{K} = 303.15$

Liquid	T/K	$\rho/10^{-3}$ kg m^{-3}		$\eta/10^3$ kg m^{-1} s^{-1}		$U/$m s^{-1}		α/k K^{-1}	$C_P/$J mol^{-1} K^{-1}
		Exp.	Literature	Exp.	Literature	Exp.	Literature		
2-Propanol	303.15	0.7815	0.7810[a]	1.6536	1.521[b]	1122.2	1107.8[c]	1.299[h]	164.5[i]
Methyl benzoate	303.15	1.0775	1.0787[d]	1.670	1.673[e]	1399.4	1392.0[f]	1.045[h]	222[i]
Ethyl benzoate	303.15	1.0420	1.042[g]	1.749	1.749[g]	1345.4	1345.4[g]	1.077[h]	250[i]

[a] Vasudha et.al. [19]

[b] Mutalik et al. [20], compared at $T/\text{K} = 308.15$

[c] Sreekanth et al. [21], compared at $T/\text{K} = 308.15$

[d] Mohan et al. [22]

[e] Riddick et al. [23]

[f] Aminabhavi et al. [24]

[g] Sreehari et al. [9]

[h] Derived from density data

[i] Estimated from group contribution method of Chueh–Swanson [25]

The viscosities were measured with Ostwald viscometer. The viscometer was calibrated at each temperature using redistilled water. The uncertainty in viscosity measurement is up to 0.001 mPa s. The flow time has been measured after the attainment of bath temperature by each mixture. The flow measurements were made with an electronic stop watch with a precision of 0.01 s. For all the pure components and mixtures, 3–4 readings were taken, and the average of these values was used in all the calculations.

The densities of the pure compounds and their mixtures were determined accurately using 10 mL specific gravity bottles in digital electronic balance (Mettler Toledo AB 135, Switzerland) with an uncertainty of $\pm 10^{-8}$ kg. The average uncertainty in the measured density was ± 0.001 kg m^{-3}.

The speed of sound was measured with a single-crystal variable path interferometer (Mittal Enterprises, New Delhi, India) operating at a frequency of 2 MHz that had been calibrated with water and benzene. The uncertainty in the speed of sound was found to be ± 0.1 m s^{-1}. In all property measurements, the temperature was controlled within ± 0.1 K using a constant temperature bath (M/s Sakti Scientific Instruments Company, India) by circulating water from the thermostat.

Theory

The values of experimentally determined density and speed of sound for the binary mixtures of methyl benzoate and ethyl benzoate with the 2-propanol at 303.15, 308.15, 313.15, 318.15, and 323.15 K over the entire composition range are given in Table 2. It can be observed from Table 2 that the values of speed of sound, density, and viscosity

show increase in trend at all the temperatures in the binary systems under study.

Using the experimentally determined values of speed of sound, density, and viscosity, various thermodynamic parameters like excess isentropic compressibility $\left(K_s^\text{E}\right)$, excess molar volume ($V^\text{E}$), excess free length $\left(L_f^\text{E}\right)$, excess Gibb's free energy ($\Delta G^{*\text{E}}$), and excess enthalpy (H^E) were calculated.

Kiyohara and Benson [26, 27] stated that the thermodynamic properties of an ideal mixture must be mutually related in the same way as for those of pure substances and real mixtures. Also Douheret et al. [28] suggested that the interpretation of the nature of molecular interactions in mixtures requires a correct calculation of a thermodynamic property of the ideal liquid mixtures by the application of correct ideal mixing rules. In the present work, the authors have calculated the excess values of isentropic compressibility and excess free length values to check the applicability of thermo dynamical ideality (the ideal mixing rules) to the components under study.

The excess values of isentropic compressibility K_s^E were calculated as follows,

$$K_s^\text{E} = K_s - K_s^\text{id}, \tag{1}$$

where K_s represents the calculated value of isentropic compressibility for the mixture

$$K_s = \frac{1}{\rho U^2}, \tag{2}$$

K_s^E is its excess value, K_s^id is the ideal isentropic compressibility value, ρ is the density, and U represents the speed of sound. K_s^id for an ideal mixture was calculated from the relation recommended by Benson and Kiyohara [26, 27] and Douheret et al. [28].

Table 2 Densities (ρ), speed of sound (U), and viscosities (η) for the binary mixtures of methyl benzoate and ethyl benzoate with 2-propanol at different temperatures

x_1	$\rho/10^{-3}$ kg m^{-3}	U/m s^{-1}	$\eta/10^3$ kg m^{-1} s^{-1}	x_1	$\rho/10^{-3}$ kg m^{-3}	U/m s^{-1}	$\eta/10^3$ kg m^{-1} s^{-1}
Methyl benzoate(1) + 2-propanol (2)							
T/K = 303.15							
0.0000	0.7815	1122.2	1.6536	0.4773	0.9600	1289.1	1.6628
0.0634	0.8117	1152.1	1.6550	0.5868	0.9892	1316.2	1.6645
0.1321	0.8417	1181.0	1.6564	0.7089	1.0185	1343.1	1.6664
0.2069	0.8715	1207.0	1.6578	0.8456	1.0478	1373.4	1.6682
0.2887	0.9013	1235.2	1.6595	1.0000	1.0775	1399.4	1.6700
0.3784	0.9307	1260.9	1.6610				
T/K = 308.15							
0.0000	0.7720	1106.2	1.4941	0.4773	0.9515	1269.9	1.4976
0.0634	0.8022	1135.1	1.4946	0.5868	0.9811	1295.9	1.4984
0.1321	0.8324	1163.1	1.4951	0.7089	1.0107	1324.1	1.4993
0.2069	0.8624	1189.1	1.4956	0.8456	1.0405	1350.9	1.5003
0.2887	0.8923	1218.1	1.4962	1.0000	1.0706	1371.6	1.5014
0.3784	0.9220	1243.0	1.4969				
T/K = 313.15							
0.0000	0.7601	1088.8	1.3195	0.4773	0.9429	1248.7	1.3444
0.0634	0.7907	1118.1	1.3229	0.5868	0.9732	1273.4	1.3499
0.1321	0.8213	1141.4	1.3264	0.7089	1.0037	1299.2	1.3561
0.2069	0.8518	1167.0	1.3304	0.8456	1.0344	1324.1	1.3634
0.2887	0.8823	1194.6	1.3347	1.0000	1.0655	1348.4	1.3710
0.3784	0.9126	1219.0	1.3394				
T/K = 318.15							
0.0000	0.7543	1075.1	1.1830	0.4773	0.9377	1232.8	1.2307
0.0634	0.7849	1101.1	1.1892	0.5868	0.9682	1258.8	1.2419
0.1321	0.8155	1126.7	1.1960	0.7089	0.9989	1281.3	1.2539
0.2069	0.8461	1152.1	1.2037	0.8456	1.0298	1302.7	1.2672
0.2887	0.8768	1179.6	1.2123	1.0000	1.0612	1326.6	1.2818
0.3784	0.9072	1204.8	1.2213				
T/K = 323.15							
0.0000	0.7470	1065.8	1.0629	0.4773	0.9333	1213.7	1.1398
0.0634	0.7779	1088.5	1.0741	0.5868	0.9645	1240.8	1.1572
0.1321	0.8089	1112.7	1.0851	0.7089	0.9960	1262.0	1.1770
0.2069	0.8400	1138.4	1.0967	0.8456	1.0277	1283.4	1.1985
0.2887	0.8712	1163.7	1.1096	1.0000	1.0600	1307.2	1.2223
0.3784	0.9022	1190.2	1.1235				
Ethyl benzoate(1) + 2-propanol (2)							
T/K = 303.15							
0.0000	0.7815	1122.2	1.6536	0.4446	0.9386	1274.2	1.6953
0.0560	0.8083	1152.1	1.6585	0.5460	0.9624	1294.3	1.7055
0.1177	0.8347	1177.5	1.6637	0.6810	0.9900	1314.5	1.7191
0.1862	0.8611	1202.0	1.6706	0.8277	1.0158	1330.4	1.7327
0.2624	0.8872	1226.4	1.6780	1.0000	1.0420	1345.4	1.7495
0.3480	0.9130	1251.8	1.6860				
T/K = 308.15							
0.0000	0.7720	1106.2	1.4941	0.4446	0.9303	1256.1	1.5415
0.0560	0.7988	1135.1	1.5011	0.5460	0.9543	1278.5	1.5509
0.1177	0.8255	1160.5	1.5083	0.6810	0.9823	1296.4	1.5628

Table 2 continued

x_1	$\rho/10^{-3}$ kg m^{-3}	U/m s^{-1}	$\eta/10^3$ kg m^{-1} s^{-1}	x_1	$\rho/10^{-3}$ kg m^{-3}	U/m s^{-1}	$\eta/10^3$ kg m^{-1} s^{-1}
0.1862	0.8519	1184.0	1.5153	0.8277	1.0085	1316.7	1.5768
0.2624	0.8783	1210.4	1.5247	1.0000	1.0351	1331.4	1.5932
0.3480	0.9043	1233.9	1.5321				
T/K = 313.15							
0.0000	0.7601	1088.8	1.3195	0.4446	0.9222	1240.2	1.3795
0.0560	0.7873	1118.1	1.3274	0.5460	0.9471	1261.5	1.3935
0.1177	0.8146	1141.4	1.3365	0.6810	0.9761	1279.6	1.4086
0.1862	0.8417	1167.0	1.3451	0.8277	1.0033	1299.7	1.4263
0.2624	0.8686	1194.6	1.3562	1.0000	1.0310	1312.0	1.4457
0.3480	0.8955	1219.0	1.3673				
T/K = 318.15							
0.0000	0.7543	1075.1	1.1830	0.4446	0.9172	1224.4	1.2537
0.0560	0.7815	1101.1	1.1922	0.5460	0.9422	1245.6	1.2697
0.1177	0.8089	1126.7	1.2026	0.6810	0.9715	1263.6	1.2906
0.1862	0.8361	1152.1	1.2129	0.8277	0.9989	1281.7	1.3132
0.2624	0.8632	1179.6	1.2252	1.0000	1.0269	1293.4	1.3391
0.3480	0.8902	1200.9	1.2385				
T/K = 323.15							
0.0000	0.7470	1065.8	1.0629	0.4446	0.9107	1213.7	1.1498
0.0560	0.7743	1088.5	1.0743	0.5460	0.9361	1233.9	1.1671
0.1177	0.8017	1112.7	1.0852	0.6810	0.9656	1250.9	1.1940
0.1862	0.8291	1138.4	1.0994	0.8277	0.9934	1266.8	1.2223
0.2624	0.8564	1163.7	1.1136	1.0000	1.0217	1285.4	1.2545
0.3480	0.8835	1190.3	1.1301				

$$K_s^{id} = \sum \phi_i \left\{ K_{s,i}^o + \frac{TV_i^o(\alpha_i^o)^2}{C_{p,i}^o} \right\}$$
$$- T\left(\sum x_i V_i^o\right)\left(\frac{\sum \phi_i \alpha_i^{o2}}{\sum x_i C_{p,i}^o}\right), \qquad (3)$$

in which $K_{s,i}^o$, V_o^i, α_i^o, $C_{p,i}^o$ are the isentropic compressibility, molar volume, isobaric thermal expansion coefficient, and molar isobaric heat capacity of pure component i, T represents temperature, ϕ_i is the volume fraction, and x_i represents the mole fraction of i in the mixture.

The density values have been used to calculate the excess volumes, V^E, using the following equation,

$$V^E = \frac{x_1 M_1 + x_2 M_2}{\rho} - \left(\frac{x_1 M_1}{\rho_1} + \frac{x_2 M_2}{\rho_2}\right), \qquad (4)$$

where ρ is the density of the mixture and x_1, M_1, and ρ_1 and x_2, M_2, and ρ_2 are the mole fraction, molar mass, and density of pure components 1 and 2, respectively.

The excess values of free length $\left(L_f^E\right)$, Gibbs free energy (ΔG^{*E}), and enthalpy (H^E) were calculated by using the expressions given in the literature [21, 29] as follows,

$$L_f^E = L_f - K_T\left(K_s^{id}\right)^{1/2}, \qquad (5)$$

where L_f represents the calculated value for the mixture and K_T represents a temperature dependent constant whose value is $K_T = (91.368 + 0.3565 \text{ T}) \times 10^{-8}$.

Excess Gibbs free energy of activation ΔG^{*E} was calculated as follows,

$$\Delta G^{*E} = RT\left[\ln\left(\frac{\eta V}{\eta_2 V_2}\right) - x_1 \ln\left(\frac{\eta_1 V_1}{\eta_2 V_2}\right)\right], \qquad (6)$$

where R represents gas constant, T is the absolute temperature, η is the viscosity of the mixture and η_1, η_2 are the viscosities of the pure compounds, V is the molar volume of mixture and V_1, V_2 are the molar volumes of the pure compounds,

Excess enthalpy H^E was calculated from usual relation.

$$H^E = H - (x_1 H_1 + x_2 H_2), \qquad (7)$$

where H represents the calculated value of enthalpy for the mixture and H_1, H_2 represent enthalpy of pure components 1 and 2, respectively

The excess values for the above parameters were fitted by the method of non-linear least-squares to a Redlich–Kister type polynomial [17].

$$Y^E = x_1(1 - x_1) \sum_{i=1}^{n} A_i(2x_1 - 1)^{i-1}, \tag{8}$$

where $Y^E = K_s^E, V^E, L_f^E, \Delta G^{*E}, H^E$. The values of coefficient A_i were determined by a regression analysis based on the least-squares method and are reported along with the corresponding standard deviations between the experimental and the calculated values of the respective functions in Table 4.

The standard deviation (σ) was calculated using the relation

$$\sigma(Y^E) = \left[\sum \left(Y_{obs}^E - Y_{cal}^E \right)^2 / (n - m) \right]^{1/2}, \tag{9}$$

where n represents the number of experimental points and m is the number of adjustable parameters.

Results and discussion

The experimental values of speed of sound, density, and viscosity in case of the binary liquid mixtures under study over the entire range of composition and at different temperatures, $T = (303.15, 308.15, 313.15, 318.15,$ and $323.15)$ K are given in Table 2. From this available data of speed of sound, density, and viscosity, the values of excess isentropic compressibility (K_s^E), excess molar volume (V^E), excess free length (L_f^E), excess Gibb's free energy (ΔG^{*E}), and excess enthalpy (H^E) were calculated. These excess parameters were plotted against mole fractions of methyl benzoate and ethyl benzoate separately over the entire mole fraction range and at different temperatures. The plots are shown in Figs. 1, 2, 3, 4 and 5. The excess parameters of isentropic compressibility (K_s^E), molar volume (V^E), free length (L_f^E), excess Gibb's free energy (ΔG^{*E}), and excess enthalpy (H^E) are fitted to the Redlich–Kister type polynomial equation and the coefficients A_i evaluated by the method of least-squares, along with standard deviation (σ) are given in Table 3.
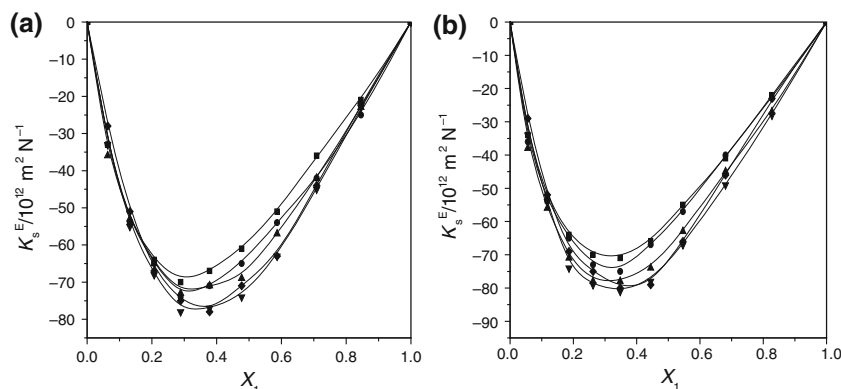
The deviations observed in the excess parameters indicate the strength of interactions present between the component molecules of the binary mixtures under study [30]. The variations in these excess parameter values reflect the interactions between the mixing species, depending upon the composition, molecular sizes, and shapes of the components and temperature. The effects which influence the values of excess thermodynamic functions may be the result of physical, chemical, and structural contributions such as:

(1) The chemical effects, like the breaking of molecular association present in the pure liquid which results in the positive values of V^E, K_s^E, L_f^E and negative ΔG^{*E}, on the other hand charge transfer forces, formation of hydrogen bonds, and other complex forming interactions result in the negative values of V^E, K_s^E, L_f^E and positive ΔG^{*E} [29].

(2) Physical contributions are from dispersion forces or weak dipole–dipole interactions causing the positive values of V^E, K_s^E, L_f^E and negativeΔG^{*E}.

(3) The structural contribution arising from the geometrical fitting of one component into the other because of the differences in the size and shape of the component molecules resulting in the negative values of V^E, K_s^E, L_f^E and positive ΔG^{*E}.

Figures 1a, b show the excess isentropic compressibility (K_s^E) for the binary liquid mixtures of methyl benzoate and ethyl benzoate with 2-propanol, respectively, over the entire mole fraction range and at different temperatures $T = (303.15, 308.15, 313.15, 318.15, 323.15)$ K. It is clear from Fig. 1a, b that the K_s^E values are negative over the entire mole fraction range for the systems under study and at investigated temperatures, this indicates the presence of strong interactions in these mixtures. As the temperature increases, it has been observed that the negative K_s^E values are found to increase in both the systems, and the changes in K_s^E values with respect to temperature are small in these mixtures. Also with the increase in temperature, the solute–

Fig. 1 Excess isentropic compressibility with respect to mole fraction at various temperatures for **a** methyl benzoate + 2-propanol, **b** ethyl benzoate + 2-propanol *filled square*, 303.15 K; *filled circle*, 308.15 K; *filled triangle*, 313.15 K; *inverted triangle*, 318.15 K; *filled rhombus*, 323.15 K
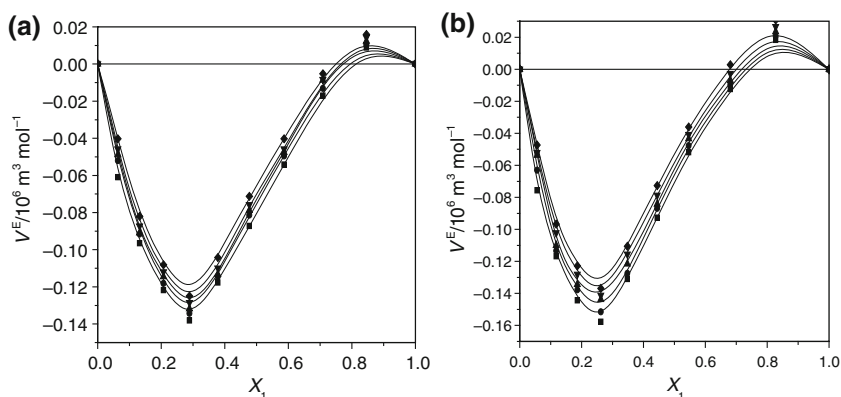
Fig. 2 Excess molar volume with respect to mole fraction at various temperatures for **a** methyl benzoate + 2-propanol, **b** ethyl benzoate + 2-propanol *filled square*, 303.15 K; *filled circle*, 308.15 K; *filled triangle*, 313.15 K; *inverted triangle*, 318.15 K; *filled rhombus*, 323.15 K
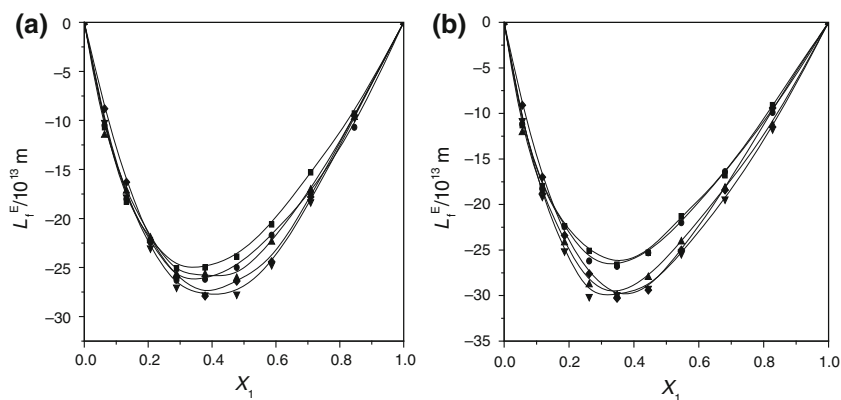
Fig. 3 Excess free length with respect to mole fraction at various temperatures for **a** methyl benzoate + 2-propanol, **b** ethyl benzoate + 2-propanol *filled square*, 303.15 K; *filled circle*, 308.15 K; *filled triangle*, 313.15 K; *inverted triangle*, 318.15 K; *filled rhombus*, 323.15 K

solvent interactions get weaker causing the excess values to decrease at higher temperature. The negative values of K_s^E are of the order (ethyl benzoate + 2-propanol) > (methyl benzoate + 2-propanol). The sign of excess isentropic compressibility plays a relevant role in assessing the compactness due to molecular interaction in liquid mixtures through charge transfer, dipole–dipole interactions, and dipole-induced dipole interactions interstitial accommodation, and orientational ordering leading to more compact structure making, which enhances excess isentropic compressibility to have negative values. Fort and Moore [31] suggested that the liquids having different molecular sizes and shapes mix well there by reducing the volume which causes the values of K_s^E to be negative. It also suggests that the liquids are less compressible when compared to their ideal mixtures signifying the chemical effects including charge transfer forces, formation of hydrogen bond, and other complex forming interactions. It can also be said that the molecular interactions are strong in these binary liquid mixtures and that the medium is highly packed. Similar results were obtained by earlier workers [32, 33].

The variation of excess molar volume (V^E), with respect to mole fraction, x_1, is given in Fig. 2a, b over the entire composition range and at different T = (303.15, 308.15, 313.15, 318.15, and 323.15) K. The strength of the intermolecular interactions in binary liquid mixtures can be explained using the sign and magnitude of the V^E values. The factors that are mainly responsible for the contraction of volume causing the V^E values to be negative are due to strong specific interactions like the association of component molecules through hydrogen bonds, due to dipole–dipole interactions, or it may be due to the induced dipole–dipole interactions, whereas the expansion of volumes leading to positive V^E values is due to breaking of one or both of the components in a solution, the geometry of molecular structure which does not allow the fitting of one component molecules into the voids created by the molecules of other component, and the steric hindrance of the molecules. In our present study, the V^E values are mostly negative in both the cases. So this kind of behavior of V^E can attributed to the formation of hydrogen bond, disruption of alcohol self-associations, and the structural characteristics like geometrical fitting of one component into the other as a result of the increase in difference of size and shape of the component molecules. As the temperature increases, it has been observed that, the negative values of V^E are found to decrease indicating the decrease of interactions between the unlike molecules. It is clear from Fig. 2a, b that the negative values of V^E are in the following order, (ethyl benzoate + 2-propanol) > (methyl benzoate + 2-propanol). The expansion in molar volume can be attributed to the presence of weak

intermolecular forces of attraction [34]. Similar results were reported by García et al. [35]. The negative values of V^E indicate that there is more compact packing of the molecules

which implies that the molecular interactions are strong, whereas the positive values indicate a loose packing of molecules in the binary mixture compared to those in the pure component. Similar results were observed by earlier workers [35, 36].

It can be observed from Fig. 3a, b that the L_f^E values have a negative trend similar to what we have observed in case of the K_s^E at all the temperatures under study. The negative values of L_f^E suggest that specific interactions are present between unlike molecules in these binary systems [37] and that the molecules may form multimers through hydrogen bonding between the hydroxyl group (–OH) of 2-propanol and –CH group of benzoates.

Figure 4a, b represent the excess Gibb's free energy of activation (ΔG^{*E}) with respect to mole fraction x_1, over the entire composition range and at T = (303.15, 308.15, 313.15, 318.51, and 323.15) K. It can be seen from Fig. 4a, b that the ΔG^{*E} values are positive at all temperatures and over the entire range of mole fraction. These positive values indicate the existence of strong intermolecular interaction through hydrogen bonding between the component molecules of the liquid mixtures under study. The maximum deviation is observed for (ethyl benzoate + 2-propanol) system indicating the strength of bond formation in this system is more compared to that of (methyl benzoate + 2-propanol) system. Similar results were observed by earlier workers [38].

From Fig. 5a, b it is clear that the excess values of enthalpy (H^E) are negative with respect to the mole fraction, x_1, over the entire composition range and at T = (303.15, 308.15, 313.15, 318.15, and 323.15) K. The negative values of H^E tend to decrease with increase in temperature, this insist the fact that there are strong specific interactions between unlike molecules in these liquid mixtures [39]. The negative H^E values also suggest the existence of inter molecular hydrogen bond and the breaking of associated structures in both cases.

The variations in these above excess parameters with mole fraction and temperature predict the presence of
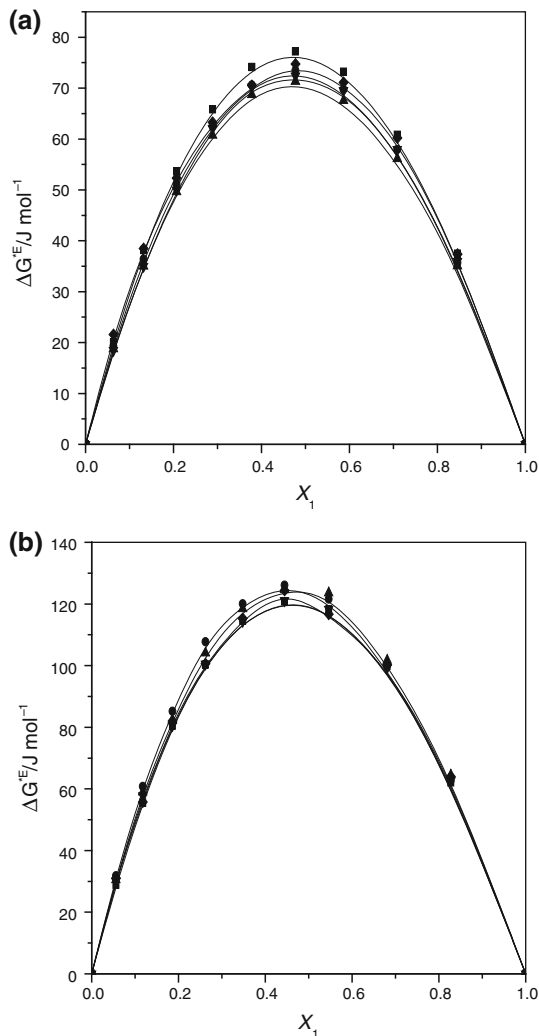
Fig. 4 Excess Gibb's free energy with respect to mole fraction at various temperatures for **a** methyl benzoate + 2-propanol, **b** ethyl benzoate + 2-propanol *filled square*, 303.15 K; *filled circle*, 308.15 K; *filled triangle*, 313.15 K; *inverted triangle*, 318.15 K; *filled rhombus*, 323.15 K

Fig. 5 Excess enthalpy with respect to mole fraction at various temperatures for **a** methyl benzoate + 2-propanol, **b** ethyl benzoate + 2-propanol *filled square*, 303.15 K; *filled circle*, 308.15 K; *filled triangle*, 313.15 K; *inverted triangle*, 318.15 K; *filled rhombus*, 323.15 K
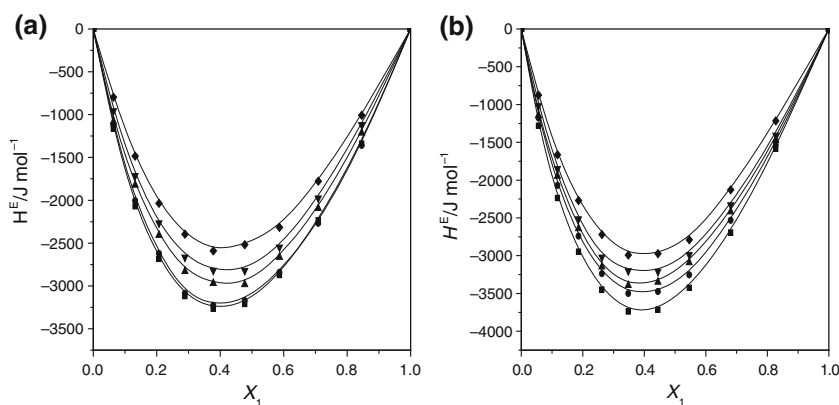
Table 3 Coefficients of Redlich–Kister equation A_i, and standard deviations σ, for excess isentropic compressibility (K_s^E), excess molar volumes (V^E), excess free length $\left(L_f^E\right)$, excess Gibb's free energy (ΔG^{*E}), and excess enthalpy (H^E) for the liquid mixtures at various temperatures

Properties	T/K	A_0	A_1	A_2	σ
Methyl benzoate + 2-propanol					
$K_s^E/10^{12}$ m^2 N^{-1}	303.15	−175.5	204.3	−227.9	0.30
	308.15	−247.6	189.4	−164.1	0.20
	313.15	−245.3	203.9	−181.8	0.37
	318.15	−279.1	203.5	−98.57	0.24
	323.15	−282.0	185.7	−44.28	0.28
$V^E/10^6$ m^3 mol^{-1}	303.15	−0.332	0.658	−0.119	0.04
	308.15	−0.330	0.630	−0.022	0.02
	313.15	−0.322	0.628	0.015	0.04
	318.15	−0.317	0.616	0.051	0.03
	323.15	−0.306	0.594	0.104	0.04
$L_f^E/10^{13}$ m	303.15	−90.54	58.14	−46.64	0.11
	308.15	−96.88	50.56	−43.26	0.06
	313.15	−95.26	55.17	−45.97	0.10
	318.15	−106.6	54.53	−17.00	0.34
	323.15	−106.5	48.77	−0.234	0.20
ΔG^{*E}/J mol^{-1}	303.15	307.4	−31.54	2.758	0.14
	308.15	292.2	−30.89	5.443	0.31
	313.15	283.3	−27.86	8.159	0.18
	318.15	291.2	−22.86	−1.053	0.12
	323.15	292.4	−31.26	44.79	0.09
H^E/J mol^{-1}	303.15	−12496	5253	−3092.0	0.81
	308.15	−12429	4790	−2870.0	0.67
	313.15	−11452	4632	−2736.0	0.90
	318.15	−10996	4299	−1480.0	0.99
	323.15	−10086	3638	−0299.9	0.57
Ethyl benzoate + 2-Propanol					
$K_s^E/10^{12}$ m^2 N^{-1}	303.15	−224.8	231.4	−232.6	0.35
	308.15	−231.4	232.5	−235.1	0.32
	313.15	−260.7	246.5	−244.4	0.16
	318.15	−286.0	241.9	−178.6	0.18
	323.15	−291.6	238.8	−61.03	0.18
$V^E/10^6$ m^3 mol^{-1}	303.15	−0.281	0.862	−0.412	0.04
	308.15	−0.288	0.828	−0.253	0.04
	313.15	−0.289	0.802	−0.138	0.02
	318.15	−0.271	0.790	−0.107	0.03
	323.15	−0.257	0.780	−0.043	0.03
$L_f^E/10^{13}$ m	303.15	−88.90	70.07	−62.27	0.08
	308.15	−90.58	68.98	−62.61	0.12
	313.15	−100.9	71.14	−63.13	0.30
	318.15	−109.0	68.58	−41.32	0.26
	323.15	−110.0	69.33	−1.023	0.30
ΔG^{*E}/J mol^{-1}	303.15	483.7	−71.78	−1.936	0.18
	308.15	498.4	−101.6	15.62	0.36
	313.15	497.8	−77.05	11.59	0.36
	318.15	480.3	−74.89	25.87	0.18
	323.15	482.6	−71.63	32.64	0.36

Table 3 continued

Properties	T/K	A_0	A_1	A_2	σ
H^E/J mol^{-1}	303.15	−14028	6795	−4376	0.97
	308.15	−13241	6032	−3917	0.85
	313.15	−12726	5868	−3709	0.77
	318.15	−12365	5385	−2466	1.02
	323.15	−11565	5067	−716.6	0.44

Table 4 Average percentage error (APE) and χ^2 fit values for speed of sound computed from different theoretical models

	U_{NOM}/m s^{-1}	U_{IMP}/m s^{-1}	U_{VDV}/m s^{-1}	U_{JM}/m s^{-1}	U_{FLT}/m s^{-1}	U_{R}/m s^{-1}
Methyl benzoate + 2-propanol						
T/K = 303.15						
APE	0.0000	0.6578	9.3196	1.1987	0.0000	−9.4502
χ^2	0.0000	0.7865	190.13	2.6600	0.0000	149.35
T/K = 308.15						
APE	0.0000	0.8254	9.3617	1.3595	0.0000	−9.5134
χ^2	0.0000	1.2178	189.54	3.3777	0.0000	149.03
T/K = 313.15						
APE	0.0000	0.6394	9.2011	1.2326	0.0000	−10.093
χ^2	0.0000	0.7261	179.70	2.7481	0.0000	163.36
T/K = 318.15						
APE	0.0000	0.7229	9.2042	1.3100	0.0000	−10.157
χ^2	0.0000	0.9910	178.72	3.2038	0.0000	162.41
T/K = 323.15						
APE	0.0000	0.5547	8.9484	1.1496	0.0000	−10.713
χ^2	0.0000	0.6197	166.63	2.5006	0.0000	176.72
Ethyl benzoate + 2-propanol						
T/K = 303.15						
APE	0.0000	1.7865	10.4969	1.6406	0.0000	−8.8963
χ^2	0.0000	5.9979	244.83	5.0363	0.0000	131.75
T/K = 308.15						
APE	0.0000	1.6826	10.4955	1.5761	0.0000	−9.1717
χ^2	0.0000	5.2330	241.64	4.5775	0.0000	137.80
T/K = 313.15						
APE	0.0000	1.7753	10.6267	1.7335	0.0000	−9.4863
χ^2	0.0000	5.7989	245.41	5.5209	0.0000	144.84
T/K = 318.15						
APE	0.0000	1.7654	10.5921	1.7356	0.0000	−9.6461
χ^2	0.0000	5.7431	241.45	5.5442	0.0000	147.12
T/K = 323.15						
APE	0.0000	1.4782	10.3961	1.4812	0.0000	−10.1097
χ^2 square	0.0000	4.2484	231.85	4.2601	0.0000	157.89

hydrogen bonding between the compounds in both the binary mixtures. The strength of bond formation between the compounds in ethyl benzoate + 2-propanol system is more than that in methyl benzoate + 2-propanol system, this is because of the increased chain length and larger effective radius of the rotating unit of pure ethyl benzoate when compared to that of pure methyl benzoate. Also, the excess parameters calculated in the present study correlate

Table 5 Various interaction parameters and the corresponding standard deviations ($\sigma/10^{-3}$ N s m^{-2}) computed from different models for viscosity

T/K	G_{12}	σ	H_{12}	σ	W_{vis}/RT	σ	Δ_{12}	σ	F_{12}	σ	T_{12}	σ
Methyl benzoate + 2-propanol												
303.15	0.0034	0.0001	0.0017	0.6670	0.2153	0.0067	0.3527	0.0124	1.6646	0.0001	1.7139	0.0001
308.15	0.0021	0.0001	0.0015	0.6002	0.2095	0.0060	0.3494	0.0112	1.4978	0.0001	1.5433	0.0001
313.15	0.0019	0.0001	0.0013	0.5393	0.2061	0.0053	0.3512	0.0101	1.3463	0.0001	1.3812	0.0001
318.15	0.0052	0.0003	0.0012	0.4944	0.2078	0.0047	0.3545	0.0091	1.2346	0.0003	1.2594	0.0003
323.15	0.0153	0.0007	0.0011	0.4586	0.2141	0.0049	0.3646	0.0090	1.1486	0.0007	1.1608	0.0006
Ethyl benzoate + 2-propanol												
303.15	0.0012	0.0006	0.0017	0.6744	0.1983	0.0038	0.4454	0.0179	1.6999	0.0006	1.7697	0.0015
308.15	0.0126	0.0036	0.0016	0.6151	0.2089	0.0052	0.4592	0.0180	1.5526	0.0013	1.6126	0.0013
313.15	0.0167	0.0005	0.0014	0.5519	0.2060	0.0035	0.4633	0.0152	1.3927	0.0005	1.4402	0.0015
318.15	0.0133	0.0003	0.0013	0.5015	0.2005	0.0032	0.4599	0.0140	1.2670	0.0003	1.3027	0.0009
323.15	0.0173	0.0007	0.0012	0.4603	0.2020	0.0030	0.4639	0.0129	1.1648	0.0007	1.1881	0.0006

T, temperature; various interactions parameters: G_{12}, Grunberg and Nissan; H_{12}, Hind, Mc Laughlin and Ubbelohde; W_{vis}/RT, Katti and Chaudari; Δ_{12}, Heric and Brewer; F_{12}, Frenkel; T_{12}, Tamura and Kurata

with one another and at the same time each parameter supports the formation of hydrogen bonding in these binary liquid mixtures.

In the present study, theoretical speed of sound values has been evaluated in the binary mixtures considering methyl/ethyl benzoate as one component and 2-propanol as the other component at all investigated temperatures. This kind of evaluation of theoretical speed of sound values proves to be useful to verify the applicability of various postulates of these theories of liquid mixtures and to arrive at some useful inferences regarding the strength of molecular interactions between component liquids in some cases. The theories due to Nomoto (U_{NOM}) [40], Impedance relation (U_{IMP}) [41], Van Dael and Vangeel (U_{VDV}) [42], Junjie's (U_{JM}) [43, 44], free length theory (U_{FLT}) [45], and Rao's (U_R) [46] are employed and the Average percentage error along with the χ^2 fit values described elsewhere [4] for the binary mixture and at all investigated temperatures are compiled in Table 4. The average percentage error values are small. On comparison, the Nomoto's relation and free length theory relation are found to give some valuable estimate of the experimental values of speed of sound values in these binary mixtures at all the temperatures.

The dynamic viscosities of the liquid mixtures have been correlated with composition using several empirical relations due to Grunberg–Nissan [47], Hind et al. [48], Katti and Chaudari [49], Heric and Brewer [50], Frenkel [51], and Tamura and Kurata [52]. The experimental and theoretical values of viscosity with their corresponding interaction terms and standard deviation values for the liquid mixtures at T = (303.15, 308.15, 313.15, 318.15,

and 323.15) K are compiled in Table 5. All the empirical models gave a reasonable fit, but there is good agreement between the theoretical and experimental values in case of (ethyl benzoate + 1-propanol) + benzene mixture. The estimated standard deviations are smaller in all cases indicating that the present mixture viscosities are well-correlated by these viscosity models.

Further, the hydrogen bond between the component systems has also been confirmed from the FT-IR [53]. The shifts observed are caused by the strong interaction between the high electro-negative charge of oxygen in 2-propanol and hydrogen of the benzoates.

Conclusions

The excess parameters like K_s^E, V^E, L_f^E, ΔG^{*E}, and H^E were calculated from the experimentally determined speed of sound, density, and viscosity values. The formation of hydrogen bond between the mixtures is identified by studying the variations in these parameters. The values of excess isentropic compressibility, excess free length, and excess enthalpy are found to be negative, excess Gibb's free energy of activation is positive over the entire range of composition at all temperatures for the liquid mixture systems considered in the present study. The excess molar volume values changed from negative to positive for the binary systems over the entire range of composition and at all the temperatures considered in the present study. This is a clear indication for the presence of hydrogen bonding between the component molecules. The difference in molar masses of the liquid molecules is also responsible for the

existing specific interactions between the molecules of the component liquids. Besides, the computed speed of sound values from different theories has been correlated with the experimentally measured values. Speed of sound values obtained from Nomoto's and free length theory relations is in good agreement with the experimental values. The experimental viscosity values are compared with the viscosity values obtained from different empirical relations and these are in good agreement with the experimental values.

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