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Thermophysical properties of binary blends of cyclohexane with some esters

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Abstract: From the densities (ρ) and viscosities (η) measured for three binary blends consisting of methyl acetate (MA), ethyl acetate (EA) and methyl salicylate (MS) over the entire composition range with cyclohexane (CH) at 298.15–318.15 K under atmospheric pressure, the excess molar volumes (V_m^E) and excess viscosities (η^E) were derived. In addition, the excess isentropic compressibilities (κ_s^E) excess intermolecular free lengths (L_f^E) and excess molar refractions (R_m^E) were derived from measured ultrasonic speeds of sound (u) and refractive indices (n_D) for the binary blends at 298.15 K. Various derived properties are discussed in terms of molecular interactions and structural effects. Partial molar volumes ($\bar{V}_{m,1}^0$ and $\bar{V}_{m,2}^0$) and excess partial molar volumes ($\bar{V}_{m,1}^{0,E}$ and $\bar{V}_{m,2}^{0,E}$) at infinite dilution are also discussed in terms of volume changes in the blends. Furthermore, the excess molar volumes (V_m^E) and viscosities (η) of the blends were correlated with the Prigogine–Flory–Paterson (PFP) theory and the Peng–Robinson Equation of State (PR-EOS).

Keywords: excess properties; cyclohexane, esters; Prigogine–Flory–Patterson theory; Peng–Robinson equation of state.

INTRODUCTION

Instead of a single pure solvent, solvent mixtures containing two or more solvents provide a range of mixtures with compositions that can be optimized for specific chemical engineering purposes, such as chemical separation, heat transfer, mass transfer, fluid flow, *etc*. Thus, knowledge of the physico-chemical properties of such liquid blends is a pre-requisite for many purposes and systematic studies on the thermodynamic and transport properties of binary liquid blends to help in the understanding intermolecular interactions and structural properties of liquid blends. Thus, the determination of density, viscosity and speed of sound, *etc.* are valuable tools for studying the liquid state[1] because local struc-

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ture and macroscopic properties of liquids/liquid blends are determined by the interactions operative amongst the molecules.[2] Excess molar volumes (V_m^E), excess viscosities (η^E), excess isentropic compressibility (κ_S^E), *etc.* help in the understanding of molecular interactions and the development of theoretical models for their description and simulation.[3,4]

Cyclohexane (CH) is a non-polar, unassociated, inert hydrocarbon with a globular structure.[5] It is used as a raw material for the industrial production of two important intermediates (*viz.*, adipic acid and caprolactam) used in the production of nylon. Esters exist as dipolar associates in their pure state.[6] Both the aliphatic esters methyl acetate (MA) and ethyl acetate (EA) are commonly used as solvents in glues, nail polish remover, *etc*. Ethyl acetate (EA) is used to decaffeinate coffee beans and tea leaves. Methyl salicylate (MS) is a phenolic ester having strong intramolecular hydrogen bonds between its hydroxyl and carbonyl group[7] and is used for the relief of muscle aches and pains when applied externally to the affected area.

Hence, from the industrial point of view, extensive information on various physico-chemical properties of binary blends consisting of cyclohexane (CH) with the esters MA, EA and MS as a function of composition, temperature and pressure is greatly needed. The present work is an attempt to explore the nature of the molecular interactions in the blends CH + MA, CH + EA and CH + MS at 298.15, 308.15 and 318.15 K under ambient pressure in terms of various excess properties. Although Rathnam *et al.*[8] studied the binary blend of CH + EA in terms of excess viscosities at 313.15 K and Roy *et al.*[9] studied binary and ternary blends of CH with MA and EA at 298.15 K only, to the best of our knowledge no comparable literature data for the studied blends are available and treated in terms of the Prigogine–Flory–Paterson (PFP) theory,[10,11] the Bloomfield–Dewan viscosity model[12] or the Peng–Robinson equation of state (PR-EOS).[13] Moreover, various derived parameters were calculated using ultrasonic speeds of sound (u) and refractive indices (n_D) and are reported and discussed accordingly.

EXPERIMENTAL

Chemicals

All the chemicals used in this work were purchased from Sigma–Aldrich (Reagent Plus, purity > 99 %) and used as received from the vendor. The purity of the solvents was ascertained by GLC and by comparing their densities and viscosities at the experimental temperatures with available literature data[14-25] (given in Table S-I of the Supplementary material to this paper).

Methods

The binary blends were prepared by mass in specially designed stoppered air-tight bottles inside a dry box at 298.15 K. Actually, for each binary system, a set of nine binary blends were prepared afresh before use with mole fractions varying from 0.1 to 0.9. The uncertainty in the mole fraction was evaluated to be ±0.0002.[26] Mass measurements were performed with a digital analytical balance (Mettler, AG285, Switzerland) with an accuracy of ±0.01 mg. The densities (ρ) were measured with a vibrating-tube density meter (Anton Paar, DMA 4500M) calibrated at the experimental temperatures with doubly distilled, degassed water and dry air under atmospheric pressure. The stated repeatability and accuracy of the densities were $\pm 1\times 10^{-5}$ g cm^{-3} and $\pm 5\times 10^{-5}$ g cm^{-3}, respectively. However, the uncertainty in the densities was found to be within $\pm 2\times 10^{-5}$ g cm^{-3}. The viscosities (η) were measured by means of a suspended Canon-type Ubbelhode viscometer, thoroughly cleaned and dried, placed vertically in a glass-sided thermostated bath maintained at ±0.01 K of the desired temperature and calibrated with triply distilled water and purified methanol[27-29] at the experimental temperatures. After attainment of thermal equilibrium, the efflux times of flow of the liquids/blends were recorded with a digital stopwatch correct to ±0.01 s in triplicate with adequate precautions to avoid evaporation losses, and the average of triplicate measurements was taken into account. The uncertainty in the viscosities was found to be within ±0.003 mPa s.[26] The ultrasonic speeds of sound (u) were measured by a single crystal variable-path ultrasonic interferometer (Mittal Enterprise, F-05, New Delhi, India) working at 2 MHz. It was calibrated with triply distilled, degassed water and methanol maintained at 298.15 K by circulating thermostated water around a jacketed cell (2 MHz) filled with the experimental liquids. The uncertainty of the ultrasonic speeds was around ±0.2 m s^{-1}.[26] Refractive indices were measured with an Abbe refractometer, calibrated with triply distilled, degassed water and purified methanol maintained at 298.15 K. The estimated uncertainty in the refractive indices was ±0.0002.[30]

RESULTS AND DISCUSSION

The experimental densities (ρ), viscosities (η), excess molar volumes (V_m^E) and excess viscosities (η^E) of the binary blends of CH + MA, CH + EA and CH + + MS at 298.15, 308.15 and 318.15 K under ambient pressure are listed in Table S-II of the Supplementary material.

Excess molar volumes

Excess molar volumes (V_m^E) can be obtained from the equation:

$$V_\mathrm{m}^\mathrm{E} = \sum_{i=1}^{2} x_i M_i (1/\rho - 1/\rho_i) \tag{1}$$

where ρ is the density of the blend and x_i, M_i and ρ_i are the mole fraction, molar mass and density of the i^th component in the mixture, respectively. The estimated uncertainty in the excess molar volumes (V_m^E) was evaluated to be ±0.006 cm^3 mol^{-1}. The V_m^E *versus* x_i curves for the blends at 298.15 K are shown in Fig. 1. They illustrate that the excess molar volumes (V_m^E) for the blend (CH + MS) showed a slight sigmoid variation with positive V_m^E values at lower mole fractions of CH ($x_1 \leq 0.2294$) but the V_m^E values become negative at CH rich regions ($x_1 \geq 0.2294$); however, the V_m^E values for the blends (CH + MA) and (CH + EA) were positive over the entire composition range at all the experimental temperatures.

The excess molar volumes (V_m^E) may be discussed in terms of several effects: physical, chemical and geometrical contributions. The physical interactions result in volume expansion and involve mainly dispersion forces as well as non-specific interactions and thus contribute to positive V_m^E values. The chemical or specific interactions result in volume contraction and may involve hydrogen bond formation, charge transfer type forces and other complex forming interactions between dissimilar species in the blends and thus contribute to negative V_m^E values. Negative V_m^E values may also arise from a variation of the degree of molecular packing, *i.e.*, interstitial accommodation of one component into the structure of the other. This accommodation depends on the difference in free volume and molar volume of the components involved.

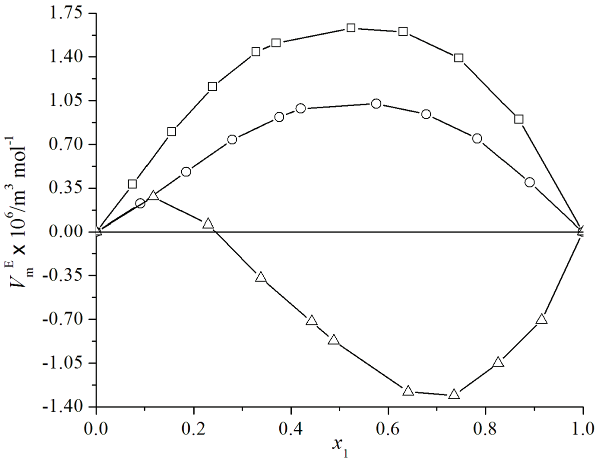

Fig. 1. Excess molar volume (V_m^E) *vs*. mole fraction of CH (x_1) for the binary blends of CH + some esters at T = 298.15 K. The graphical points represent excess molar volumes (V_m^E): □, MA; ○, EA; Δ, MS.

Esters can exist as dipolar associates and an approximate estimate of the nature and the strength of molecular interactions between similar ester molecules can be guessed from knowledge of their dipole moments (μ_D). The dipole moment of different components[31] used in this work increases in the following order (μB): $\mu_{D,CH}$ (0.00) < $\mu_{D,MA}$ (1.72) < $\mu_{D,EA}$ (1.78) < $\mu_{D,MS}$ (2.47). Thus the expected order of molecular interactions (based on dipole-induced dipole interactions) between the unlike components of the binary blends is (CH + MS) > (CH + EA) > (CH + MA). Representative plots of V_m^E *versus* x_1 at 298.15 K reveals that the intermolecular interactions amongst the unlike components is truly highest for the blend (CH + MS) and lowest for the blend (CH + MA). The observed positive V_m^E values for the blends (CH + MA) and (CH + EA) over the entire composition range suggest the dominating role of dispersion interactions between the dissimilar components in these blends. Dispersion interaction may arise from breaking of dipole–dipole cohesive forces present between similar molecules (ester–ester) on addition of CH to the studied esters. However, for the blends (CH + MS), the negative V_m^E values suggest that the interactions between dissimilar molecules are greater than those between similar molecules (ester––ester), probably due to strong dipole-induced dipole interactions.

This order of molecular interactions for the binary blends is actually the overall state of the combined effects of several factors, such as the molecular size, shape and nature of the components, *etc*. CH is a ring structured globular molecule and can exist either in the chair form or a twisted boat form or in a skew-boat form.[32] A spectroscopic study by Garcia and Redondo[33] showed that the stable conformer of CH is the chair form with D_{3d} symmetry and CH rotates freely between chair and boat conformations at high temperature (even just greater than room temperature)[34] and occupies a small space with its flexible ring structure.[35] MS molecules are almost planer in shape due to favorable intra-molecular hydrogen bonding rather than inter-molecular hydrogen bonding, because intra-molecular hydrogen bonding requires the –OH group to be out of plane and interaction between neighboring MS molecules originate predominantly from dipolar interactions; the intra-molecular hydrogen bonding in liquid MS persists even at higher temperatures.[7] Again the order of molar volumes: MS > EA > MA suggests that the inter-molecular spacing or vacancies in EA is larger than that in MA. Alkyl esters exist as dipolar associates and are hydrogen bond acceptors. The addition of the CH (component 1) breaks the inter-molecular association (dipole–dipole interaction in the case of MA and EA) in the structure of the pure component (2) making enough space available for mutual fitting. Therefore, the molecular packing in the CH + EA system is more compact than that of the CH + MA system, that is why the excess molar volumes (V_m^E) of the blend CH + MA are greater than those of the blend CH + EA. In case of the blend CH + MS the initial positive V_m^E values could be attributed to the breaking up of the three dimensional hydrogen bonded (inter-molecular and intra-molecular) network or dipolar interactions in liquid MS due to the addition of CH and beyond the mole fraction of CH ($x_1 \geq 0.2294$), as the amount of CH increases further in the blend, the CH molecules are interstitially accommodated or geometrically fitted in the free space between the voids of planar MS molecules ($V_{m,MS} - V_{m,CH}$ = 20.26 cm^3 mol^{-1} at 298.15 K). This effect increases the intermolecular compactness, thereby imparting negative contributions to the solution volume and compressibility of the blend CH + MS. Thus, the order of molecular interactions based on excess molar volumes (V_m^E) is CH + MA < CH + EA < CH + MS. Nevertheless, it was observed that the V_m^E values increased with increasing experimental temperature for all the blends over the entire composition range. Such a trend in temperature dependence of the V_m^E values suggests that temperature enhancement disrupts the developing specific and non-specific interactions between the component molecules in the blends due to thermal agitations at elevated temperatures.

Partial molar volumes ($\bar{V}_{\mathrm{m},i}$) of the i^{th} component in the binaries at 298.15 K were obtained from the relation:[36,37]

$$\bar{V}_{\mathrm{m},i} = V^{\mathrm{E}}_{\mathrm{m},i} + V^{*}_{\mathrm{m},i} + (1 - x_i)(\mathrm{d}V^{\mathrm{E}}_{\mathrm{m},i} / \mathrm{d}x_i)_{T,p} \tag{2}$$

where $V^{*}_{\mathrm{m},i}$ is the molar volume of the i^{th} component in the binaries. The derivatives, $(\mathrm{d}V^{\mathrm{E}}_{\mathrm{m},i}/\mathrm{d}x_i)_{T,p}$ used in Eq. (2) were obtained following an earlier described procedure.[37] For this purpose, the $V^{\mathrm{E}}_{\mathrm{m}}$ values were fitted to the Redlich–Kister polynomial[38] by the method of least squares regression using the Marquardt algorithm[39] to derive the following Redlich–Kister coefficients (a_i): $a_0 = 6.5322$, $a_1 = 0.6065$, $a_2 = 2.0832$, $a_3 = 1.2945$, $a_4 = -2.5250$ for the blend CH + MA; $a_0 = 4.1742$, $a_1 = 0.8079$, $a_2 = -1.0677$ for the blend CH + EA and $a_0 = -3.7627$, $a_1 = -6.3862$, $a_2 = 1.4985$ $a_3 = -1.3304$ for the blend CH + MS with standard deviations (σ) of 0.006, 0.011 and 0.029[40] for the three binaries, respectively. The number of these coefficients during regression was determined following Marquadrat algorithm.[39] The partial molar volumes ($\bar{V}^{0}_{\mathrm{m},1}$ and $\bar{V}^{0}_{\mathrm{m},2}$) at infinite dilution, the excess partial molar volumes ($\bar{V}^{\mathrm{E}}_{\mathrm{m},i}$) and the excess partial molar volumes ($\bar{V}^{0,\mathrm{E}}_{\mathrm{m},i}$) at infinite dilution were obtained from the standard relations as described earlier.[36,37] The partial molar volumes ($\bar{V}^{0}_{\mathrm{m},1}$ and $\bar{V}^{0}_{\mathrm{m},2}$) and excess partial molar volumes ($\bar{V}^{0,\mathrm{E}}_{\mathrm{m},i}$) at infinite dilution for each component in the binary blends are listed in Table S-III of the Supplementary material.

The excess partial molar volumes ($\bar{V}^{\mathrm{E}}_{\mathrm{m},1}$ and $\bar{V}^{\mathrm{E}}_{\mathrm{m},2}$) of each component in the binary blends are depicted in Fig. 2 against the mole fraction of CH (x_1). Figure 2 shows that the $\bar{V}^{\mathrm{E}}_{\mathrm{m},1}$ values gradually decreased (*i.e.*, a decreasing trend as the alkyl chain length increased[9]) but the $\bar{V}^{\mathrm{E}}_{\mathrm{m},2}$ values increased with increasing mole fraction of CH (x_1) for the studied blends. The partial molar volumes ($\bar{V}^{0}_{\mathrm{m},1}$ and $\bar{V}^{0}_{\mathrm{m},2}$) at infinite dilution of each liquid were found to be greater than the molar volume of the respective pure liquid for the studied blends, except for the blend CH + MS. Again, the excess partial molar volumes ($\bar{V}^{0,\mathrm{E}}_{\mathrm{m},1}$ and $\bar{V}^{0,\mathrm{E}}_{\mathrm{m},2}$) at infinite dilution were found to be positive for both components in the blends CH + MA and CH + EA but for the blend CH + MS, $\bar{V}^{0}_{\mathrm{m},2}$ was found to be negative. That is, while the blends CH + MA and CH + EA are characterized by volume expansion, the blend CH + MS is characterized by volume contraction on mutual mixing with CH, *i.e.*, the blend CH + MS is characterized by a better packing efficiency,[41] most probably due to combined effects of dipole-induced dipole interactions and interstitial accommodation.

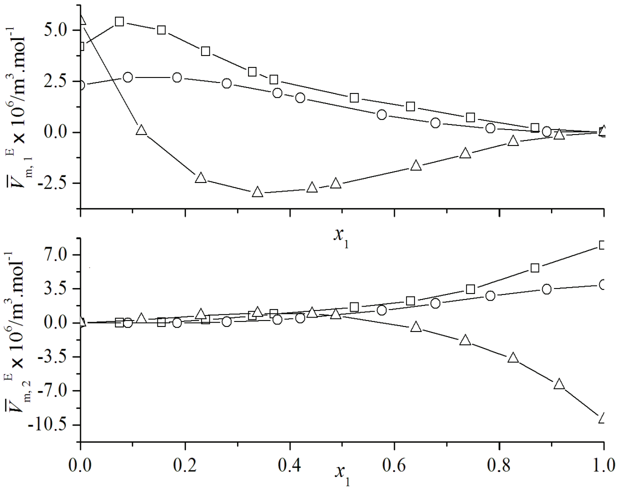

Fig. 2. Excess partial molar volume ($\overline{V}_{m,i}^{E}$) for the i^{th} component against mole fraction of CH (x_1) for the binary blends of CH + some esters at $T = 298.15$ K. The graphical points represent the $\overline{V}_{m,i}^{E}$ values: □, MA; ○, MA; Δ, MS.

Excess viscosities

The excess viscosity (η^E) can be obtained from the difference between the measured viscosity (η) and the ideal viscosity (η_{id}) of a solution as follows:[30,40]

$$\eta^E = \eta - \eta_{id} \tag{3}$$

and the ideal viscosity (η_{id}) is given by:[42]

$$\eta_{id} = \exp(\sum_{i=1}^{2} x_i \ln \eta_{id}) \tag{4}$$

The uncertainty in excess viscosities (η^E) was estimated to be within ±0.004 mPa s. Figure 3 shows that the η^E values are negative for the blends CH + MA and CH + EA, but for the blend CH + MS, the η^E values are positive (initially negative at MS rich regions with $x_1 \leq 0.229$) over the whole composition range.

Similar trends in the η^E values were observed at the other experimental temperatures. The negative η^E values suggest easier flow of the liquid blend as compared to the pure liquids. This may be due to differences in the size and shape of the mixing components, dispersion due to breaking of the liquid order on mixing with a second component and the presence of unfavorable non-specific interactions amongst the unlike molecules. However, positive η^E values suggest the presence of specific intermolecular interactions amongst the unlike molecules, resulting into more compact structure. Thus, the η^E values for the studied blends suggest the same order of molecular interactions: CH + MS > CH + EA > CH + + MA, as discussed earlier based on the excess molar volumes (V_m^E). Moreover, the decrease in η^{E} values as the experimental temperature increases for each blend suggests that the interactions between the unlike molecule become weaker at higher temperatures (Table S-II).

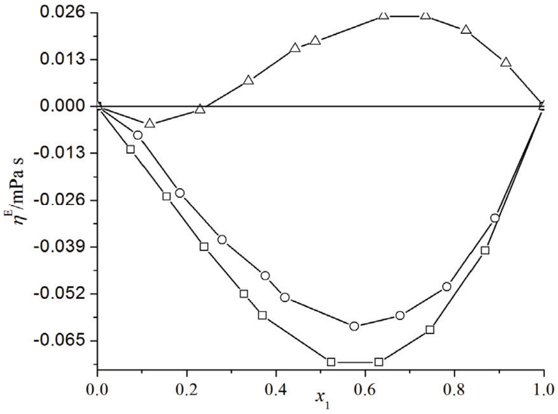

Fig. 3. Excess viscosities (η^{E}) *vs.* mole fraction of CH (x_1) for the binary blends of CH + some esters at T = 298.15 K. The graphical points represent the η^{E} values: □, MA; ○, EA; Δ, MS.

Based on the theory of absolute reaction rates, the free energy of activation of viscous flow (ΔG^*) and its excess function ($\Delta G^{*\mathrm{E}}$) for the liquid blends can be obtained using the Eyring viscosity relation:[42]

$$\eta = (hN / V)\exp(\Delta G^* / RT) \tag{5}$$

$$\Delta G^{*\mathrm{E}} = \Delta G^* - \sum_{i=1}^{2} \Delta G_i^{*\mathrm{E}} \tag{6}$$

where N, h and ΔG^* are Avogadro's number, Planck's constant and free energy of activation of viscous flow required to move the fluid particles from the ground state to the activated state. Other symbols have their usual meanings. Rearranging Eq. (5) and substituting $\Delta G^* = \Delta H^* - T\Delta S^*$, one obtains the relation:

$$R\ln(\eta V / hN) = \Delta H^* / T - \Delta S^* \tag{7}$$

Thus, the linear regression of $R\ln(\eta V/hN)$ against ($1/T$) gives the changes of enthalpy (ΔH^*) and entropy (ΔS^*) of activation for viscous flow from the corresponding slope and negative intercept, respectively. The values of ΔG^*, ΔH^*, ΔS^* and the regression coefficients (R^2) are given in Table S-IV of the Supplementary material. It could be seen that while the ΔH^* values are positive, the ΔS^* values are mostly negative for the binary blends CH + EA and CH + MS, but are mostly positive for the blend CH + MA. Such trends in the ΔH^* and ΔS^* values indicate that the formation of a transition state for viscous flow is accompanied by disruption of the developing forces or specific interactions between the components of the liquid blends. The ΔG^{*E} values are plotted in Fig. 4 against the mole fraction of CH (x_1) at 298.15 K. Interestingly, the ΔG^{*E} and η^E values follow similar trends against the mole fraction of CH (x_1). Reid and Taylor[43] suggested that positive ΔG^{*E} values stand for molecular interactions or compactness due to geometrical fittings of one component into the other on mixing and negative ΔG^{*E} indicate the dominance of dispersion forces leading to easier flow of the liquid blend as compared with the pure liquids. From Fig. 4, it is evident that the ΔG^{*E} values are negative for the blends CH + MA and CH + EA but positive for the blend CH + MS over the whole composition range (similar trends in ΔG^{*E} *versus* x_1 were found at the other experimental temperatures). These facts suggest the breaking of liquid order on mutual mixing and presence of unfavorable non-specific interactions between the unlike molecules.

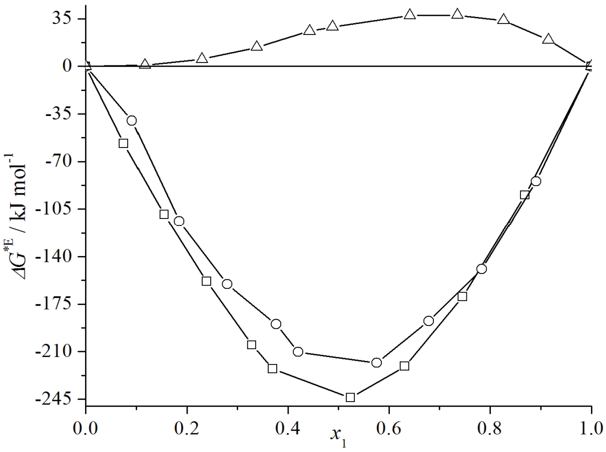

Fig. 4. The change of excess free energy of activation of viscous flow (ΔG^{*E}) *vs.* mole fraction of CH (x_1) for the binary blends of CH + some esters at T = 298.15 K. The graphical points represent values: □, MA; ○, EA; Δ, MS.

Ultrasonic speed of sound and derived acoustic functions

In order to explore the nature of the molecular interactions, the measured speeds of sound (u) and solution densities (ρ) at 298.15 K were used to determine the isentropic compressibility (κ_S) and the intermolecular free length (L_f) along with their excess functions. The excess isentropic compressibilities (κ_S^E) were obtained from the relation:

$$\kappa_S^E = \kappa_S - \kappa_S^{id} \tag{8}$$

where $\kappa_S = 1/\rho u^2$ and κ_S^{id} is the isentropic compressibility for an ideal mixture. According to Benson-Kiyohara[44] and Acree,[45] κ_S^{id} is given by the relation:

$$\kappa_{\mathrm{s}}^{\mathrm{id}} = \sum_{i=1}^{2} \tau_i \left[\kappa_{\mathrm{s},i} + \frac{T V_{\mathrm{m},i}^{*} \alpha_i^{2}}{C_{\mathrm{P},i}} \right] - \left\{ \frac{T \sum_{i=1}^{2} (x_{\mathrm{i}} V_{\mathrm{m},i}^{*}) \sum_{i=1}^{2} (\tau_i \alpha_i)^2}{\sum_{i=1}^{2} (x_i C_{\mathrm{P},i})} \right\} \tag{9}$$

where τ_i is the volume fraction of the i^{th} component in the mixture and $\kappa_{\mathrm{s},i}$, $V_{\mathrm{m},i}^{*}$, α_i and $C_{\mathrm{P},i}$ are the isentropic compressibility, the molar volume, the expansion coefficient and the molar isobaric heat capacity of the pure components, respectively. The expansion coefficients (α_i) were obtained from experimental density values and $C_{\mathrm{P},i}$ values were taken from the literature.[31] The intermolecular free lengths (L_{f}), excess intermolecular free lengths ($L_{\mathrm{f}}^{\mathrm{E}}$), free volumes ($V_{\mathrm{f}}$) and excess free volumes ($V_{\mathrm{f}}^{\mathrm{E}}$) were calculated using the standard relations.[46] Various acoustic parameters and their excess functions at 298.15 K are listed in Table S-V of the Supplementary material. The experimental speeds of sound for each pure liquid were in good agreement with the literature values[23,25,47,48] at 298.15 K. The variation of the excess isentropic compressibility ($\kappa_{\mathrm{s}}^{\mathrm{E}}$) of the blends with the mole fraction of CH (x_1) at 298.15 K is illustrated in Fig. 5, it could be seen that the $\kappa_{\mathrm{s}}^{\mathrm{E}}$ values for the blends CH + MA and CH + EA are positive but mostly negative for the blend CH + MS over the entire composition range. The positive $\kappa_{\mathrm{s}}^{\mathrm{E}}$ values for the blends CH + MA and CH + EA reveal that the component molecules in the blends become more compressible or less compact than in their pure state. This suggests disruption of the dipolar associated structure or molecular order present in the pure liquids (alkyl acetates), *i.e.*, the dipole–dipole

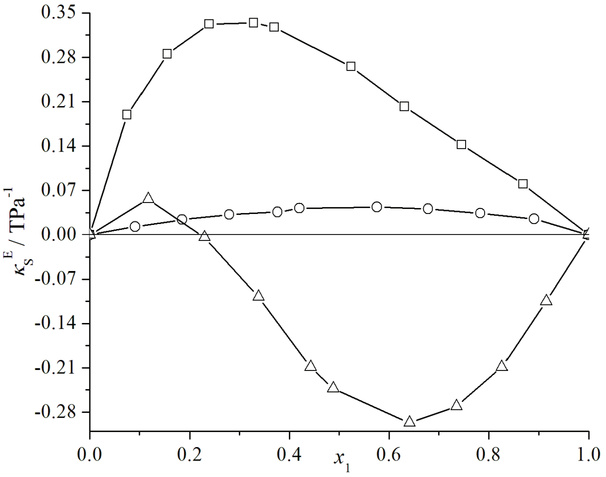

Fig. 5. Excess isentropic compressibility ($\kappa_{\mathrm{s}}^{\mathrm{E}}$) *vs.* mole fraction of CH (x_1) for the binary blends of CH + some esters at T = 298.15 K. The graphical points represents the values: □, MA; ○, EA; Δ, MS.

cohesive forces present amongst the individual MA and EA molecules (in the pure state) break up on mixing with CH. For the blend CH + MS, the initial positive κ_s^E value at $x_1 = 0.1168$ probably arises from the sudden perturbation of the three dimensional hydrogen bonded (intermolecular and intramolecular) network in liquid MS on addition of CH; however, the negative κ_s^E values over moderate to CH-rich regions are most probably associated with favorable mutual (geometrical) fitting of the CH and MS molecules through interstitial accommodation, as well as dipole-induced dipole interactions caused by the dipoles of MS.

According to Eyring and Kincaid,[49] isentropic compressibility (κ_s) and intermolecular free length (L_f) inversely vary with the speeds of sound (u). It was observed that the speeds of sound (u) increased with increasing mole fraction of CH (x_1) for the blends CH + MA and CH + EA but decreased for the blend CH + + MS; such an increase in the speeds of sound (u) led to a decrease in isentropic compressibility (κ_s) and intermolecular free lengths (L_f). However, for the blend CH + MS, as the speeds of sound (u) decreased with increasing mole fraction of CH (x_1), the isentropic compressibility (κ_s) and intermolecular free length (L_f) increased monotonously. The positive excess intermolecular free lengths (L_f^E) for the blends CH + MA and CH + EA suggest their less compact structure as compared to the blend CH + MS with a more compact structure and negative L_f^E values. Interestingly, it was observed that the free volumes (V_f) and excess free volumes (V_f^E) for the studied blends followed the order: CH + MA > CH + EA > CH + MS, *i.e.*, the reversed order of molecular interactions in parallel to the degree of their structural compactness. Thus, the study of the various acoustic and their excess functions also stand in support of the order of molecular interactions: CH + MS > CH + EA > CH + MA, as found earlier based on excess molar volumes and excess viscosities.

Excess molar refractions

The excess molar refractions (R_m^E) for the blends were obtained from the relation:[50]

$$R_m^E = R_m - \sum_{i=1}^{2} x_i R_{m,i} \tag{10}$$

where $R_{m,i} = \{(n_{D,i}-1)/(n_{D,i}+2)\}M_i/\rho_i$, $n_{D,i}$ and ρ_i stand for the molar refraction, refractive index and density of the i^{th} component in the blend, respectively. The molar refractions (R_m) for a blend can be obtained from the relation:[50]

$$R_m = \frac{n_D^2 - 1}{n_D^2 + 2}\,\frac{\sum_{i=1}^{2} x_i M_i}{\rho} \tag{11}$$

where ρ and n_D are the mixture density and refractive index, respectively, M_i is the molar mass of the i^{th} component in a blend. The excess molar refractions (R_m^E) and the experimental refractive indices (n_D) for the three binaries are listed in Table S-IV of the Supplementary material. The experimental refractive indices (n_D) of the pure liquids were in good agreement with literature values[20,24,48] at 298.15 K. The dependence of the excess refractive indices (R_m^E) on the mole fraction of CH (x_1) at 298.15 K also gives the same order of molecular interactions for the studied binaries as discussed above. Furthermore, the refractive indices of the blends were predicted by several models, *i.e.*, the Lorentz–Lorenz (LL), Gladstone–Dale (GD), Arago–Biot (AB), Newton (NEW), Eykman (EYK), Eyring–John (EJ), Heller (HEL) and Weiner (WEI), as detailed elsewhere[51,52] and references therein. The goodness of fitting of these models was judged by absolute maximum percentage average deviations (*PD*$_{max}$,[53] Table IV and Fig. S-4 of the Supplementary material). It is evident that most of the models were able to predict the refractive indices of the studied binary blends.

TABLE IV. Absolute maximum percentage average deviations (*PD*$_{max}$) for the prediction of refractive indices of the blends by different empirical theories

Blend	LL	DG	AB	NEW	EYK	EJ	HEL	WEI
CH (1) + MA (2)	0.11	0.13	0.13	0.14	0.08	0.12	0.11	0.26
CH (1) + EA (2)	0.13	0.14	0.14	0.15	0.11	0.13	0.13	0.23
CH (1) + MS (2)	0.14	0.09	0.09	0.04	0.21	0.12	0.14	0.29

CONCLUSIONS

In summary, the various derived properties revealed the following order of molecular interactions: CH + MS > CH + EA > CH + MA for the studied blends. Such an order of molecular interactions originates from the combined effect of factors such as the molecular size, shape and nature of the components; herein this order was attributed to the breaking up of dipolar interactions or the three-dimensional hydrogen bonded network, as well as interstitial accommodation on mutual mixing of the components. A comparison of the excess partial molar volumes ($\overline{V}_{m,1}^{0,E}$ and $\overline{V}_{m,2}^{0,E}$) at infinite dilution to the molar volumes of the pure components in the blends suggests that the blends CH + MA and CH + EA are characterized by volume expansion but that the blend CH + MS is characterized by volume contraction. The overall performance of PFP and PR-EOS based models for correlation of the excess molar volumes and viscosities was judged by the absolute maximum percentage average deviations (*PD*$_{max}$). Based on the *PD*$_{max}$ values for both these models, it seems that these models can reasonably correlate the excess molar volumes (V_m^E) for the binary blends with MA and EA but not MS. Also based on *PD*$_{max}$ values, the BD model was found to correlate badly the viscosities for all the studied blends as compared to the PR-EOS model.

SUPPLEMENTARY MATERIAL

Additional experimental and derived parameters, as well as descriptions of theoretical and empirical models, are available electronically from http:// //www.shd.org.rs/JSCS or from the corresponding author on request.

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ИЗВОД

ТЕРМОФИЗИЧКЕ ОСОБИНЕ БИНАРНИХ СМЕША ЦИКЛОХЕКСАНА СА НЕКИМ ЕСТРИМА

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Коришћењем експериментално измерених података за густине (ρ) и вискозности (η) за три бинарне смеше састављене од метил-ацетата (MA), етил-ацетата (EA) и метил-салицилата (MS) са циклохексаном (CH), на темепратурама 298,15–318,15 K и на атмосферском притиску, израчунате су допунска моларна запремина (V_m^E) и допунске вискозности (η^E) за цео концетрациони опсег посматраних смеша. Такође, подаци за допунску изентропску компресибилност (κ_s^E), допунску међумолекулску слободну дужину (L_f^E) и допунске моларне индексе рефракције (R_m^E), одређени су из измерених брзина звука (u) и индекса рефракција (n_D) за бинарне смеше на 298,15 K. Различите изведене особине анализиране су у смислу молекулских интеракција и структурних ефеката. Парцијалне моларне запремине ($\bar{V}_{m,1}^0$ and $\bar{V}_{m,2}^0$) и допунске парцијалне моларне запремине ($\bar{V}_{m,1}^{0,E}$ and $\bar{V}_{m,2}^{0,E}$) при бесконачном разблажењу, такође су анализиране у смислу промене запремине смеша. Поред тога, допунске моларне запремине (V_m^E) и вискозности (η) смеша су корелисане уз помоћ Prigogine–Flory–Paterson теорије (PFP) и Peng–Robinson једначине стања (PR-EOS).

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