

Thermoacoustic and phase equilibrium studies of cyclohexanone, cyclohexylamine and cyclohexanol in ethyl lactate at different temperatures at 95.3 kPa

P.V.S. Sairam¹, M. V. D. N. S. Madhavi², G. Srinivasa Rao^{3*}, K. Rayapa Reddy⁴

^{1,3} Faculty of Physics, Andhra Loyola College, Krishna University, AP

² Asst. Professor in Mathematics V.R.S.E.C, Kanuru, Vijayawada, Andhra Pradesh, India

³ Faculty of Chemistry, Andhra Loyola College, AP

ABSTRACT

Molecular associations in the mixtures of the liquids cyclohexanone (CHN), cyclohexylamine (CHA) and cyclohexanol (CHO) with ethyl lactate (EL) as major composition are sighted in this investigation from the investigational estimations of U , ρ and η . U , ρ and η of the mixtures of solvents EL+CHN, EL + CHA and EL + CHO are estimated at temperatures from 303.15 K to 318.15 K at an interval of 5 K at ambient pressure. From exploratory information, different thermodynamic parameters which are significant in the estimation of interactions among molecules in the mixture of solvents are figured. The excess parameters are computed and are fitted to a RK polynomial and the relating standard deviations are registered. The variation of these estimations are reflected in connection to intermolecular association existing in the solvent mixtures. Excess functions of molar volume (V_m^E) are observed as negative while the viscosity deviations ($\Delta\eta$) are seen as positive in all the cases. The phase equilibrium data is obtained experimentally at 95.3 kPa pressure. The liquid phase activity coefficients are interrelated with the mole fraction using Wilson, Non Random Two-Liquid, Van Laar and Margules models. The volumetric and VLE studies showed that the interactions between EL and CHN, CHA and CHO pursue the order: EL + CHN > EL + CHA > EL + CHO.

Keywords

Thermodynamic parameters, excess parameters, molecular associations, phase equilibrium.

VLE	: Vapor Liquid Equilibriums
EL	: Ethyl lactate
CHN	: Cyclohexanone
CHA	: Cyclohexylamine
CHO	: Cyclohexanol
x_1	: Mole fraction
U	: Speed of sound
ρ	: Density
η	: Coefficient of viscosity
V_m^E	: Excess molar volume
$\Delta\kappa_s$: Deviation in isentropic compressibility
$\Delta\eta$: Deviation in viscosity
L_f	: Intermolecular free length
κ_s	: Isentropic compressibility
RK	: Redlich - Kister
PMV	: Partial Molar Volume
PFP	: Prigogine Flory Patterson
P^*	: Characteristic pressure
V^*	: Characteristic volume
α	: Thermal expansion
BP	: Boiling Point

P	: Saturated vapor pressure
T	: Temperature
T _{exp}	: Experimental boiling point temperature
y _i	: Vapor phase mole fractions
G ^E	: Excess Gibbs energy
γ ₁ , γ ₂	: Activity coefficients

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1. Introduction

The need for the experimental determination, theoretical estimation and correlation of physical and chemical properties *viz.*, acoustic, volumetric, thermodynamic viscometric and phasetransition information of pure fluids and fluid mixtures is ever expanding to make processes progressively practical and to help researchers and technologists in their areas of study. The information on thermodynamic parameters in fluid mixtures utilizing the U, ρ and η with reference to mole fraction and temperature has drawn the consideration of different analysts [1-3]. Thermo acoustic, volumetric and thermodynamic studies provide reliable and detailed information for analyzing the physicochemical properties of fluids and fluid mixtures in terms of interactions among molecules [4-6]. The computational information of excess thermodynamic properties of fluid mixture gives information about the nature and depth of atomic associations and can be utilized for the molecular modelling [7-9]. The viscosity information of fluid mixtures is important for process industries in quality control, for configuration designs in fixing the ideal conditions for the compound procedures.

In addition to the information on the thermodynamic nature of the chemicals included, precise vapor–liquid balance (VLE) information is required in design processing, which has increased a lot of consideration as a dependable device for achieving viable, clean, and ideal new advances, in the course of recent decades [10-12]. Estimations of VLE in chemical industries are generally performed with an equation of state dependent on pure liquid/liquid mixture properties. The equilibrium state determines distribution of compounds in a mixture between phases. VLE related data finds wide applications in extractive refining method and for ideal estimations of parameters in the thermodynamic simulations [13, 14].

The selection of a suitable solvent which plays a crucial role in many chemical equations for a specific process mainly be subject to the availability of its physical characteristics. Green solvents are developed for the sustainable chemical processes as a safer alternative to traditional petrochemical solvents [15] as the conventional solvents have very poor environmental and toxicological profiles and cause severe insinuations on the environment. Ethyl lactate (ethyl alpha-hydroxy propionate), one of the most promising green solvents among

lactate esters family [16,17], is slowly replacing the traditional solvents as it is bio-based and derived from carbohydrate feed stock with wide applications. EL because of its unique properties fulfils most of the basic principles of Green chemistry [18, 19].

Cyclic ketones like CHN acts as a good solvent for paints, cellulose ethers, etc. [20]. Amines are significant because of their strong electron giving ability. They can form Hydrogen bonds in self-associated clusters. CHA has wide applications in the production processes and is significant due to its miscible nature with other solvents [21]. CHO is used as an intermediary material [22] in the nylon and other plastic materials production

Review of literature indicates that studies on the thermodynamic and phase equilibrium investigations and the related data of VLE with the binary liquid mixtures of EL with CHN, CHA and CHO are very limited. The main intention of the present investigation is to report the volumetric, thermo-acoustic and vapor liquid equilibrium investigations of the associations among molecules in the fluid mixtures of EL with CHN, CHA and CHO at 303.15, 308.15, 313.15 and 318.15 K. The VLE information on various activity coefficients suitable for the reenactment and structure of refining process for each of the three liquid mixtures at 95.3 kPa are reported and the data are correlated with various phase equilibrium models viz., Wilson, NRTL, Van Laar and Margules.

2. Experimental Section

2.1 Materials

The solvents used in this study are EL obtained from Merk Enterprises with purity more than 99% and cyclohexanone (CHN), cyclohexylamine (CHA) and cyclohexanol (CHO) (with purities more than 99%) obtained from S D Chemicals refined utilizing customary methods [30,31]. The masses of various mixtures of liquids were measured by using Shimadzu AY120 model analytical balance with an uncertainty of $\pm 1 \times 10^{-7}$ kg. U of pure compounds and solvents is estimated by a single crystal ultrasonic interferometer at a frequency of 2 MHz from Mittal Enterprises at different temperatures. The temperature of the liquid/liquid mixture is maintained constant with the help of a chip assisted circulating water bath (provided by Mittal Enterprises, New Delhi) regulated to ± 0.01 K, using a proportional temperature controller. The accuracy in speed measurements is within $\pm 0.2\%$. The densities of liquids/liquid mixtures were measured by an Analytical density meter designed by Rudolph and the uncertainty for the density (ρ) estimations is $\pm 1 \times 10^{-5}$ gcm^{-3} . Brookfield Viscometer was used to measure the viscosities (η) and the uncertainty for these measurements is $\pm 1 \times 10^{-3}$ mPas. An ebulliometer is used to measure the BPs of the systems and the procedure was described by Matsuda et al [33].

The names, CAS number, the supplier, purification method, purity and the molar mass of the chemicals selected for synthesis and preparation of the three mixtures for the experimental determination of various properties viz., speed of sound, liquid density, coefficient of

viscosity and the fluid phase equilibrium data are shown in table 1. Table 2 shows the comparison of experimental speeds of sound (U), densities (ρ) and viscosities (η) with literature values at 303.15K. From this table, it is observed that the experimental values are very close to literature values [23-32].

3. Results and Discussion

3.1 Volumetric Studies

Thermodynamic parameters and corresponding excess parameters and deviation in viscosity are calculated from the experimentally determined values of U, η and ρ of the systems under study. Based on the computed data, we can estimate nature of molecular associations in the binary liquid mixtures

The compressibility at constant entropy can be evaluated from the relation as

$$\kappa_s = \left(\frac{1}{\rho U^2} \right)$$

The intermolecular free length of the mixture is given by

$$L_f = K(\beta_{ad})^{\frac{1}{2}}$$

Excess function of volume per mole (V_m^E) is given by the change between the volume of mixing of a real mixture and the value analogous to the ideal case is and is given as:

$$V_m^E = V - (V_1x_1 + V_2x_2)$$

Deviation in compressibility at constant entropy ($\Delta\kappa_s$) is the variance between isentropic compressibility and the sum of the fractional associations of the pure liquids expressed as

$$\Delta\kappa_s = \kappa_s - (\kappa_{s1}x_1 + \kappa_{s2}x_2)$$

where κ_{s1} is the compressibility at constant entropy of liquid 1 and κ_{s2} that of liquid

Fort and Moore [41] investigated many liquid mixture systems and suggested an expression for deviance in viscosity as

$$\Delta\eta = \eta_{mix} - (x_1\eta_1 + x_2\eta_2)$$

Here η_{mix} is the coefficient of viscosity of the mixture and η_1 and η_2 are that of pure liquids

RK expression was used to fit these excess functions of thermodynamic parameters and is given by

$$Y_{cal}^E = x_1x_2 \sum A_{j-1} (x_2 - x_1)^{j-1}$$

where $Y = V_m^E$ or κ_s^E or $\Delta\eta$ and A_{j-1} are absolute parameters and the mole fractions of components are given by x_1 and x_2

By using least squares method, the coefficients A_{j-1} are evaluated and the standard deviations are computed by using:

$$\sigma_Y^E = \Sigma (Y_{exp}^E - Y_{cal}^E)^2 / (m - n)^{0.5}$$

It is familiar that the thermo acoustic properties of the mixtures of liquids such as U, ρ and η are firmly related in terms of the associations among the molecules present in different liquid systems. The experimentally determined values of U, η and ρ of the three systems under investigation viz., EL + CHN, EL + CHA and EL + CHO in the given temperature range are presented in Table 3. It is worth mention here that determined values of U, ρ and η of pure solvents and that of the mixtures of solvents are taken 5 times and the average values are taken. The average values then are fitted to suitable polynomial using the principle of least squares to smoothen the data. Figures 1 and 2 indicates the

variation of speed of sound and density of the pure ones with the temperature while Figure 3 gives the variation of logarithmic viscosity of the pure ones with the reciprocal of absolute temperature. The best linear fit equations obtained from principle of least squares representing the variation of these parameters of the pure liquids with the temperature are incorporated in Figures 1, 2 and 3 along with the error estimations. The compositional dependence of these of the mixtures of the liquids with the mole fraction of EL at all the temperatures under study and diagrammatically depicted in Figures 4, 5 and 6 respectively.

Fig. 1 and Fig. 2 indicates that the U and ρ of the pure liquids viz., EL, CHN, CHA and CHO decrease linearly with the increase in temperature and from Table 3 confirms that the U and ρ of the solvent system declines with the rise in temperature. With the growth in the temperature, the mean free length of the molecules of a liquid/liquid system increases resulting a decline in the U value. Additionally, increment in the temperature results less ordered structure and more spacing between the molecules. The fall in density with raise in temperature of the pure fluids as in Figure 2 and fluid mixtures as in Table 3 demonstrates the reduction in intermolecular forces because of increment in the temperature of the framework, which causes more volume expansion and subsequently increment in free path length.

Density is an important property of solvent system which is used to interpret solvent effects

on transport phenomena and other mechanism occurring in the mixtures of liquids. The nonlinear variation of speed and density with EL (Figures 4 and 5) at all the temperatures indicates some sort of association between the EL molecules, with CHN, CHA and CHO molecules. This nonlinear variation favors the breaking and forming of the associations between the unlike molecules extending throughout the whole solution resulting in the existence of molecules of one liquid dispersed throughout the bulk of the other with the possibility of the formation of intermolecular associations

The knowledge of the thermoacoustic and thermodynamic parameters in binary liquid mixtures confirms that there are interactions between component molecules. But they failed to give the detailed associations between the molecules. The excess thermodynamic parameters give the information that whether the molecular associations are strong or weak; hydrogen bonded or dipole-dipole or dipole-dipole induced. The excess thermodynamic functions directly gives the deviance of a solution from ideal conduct. The variation of these excess functions gives the scope and strength of interactions among molecules of the compositions. The evaluation of the excess values and their investigation in the light of new approaches are very important for the interpretation of associations of the molecules and for the assessment of the various solvents behavior.

V_m , κ_s and L_f of EL + CHN, CHA and CHO at different temperatures are mentioned in Table 4

and excess functions viz., $V_m^E, \Delta\kappa_s$ and $\Delta\eta$ are mentioned in Table 5. Figures 7 and 8 shows the variation of V_m^E and $\Delta\kappa_s$ at different temperatures. The observed negative V_m^E and $\Delta\kappa_s$ values because of the compression in the volume can be ascribed to (i) the structural influence including the structural impact permitting the correction of two molecules of various sizes into one another's structure (ii) the chemical commitment including explicit associations because of closer pressing of molecules because of the conceivable hydrogen bond development among hetero molecules and more dipole-dipole associations between compound molecules [34]. The perceived growth in the total estimations of V_m^E with the temperature can be because of the way that the kinetic energy of a body raises with the rise in temperature, prompting a reduction in the existing associations among EL and cyclic components. The fitting coefficients of the RK [35] equation (Aj-1) alongside the standard deviances are mentioned in Table 6. The pattern in the variation of V_m^E of the mixtures keep on the order $EL + CHN > EL + CHA > EL + CHO$ at all the temperatures in investigation.

Additionally, by reviewing partial molar volumes, the results of V_m^E are validated. The partial molar volumes of solvents 1 (EL) and 2 (cyclic compounds) in the mixture of two liquids from their molar volumes are computed from the equations [36]

$$\bar{V}_{m,1} = V_m^E + V_1^0 + (1 - x_1) \left(\frac{\partial V_m^E}{\partial x_1} \right)_{T,P} \quad \dots(1)$$

$$\bar{V}_{m,2} = V_m^E + V_2^0 - x_1 \left(\frac{\partial V_m^E}{\partial x_1} \right)_{T,P} \quad \dots(2)$$

Here V_1^0 and V_2^0 are the molar volumes of pure EL and cyclic compound correspondingly. The derivatives $\left(\frac{\partial V_m^E}{\partial x_1} \right)_{T,P}$ of the above equations are attained by differentiating V_m^E equation with respect to x_1 . This results the partial molar volumes which are given by the expressions

$$\bar{V}_{m,1} = V_1^0 + x_2^2 \sum_{i=0}^n A_i (1 - 2x_2)^i - 2x_2^2 (1 - x_2) \sum_{i=1}^n i A_i x_2^{i-1}$$

$$\bar{V}_{m,2} = V_2^0 + (1 - x_2)^2 \sum_{i=0}^n A_i (1 - 2x_2)^i + 2x_2 (1 - x_2) \sum_{i=1}^n i A_i x_2^{i-1}$$

V_m^E values are obtained from the above equations and are given by

$$\bar{V}_{m,1}^E = \bar{V}_{m,1} - V_1^*$$

$$\bar{V}_{m,2}^E = \bar{V}_{m,2} - V_2^*$$

The estimations of partial molar volumes $\bar{V}_{m,1}$ and $\bar{V}_{m,2}$ alongside excess molar volumes are provided in Tables 7(a) and (b). From Tables 7(a) and (b), it is inferred that $\bar{V}_{m,1}$ and $\bar{V}_{m,2}$ for the compounds in the mixture are smaller than their particular molar volumes in the pure state, i.e., a reduction in volume occurs on mixing EL with cyclic ones under examination. The outcomes backing the detected negative values of V_m^E in all the systems at all temperatures under study.

Fig. 8 shows the computed outcomes for excess PMV of cyclic compounds ($\bar{V}_{m,2}^E$) in their binary systems with EL ($\bar{V}_{m,1}^E$) at 303.15 K. From Fig.8, it is observed that compression in PMV happens either EL is mixed with the cyclic mixes (solid line) or vice versa (dashed line) affirming the more associations between the dissimilar molecules which bolster the inferences

drawn from V_m^E values. The $(\bar{V}_{m,i}^E)$ values at other temperatures keep on the similar patterns however show altered values, and subsequently the data isn't graphically shown to limit the quantity of figures.

For the binary systems of solvent mixtures of EL with CHN, CHA and CHO, V_m^E was assessed using the Prigogine Flory Patterson (PFP) theory [37]. This PFP theory assumes that the contribution of V_m^E can be ascribed to the three terms of pressure, free volume and interaction contributions according to the following equations (5-8):

$$\frac{V^E}{x_1V_1^*+x_2V_2^*} = V_{Pressure}^E + V_{Interaction}^E - V_{Free\ volume}^E \quad ..(5)$$

$$V_{Pressure}^E = \frac{(\bar{V}_1 - \bar{V}_2)(P_1^* - P_2^*)\psi_1\psi_2}{P_2^*\psi_1 + P_1^*\psi_2} \quad ..(6)$$

$$V_{Interaction}^E = \frac{(\bar{V}_1^{\frac{2}{3}} - 1)\bar{V}_2^{\frac{2}{3}}(\psi_2\theta_2\chi_{12})}{\left(\left(\frac{4}{3}\right)\bar{V}_1^{\frac{2}{3}} - 1\right)P_1^*} \quad ..(7)$$

$$V_{Free\ volume}^E = \frac{(\bar{V}_1 - \bar{V}_2)^2 \left(\left(\frac{4}{3}\right)\bar{V}_1^{\frac{2}{3}} - 1\right)\psi_1\psi_2}{\left(\left(\frac{4}{3}\right)\bar{V}_1^{\frac{2}{3}} - 1\right)\bar{V}_1} \quad ..(8)$$

For the calculation of the P^* and V^* parameters in the PFP equation, the Flory's equation of state [38] was used. The values for the coefficients of thermal expansion (α) and isothermal compressibility (κ_s) were found experimentally and used for the calculation of the reduced volume and pressure according to the following equation (9-10):

$$\bar{V}_i = \frac{(1 + (\frac{4}{3})\alpha_i T)^3}{1 + \alpha_i T} \quad ..(9)$$

$$P_i^* = \frac{T\bar{V}_i\alpha_i}{\kappa_i} \quad ..(10)$$

For calculating the fraction of the molecular contact energy, the hard-core volume and the molecular surface, the following equations (11-13) were used

$$\psi_1 = 1 - \psi_2 = \frac{(P^*\phi)_1}{[(P^*\phi)_1 + (P^*\phi)_2]} \quad ..(11)$$

$$\psi_1 = 1 - \phi_2 = \frac{(XV^*)_1}{[(XV^*)_1 + (XV^*)_2]} \quad ..(12)$$

$$\theta_1 = 1 - \theta_2 = \frac{\phi_1}{[\phi)_1 + \frac{(S\phi)_2}{S_1}]} \quad ..(13)$$

And the ratio of the contact surface was calculated according to the equation

$$\frac{S_1}{S_2} = \left(\frac{V_1^*}{V_2^*} \right)^{\frac{1}{3}} \quad ..(14)$$

Table 8(a) shows reduced volume (V), characteristic volume (V^*) and characteristic pressure (P^*) of the pure solvents used and Table 8(b) gives χ_{12} (interaction parameter) and the three contributions to the (V_m^E) at equi-molar mixture ($x = 0.5$) using PFP theory along with measured V_m^E values at different temperatures. Fig.9 shows the comparison of V_m^E of the binary mixtures of EL + CHN (a), + CHA (b) and + CHO (c) with EL at various temperatures.

PFP equation associated the experimental data of V_m^E appropriately. The interactional term in the PFP equation indicated a fundamental

impact on the V_m^E contrasted with the free volume and the pressure term impact. The least impact was the impact of the pressure term. The excess volume demonstrated a negative peak for the entire composition range. The values become increasingly negative with raise in the temperature, which was clarified by increasing the associations between the molecules.

To reinforce and validate the outcomes acquired from excess molar volume data, viscometric investigations are embraced. The variation in $\Delta\eta$ with the EL mole fraction is plotted in Fig. 10. It is noticed that the $\Delta\eta$ esteems are positive for all the systems under investigation at all the temperatures under study. Extreme estimations of $\Delta\eta$ are seen at $x = 0.5$ composition in all the systems at all the temperatures under scrutiny.

By and large, the $\Delta\eta$ relies upon the states of the associating components and the forces among molecules. The noticed positive estimations of $\Delta\eta$ for all the systems under study are because of the hydrogen bonding association between the solvent molecules [39, 40], as per Fort and Moore [41] the solvents of dissimilar molecular size stir up with decline in volume, resulting negative V_m^E and positive $\Delta\eta$ values.

The estimations of $\Delta\eta$ decrease in all cases with the raise in temperature of the mixture. As temperature builds, the heat energy of the system expands prompting a disruption in the self-association of pure compounds in hetero association among dissimilar molecules. This

prompts less positive $\Delta\eta$ estimations with the raise in temperature, as reflected in this study.

Fig.11 represents the variation of V_m^E , $\Delta\kappa_s$ and $\Delta\eta$ of the binary mixtures of EL + CHN + CHA and + CHO with EL composition at 303.15 K. The tendency perceived in the variation of $\Delta\eta$ (EL + CHN > EL + CHA > EL + CHO) is similar to that of V_m^E with opposite signs.

3.2 Vapor liquid equilibrium studies

Usually, the deviations from ideal behavior occurs in the fluid stage than in the vapor phase on the grounds that the forces of interaction among the molecules in the liquid are much resilient because of less intermolecular separations. But the vapor phase can be made-up to behave idealistically at temperate pressures. The phase behavior of the liquids is generally depicted by means of the activity coefficients. The method for determining the phase equilibrium in systems that are non-ideal in fluid phase is established on the activity coefficient representations such as Wilson, NRTL, Van Laar and Margules. For a useful explanation of the behavior of the mixtures of liquids and process engineering design, consistent and precise VLE data are required. The boiling points of the pure liquids viz., EL, CHN, CHA and CHO are determined experimentally at various pressures are listed in Table 9.

The experimental boiling point temperatures and vapor pressures and of the pure systems are interrelated by the three variable Antoine [42] and five variable Riedel [43] equations.

Antoine equation is given by:

$$\ln[P/(kPa)] = \left\{ \frac{A-B}{T/(K)+C} \right\}$$

where the Antoine constants A, B, and C are attained by fitting the pressure-temperature data using the nonlinear optimization technique. Fig. 13 represents investigational saturated vapor pressure (P) vs temperature (T) along with the supporting Antoine's equations for EL + CHN, EL + CHA and EL + CHO.

Riedel equation is given by:

$$\ln P = A + \left(\frac{B}{T}\right) + C * \ln(T) + DT^E \quad ..(2)$$

Here the Riedel constants A, B, C, D and E are also obtained by appropriate the pressure-temperature data using the nonlinear optimization technique and are mentioned in Table 10 along with Antoine constants.

Wilson's Model:Based on molecular contemplations, Wilson proposed [44]a model for the excess Gibbs energy (G^E) of a binary solvent in reference to the mole fractions of the compound liquids (x_1, x_2), the temperature of the mixture T and the adjustable parameters A_{12} and A_{21} , is:

$$\frac{G^E}{RT} = -x_1 \ln(x_1 + A_{12}x_2) - x_2 \ln(x_2 + A_{21}x_1)$$

Activity coefficients γ_1 and γ_2 obtained from this equation are:

$$\ln \gamma_1 = -\ln(x_1 + A_{12}x_2) + x_2 \left[\frac{A_{12}}{x_1 + A_{21}x_2} - \frac{A_{21}}{x_2 + A_{21}x_1} \right] \quad ..(4)$$

$$\ln \gamma_2 = -\ln(x_2 + A_{21}x_1) - x_1 \left[\frac{A_{12}}{x_1 + A_{12}x_2} - \frac{A_{21}}{x_2 + A_{21}x_1} \right] \quad ..(5)$$

The interaction parameters A_{12} and A_{21} are correlated with the pure-compound molar volumes and characteristic energy differences by:

$$A_{12} = \frac{v_2}{v_1} \exp \left[-\frac{\lambda_{12} - \lambda_{11}}{RT} \right] \quad ..(6)$$

$$A_{21} = \frac{v_1}{v_2} \exp \left[-\frac{\lambda_{21} - \lambda_{22}}{RT} \right] \quad ..(7)$$

Here v_i is the molar liquid volume of pure component i and $\lambda_{12}, \lambda_{11}, \lambda_{21}$ and λ_{22} are energies of interactions between the molecules.

The investigational data are interrelated by Wilson's method. The activity coefficients and G^E are computed from this by taking into consideration the non-ideal behavior of the vapor phase and liquid phase. Interactional binary parameters presumed here are assessed by nonlinear regression analysis. VLE data, viz., $x_i, T_{exp}, y_i, \gamma_1, \gamma_2$ and G^E of the three systems EL + CHN, CHA and CHO at 95.3 kPa are reported in Tables 11(a), 11(b) and 11(c).

It is seen that the estimations of activity coefficients are less than unity for all the three systems under scrutiny. This shows non-ideal nature of these mixes with a negative aberrance from Raoult's law. The apparent negative deviations from Raoult's law in all the systems may be a direct result of the nearness of strong intermolecular forces like hydrogen bonding between the components of two solvents. The positive and negative deviations for non-ideal solutions from vapor liquid investigations are well pronounced by Harrison et al. [45].

NRTL equation: The Non Random Two Liquid (NRTL)[46] equation, pertinent to partially dissolvable solvents and completely dissolvable systems, for excess Gibbs energy is:

$$g^E = x_1 x_2 \left(\frac{\tau_{21} G_{21}}{x_1 + x_2 G_{21}} + \frac{\tau_{12} G_{12}}{x_1 + x_2 G_{12}} \right) \quad \dots(8)$$

$$\tau_{12} = (\Delta g_{12} - \Delta g_{22})/RT \quad \dots(9)$$

$$\tau_{21} = (\Delta g_{21} - \Delta g_{11})/RT \quad \dots(10)$$

$$G_{12} = \exp(-\alpha_{12} \tau_{12}) G_{21} = \exp(-\alpha_{12} \tau_{21}) \quad \dots(11)$$

Here α_{12} is interrelated to the non-randomness in the system; when α_{12} is zero, the mixture is totally random and the equation reduces to the 2-suffix Margules equation. The activity coefficients are:

$$\ln \gamma_1 = -x_2^2 \left[\tau_{21} \left\{ \frac{G_{12}}{x_1 + x_2 G_{21}} \right\}^2 + \frac{\tau_{12} G_{12}}{(x_2 + x_1 G_{12})^2} \right]$$

$$\ln \gamma_2 = -x_1^2 \left[\tau_{12} \left\{ \frac{G_{12}}{x_2 + x_1 G_{12}} \right\}^2 + \frac{\tau_{21} G_{21}}{(x_1 + x_2 G_{21})^2} \right]$$

Van Laar Equation: Van Laar [47] stated the G^E of the mixtures of two liquids as:

$$\frac{g^E}{RT} = \frac{A_{12} x_1 x_2}{x_1 \left(\frac{A_{12}}{A_{21}} \right) + x_2} \quad \dots(14)$$

where the constants A_{12} & A_{21} are obtained by regression of investigational VLE data. The activity coefficients of the components are:

$$\ln \gamma_1 = A_{12} \left[\frac{A_{21} x_2}{A_{12} x_2 + A_{21} x_1} \right]^2 \quad \dots(15)$$

$$\ln \gamma_2 = A_{21} \left[\frac{A_{12} x_1}{A_{12} x_1 + A_{21} x_2} \right]^2 \quad \dots(16)$$

This indicates that the A_{12} and A_{21} are equal to logarithmic limiting activity coefficients $\ln \gamma_1^\infty$ and $\ln \gamma_2^\infty$.

Four suffix Margules equation: For G^E of mixture of two liquids, Margules proposed a model

which is used to develop an expression for the activity coefficients γ_i of i^{th} component of a system and the activity coefficient gives the deviation from ideal solubility. The Margules activity coefficient model and given by:

$$\frac{g^E}{RT} = x_1 x_2 [A x_2 + B x_1 - C x_1 x_2] \quad \dots(17)$$

with the respective activity coefficients:

$$\ln \gamma_1 = x_2^2 [A + 2(B - A - C)x_1 + 3C x_1^2] \quad \dots(18)$$

$$\ln \gamma_2 = x_1^2 [B + 2(A - B - C)x_2 + 3C x_2^2] \quad \dots(19)$$

Parameters A, B, and C were obtained using the non-linear regression analysis.

Binary interaction parameters for the systems of EL + CHN, +CHN and CHO using Wilson, NRTL, Van Laar and Margules models at ambient pressure listed in Table 12.

The experimental data of the three liquid mixtures under investigation are correlated with the Wilson technique from which the activity coefficients and excess Gibbs energy are determined considering the non-ideal behavior of the vapor-liquid states. The adjustable interaction parameters presumed in these conditions are assessed by nonlinear regression principle.

VLE data, viz., information on fluid phase and vapor phase mole fractions (x_1, y_1), experimental boiling point temperature (T_{exp}), the activity coefficients (γ_1 and γ_2), and excess Gibbs energy (G^E) values are computed theoretically at a pressure 95.3 kPa are listed in tables 11(a), 11(b) and 11(c). The corresponding binary interaction parameters viz., Wilson model (A_{12} and A_{21}),

NRTL model (Δg_{12} , Δg_{12} and α_{12}), Van Laar model (A and B) and Margules model (A, B, D) obtained from regression analysis for the mixtures at a pressure 95.3 kPa are presented in Table 12.

The identified negative deviations might be because of the existence of intermolecular forces like H-bonding among the constituents of the combination of solvents. The positive and negative deviations for non-ideal solutions from vapor–liquid investigations are all explained by Harrison et al. [45].

The variation in the mole fractions of vapor phase (y_1) with reference to the liquid phase (x_1) of ethyl lactate are presented in figure 12. From Fig. 12, it is seen that the curves are nonlinear in nature for all the three binary liquid mixtures under investigation indicating that each mixture forms a non-ideal solution deviating negatively from Raoult's law over the entire concentration range. The observed negative deviations from Raoult's law in all the nine binary mixtures of three systems under study may be due to the presence of strong intermolecular forces due to H-bonding/dipole-dipole interactions between the components of the mixtures.

Figures 13 show the variation of the activity coefficients (γ_1 of component-1 and γ_2 of component-2) with the mol% of ethyl lactate of binary mixtures. It is noticed from these figures for the combinations of liquids under study that the coefficient γ_1 increases with the ethyl lactate composition and reaches unity while the coefficient γ_2 decreases from unity with ethyl

lactate composition in all the combinations of liquids under study.

It is also observed that the activity coefficients are less than unity for all the three mixtures under study, showing non-ideal behavior of these combinations with a negative deviation from Raoult's law. The noticed negative deviations from Raoult's law in all the three combinations of liquids might be because of the occurrence of strong intermolecular forces like H-bonding between the constituents of the solvents. The positive and negative deviations for non-ideal solutions from VLE investigations are all well explained by Harrison et al [45]. The degree of deviation from linearity indicates measure of interaction between unlike molecules. Even though, T-x-y graphs for the mixtures EL+CHN (Fig. 12) is very close for the components of the mixture, it is evident from the variation of the activity coefficients plots that even in these two mixtures also considerable interactions take place between the unlike molecules.

In order to check thermodynamic consistency of the mixtures, the variation in the logarithmic ratio of activity coefficients i.e., $\ln(\gamma_1/\gamma_2)$ with the liquid phase mole fraction of ethyl lactate (x_1) for the nine combinations of liquids is represented in Figure 13 for (EL+CHN, +CHA, +CHO). From these figures, both positive and negative values are observed. From this, the region above and below the axis is computed to check the consistency thermodynamically. It is noticed that all the combinations under study passed through the Herigton's thermodynamic consistency test.

Figure 14 shows the activity coefficients variation of the combinations of liquids under study with the increase in ethyl lactate composition. From the figure, it is noticed that the coefficient γ_1 increases with the ethyl lactate composition and reaches unity while γ_2 decreases from unity with ethyl lactate composition in all the combinations of liquids under study. The degree of deviation from linearity indicates measure of interaction between unlike molecules.

The excess values of Gibbs energy (GE) of the combinations of liquids under study are plotted against the ethyl lactate mol% in Figure 14 for system-I (EL+CHN, +CHA, +CHO). The observed negative excess Gibbs energy (GE) values for all binary mixtures indicate that more intermolecular forces operating between dissimilar molecules. From the GE plots (Figure 14) of liquids under system –I investigated; it can be concluded that in the combinations; the absolute GE values follow the order:



In ethyl lactate, the atoms are self-associated through the dipolar interactions but in cyclic compounds considered, associations among molecules are through both intermolecular H-bonding and dipolar associations. Mixing of ethyl lactate with cyclic compounds results the mutual dissociation of the structures present in pure compounds with corresponding formation of new H-bonds between proton acceptor oxygen atoms of ethyl lactate molecules and hydrogen molecules of cyclic ones. It is notable that the dispersion forces cause positive contributions to excess

values, while dipole–dipole, dipole-initiated dipole, charge-transfer interaction and H-bonding between the molecules of unlike molecules of the combinations makes negative contributions. In the case of ethyl lactate and cyclohexanone combination, the intermolecular H-bond between the like molecules of cyclohexanone breaks and forms new H-bonds more readily with ethyl lactate molecules. Whereas, in the binary mixture of ethyl lactate and cyclohexylamine indicates a lesser negative value of GE. In ethyl lactate and cyclohexanol mixture, the excess GE values are less negative than the other combinations.

4. Conclusions

U, ρ and η of three systems have been accounted at various temperatures from 303.15 to 318.15 K in an interval of 5 K in the entire composition range. V_m^E , $\Delta\kappa_s$ and $\Delta\eta$ have been computed from the measured data were interrelated well using the RK polynomial. The possible association between the structures of solvent molecules, their associations and properties were discoursed for all the solvent mixtures under study. The pattern in the variation of V_m^E , $\Delta\kappa_s$ and partial molar volumes for the systems shows the order EL + CHN > EL + CHA > EL + CHO at all the temperatures under investigation which is supported by PFP theory. This is reinforced by the observed positive values of $\Delta\eta$.

The outcomes of the experiments are seen to be well represented by Wilson model. It is inferred from the investigation that all the three systems are non-ideal liquid mixtures deviating

from Raoult's law. Also, it is seen that each of the three systems under study display negative estimations of G^E due to intense intermolecular hydrogen bonding between dissimilar molecules. Thermodynamic consistencies of the systems are checked by Herington's test. From the observed negative G^E values, it is construed that solid

intermolecular forces operating between unlike molecules. From the observations of G^E values, it is concluded that the interactions between the three binary solvent mixtures follow the order:
EL + CHN > EL + CHA > EL + CHO

Table 1. Details of Studied Chemicals, CAS Number, Source, Purification Method, chemical structure and molar mass

Chemical	CAS number	Supplier	Purification Technique (Purity% GC)	Molar mass $10^{-3} \text{ kg mol}^{-1}$
Ethyl lactate	97-64-3	Merck	Vacuum distillation(99.7)	118.13
Cyclohexanone	108-94-1	S.D. fine	Fractional distillation(99.6)	98.14
Cyclohexylamine	108-91-8.	S.D. fine	Fractional distillation(99.3)	99.17
Cyclohexanol	108-93-0	S.D. fine	Fractional distillation(99.5)	100.16

Table 2. Comparison of experimental speeds of sound (U), densities (ρ) and viscosities (η) with literature values at 303.15K

Compound	Speed of sound (U/ms^{-1})		Density ($\rho/\text{kg m}^{-3}$)		Viscosity ($\eta/\text{mPa}\cdot\text{s}$)	
	Expt.	Lit.	Expt.	Lit.	Expt.	Lit.
Ethyl lactate (EL)	1261.14	1261.17[23]	1022.74	1022.81[24]	2.095	2.096[25]
Cyclohexanone (CHN)	1388.34	1388.30[26]	937.35	937.5[27]	1.845	1.847[28]
Cyclohexylamine (CHA)	1397.74	1397.8[29]	857.64	857.671[30]	1.739	1.737[31]
Cyclohexanol (CHO)	1443.13	1443.2[29]	941.43	941.32[30]	39.587	39.546[32]

Table 3. Speeds of sound ($U/\text{m}\cdot\text{s}^{-1}$), densities ($\rho/\text{kg}\cdot\text{m}^{-3}$), dynamic viscosities ($\eta/\text{mPa}\cdot\text{s}$) of EL + CHN, CHA and CHO at 303.15 K, 308.15 K, 313.15 K and 318.15 K

x_1	U	ρ	η	x_1	U	ρ	η	x_1	U	ρ	η
EL (1) + CHN (2)				EL (1) + CHA (2)				EL (1) + CHO (2)			
303.15 K											
0.0000	1388.34	937.35	1.845	0.0000	1397.74	857.64	1.739	0.0000	1443.13	941.43	39.587
0.0915	1376.19	947.17	1.890	0.1001	1383.69	874.85	1.792	0.0928	1422.85	949.90	36.122
0.1847	1363.85	956.68	1.931	0.2002	1369.58	891.94	1.841	0.1872	1403.08	958.32	32.595
0.2798	1351.33	965.90	1.968	0.3002	1355.49	908.90	1.886	0.2830	1383.80	966.67	29.012
0.3767	1338.68	974.83	2.002	0.4003	1341.48	925.71	1.928	0.3804	1364.99	974.95	25.365
0.4755	1325.91	983.48	2.032	0.5003	1327.60	942.35	1.966	0.4795	1346.63	983.15	21.651
0.5762	1313.06	991.86	2.055	0.6003	1313.89	958.82	2.000	0.5801	1328.72	991.25	17.877
0.6790	1300.14	999.96	2.072	0.7002	1300.36	975.10	2.029	0.6825	1311.22	999.27	14.033
0.7838	1287.16	1007.81	2.085	0.8002	1287.06	991.19	2.055	0.7865	1294.14	1007.19	10.126
0.8908	1274.16	1015.40	2.093	0.9001	1273.98	1007.07	2.077	0.8924	1277.45	1015.01	6.144
1.0000	1261.14	1022.74	2.095	1.0000	1261.14	1022.74	2.095	1.0000	1261.14	1022.74	2.095

308.15 K

0.0000	1370.36	933.18	1.684	0.0000	1379.12	853.18	1.571	0.0000	1419.48	937.18	27.956
0.0915	1359.89	943.13	1.717	0.1001	1365.81	870.63	1.615	0.0928	1400.84	945.96	25.546
0.1847	1348.87	952.77	1.750	0.2002	1352.45	887.84	1.656	0.1872	1382.41	954.57	23.094
0.2798	1337.31	962.09	1.779	0.3002	1339.04	904.83	1.694	0.2830	1364.20	962.99	20.602
0.3767	1325.25	971.08	1.806	0.4003	1325.57	921.58	1.729	0.3804	1346.21	971.25	18.066
0.4755	1312.69	979.74	1.829	0.5003	1312.03	938.12	1.761	0.4795	1328.45	979.34	15.482
0.5762	1299.66	988.04	1.844	0.6003	1298.42	954.42	1.790	0.5801	1310.91	987.27	12.856
0.6790	1286.16	995.97	1.855	0.7002	1284.72	970.51	1.815	0.6825	1293.60	995.04	10.181
0.7838	1272.22	1003.53	1.863	0.8002	1270.92	986.38	1.837	0.7865	1276.51	1002.66	7.462
0.8908	1257.83	1010.70	1.869	0.9001	1257.03	1002.03	1.856	0.8924	1259.65	1010.13	4.691
1.0000	1243.02	1017.46	1.872	1.0000	1243.02	1017.46	1.872	1.0000	1243.02	1017.46	1.872

313.15 K

0.0000	1352.39	928.87	1.539	0.0000	1360.57	848.73	1.417	0.0000	1395.13	932.69	19.965
0.0915	1342.48	938.93	1.562	0.1001	1348.06	866.31	1.453	0.0928	1377.32	941.80	18.275
0.1847	1331.92	948.65	1.585	0.2002	1335.28	883.67	1.487	0.1872	1359.76	950.59	16.556
0.2798	1320.70	958.02	1.607	0.3002	1322.25	900.78	1.519	0.2830	1342.41	959.09	14.810
0.3767	1308.85	967.02	1.627	0.4003	1308.98	917.63	1.548	0.3804	1325.24	967.32	13.032
0.4755	1296.37	975.63	1.643	0.5003	1295.48	934.20	1.575	0.4795	1308.22	975.30	11.221
0.5762	1283.27	983.82	1.654	0.6003	1281.76	950.46	1.599	0.5801	1291.34	983.04	9.379
0.6790	1269.54	991.58	1.661	0.7002	1267.81	966.39	1.620	0.6825	1274.56	990.56	7.502
0.7838	1255.21	998.87	1.665	0.8002	1253.65	981.96	1.639	0.7865	1257.87	997.88	5.594
0.8908	1240.25	1005.67	1.668	0.9001	1239.28	997.16	1.656	0.8924	1241.25	1005.00	3.649
1.0000	1224.68	1011.94	1.671	1.0000	1224.68	1011.94	1.671	1.0000	1224.68	1011.94	1.671

318.15 K

0.0000	1334.41	924.52	1.409	0.0000	1342.04	844.14	1.285	0.0000	1370.67	928.24	14.538
0.0915	1325.22	934.74	1.423	0.1001	1330.12	861.98	1.314	0.0928	1354.19	937.64	13.333
0.1847	1315.25	944.60	1.437	0.2002	1317.89	879.52	1.341	0.1872	1337.74	946.64	12.107
0.2798	1304.48	954.08	1.451	0.3002	1305.32	896.73	1.366	0.2830	1321.31	955.27	10.861
0.3767	1292.92	963.14	1.463	0.4003	1292.41	913.61	1.389	0.3804	1304.90	963.55	9.593
0.4755	1280.56	971.75	1.473	0.5003	1279.11	930.13	1.410	0.4795	1288.48	971.48	8.301
0.5762	1267.38	979.88	1.479	0.6003	1265.42	946.26	1.429	0.5801	1272.06	979.08	6.988
0.6790	1253.37	987.47	1.483	0.7002	1251.31	961.99	1.446	0.6825	1255.62	986.37	5.649
0.7838	1238.51	994.47	1.485	0.8002	1236.75	977.30	1.462	0.7865	1239.17	993.36	4.288
0.8908	1222.78	1000.84	1.487	0.9001	1221.70	992.14	1.476	0.8924	1222.68	1000.06	2.900
1.0000	1206.15	1006.49	1.489	1.0000	1206.15	1006.49	1.489	1.0000	1206.15	1006.49	1.489

Standard uncertainties u are $u(x_1) = \pm 1.0 \times 10^{-4}$, $u(T) = 0.01 K$ and the combined uncertainties $U_c, U_c(\rho) = 0.2 kg.m^{-3}$ and $U(u) = 0.8 m s^{-1}$ with level of confidence = 0.95

Table 4. Molar volume ($V_m/10^{-6} m^3 mol^{-1}$), isentropic compressibility ($\kappa_s/10^{-10} Pa^{-1}$) and intermolecular free length ($L_f/10^{-12} m$) of EL + CHN, CHA and CHO at 303.15, 308.15, 313.15 and 318.15 K

x_1	V_m	κ_s	L_f	x_1	V_m	κ_s	L_f	x_1	V_m	κ_s	L_f
EL (1) + CHN (2)				EL (1) + CHA (2)				EL (1) + CHO (2)			
303.15 K											
0.0000	104.699	5.5349	48.830	0.0000	115.631	5.9682	50.706	0.0000	106.391	5.1004	46.874
0.0915	105.545	5.5746	49.005	0.1001	115.526	5.9702	50.714	0.0928	107.199	5.2000	47.330
0.1847	106.444	5.6195	49.202	0.2002	115.440	5.9771	50.743	0.1872	108.026	5.3006	47.786
0.2798	107.395	5.6694	49.420	0.3002	115.373	5.9881	50.790	0.2830	108.875	5.4023	48.242
0.3767	108.398	5.7242	49.659	0.4003	115.327	6.0029	50.853	0.3804	109.746	5.5050	48.698
0.4755	109.453	5.7837	49.916	0.5003	115.302	6.0208	50.929	0.4795	110.640	5.6090	49.156
0.5762	110.559	5.8477	50.191	0.6003	115.299	6.0415	51.016	0.5801	111.560	5.7141	49.615
0.6790	111.717	5.9162	50.484	0.7002	115.317	6.0648	51.115	0.6825	112.506	5.8206	50.075
0.7838	112.927	5.9890	50.794	0.8002	115.357	6.0904	51.222	0.7865	113.478	5.9283	50.536
0.8908	114.189	6.0662	51.120	0.9001	115.419	6.1181	51.338	0.8924	114.477	6.0373	50.998
1.0000	115.503	6.1476	51.462	1.0000	115.503	6.1476	51.462	1.0000	115.503	6.1476	51.462
308.15 K											

0.0000	105.167	5.7064	50.029	0.0000	116.236	6.1625	51.990	0.0000	106.874	5.2956	48.195
0.0915	105.997	5.7335	50.148	0.1001	116.086	6.1573	51.968	0.0928	107.645	5.3870	48.609
0.1847	106.881	5.7686	50.301	0.2002	115.972	6.1577	51.970	0.1872	108.451	5.4818	49.035
0.2798	107.820	5.8119	50.489	0.3002	115.892	6.1638	51.995	0.2830	109.290	5.5798	49.471
0.3767	108.816	5.8634	50.712	0.4003	115.843	6.1753	52.044	0.3804	110.164	5.6812	49.919
0.4755	109.871	5.9233	50.971	0.5003	115.823	6.1923	52.116	0.4795	111.070	5.7860	50.377
0.5762	110.986	5.9920	51.266	0.6003	115.830	6.2148	52.210	0.5801	112.011	5.8941	50.845
0.6790	112.165	6.0696	51.597	0.7002	115.863	6.2429	52.328	0.6825	112.984	6.0056	51.324
0.7838	113.408	6.1567	51.965	0.8002	115.920	6.2765	52.469	0.7865	113.990	6.1206	51.813
0.8908	114.720	6.2536	52.373	0.9001	116.001	6.3158	52.633	0.8924	115.030	6.2391	52.312
1.0000	116.103	6.3610	52.821	1.0000	116.103	6.3610	52.821	1.0000	116.103	6.3610	52.821
313.15 K											
0.0000	105.655	5.8863	51.266	0.0000	116.845	6.3649	53.310	0.0000	107.388	5.5085	49.594
0.0915	106.472	5.9095	51.367	0.1001	116.665	6.3520	53.256	0.0928	108.122	5.5972	49.992
0.1847	107.345	5.9421	51.509	0.2002	116.520	6.3470	53.235	0.1872	108.905	5.6896	50.403
0.2798	108.279	5.9843	51.692	0.3002	116.413	6.3497	53.246	0.2830	109.735	5.7859	50.828
0.3767	109.274	6.0365	51.916	0.4003	116.342	6.3601	53.290	0.3804	110.611	5.8863	51.267
0.4755	110.334	6.0990	52.185	0.5003	116.309	6.3782	53.366	0.4795	111.531	5.9910	51.720
0.5762	111.462	6.1723	52.497	0.6003	116.314	6.4041	53.474	0.5801	112.493	6.1003	52.190
0.6790	112.662	6.2572	52.857	0.7002	116.358	6.4378	53.614	0.6825	113.495	6.2144	52.676
0.7838	113.937	6.3542	53.265	0.8002	116.442	6.4796	53.788	0.7865	114.537	6.3336	53.179
0.8908	115.293	6.4643	53.725	0.9001	116.567	6.5298	53.996	0.8924	115.618	6.4583	53.700
1.0000	116.736	6.5887	54.239	1.0000	116.736	6.5887	54.239	1.0000	116.736	6.5887	54.239
318.15 K											
0.0000	106.152	6.0744	52.541	0.0000	117.481	6.5774	54.673	0.0000	107.903	5.7342	51.049
0.0915	106.949	6.0916	52.616	0.1001	117.251	6.5572	54.590	0.0928	108.601	5.8157	51.410
0.1847	107.806	6.1198	52.737	0.2002	117.071	6.5463	54.544	0.1872	109.359	5.9030	51.794
0.2798	108.726	6.1594	52.908	0.3002	116.939	6.5449	54.538	0.2830	110.174	5.9960	52.201
0.3767	109.714	6.2111	53.129	0.4003	116.854	6.5530	54.572	0.3804	111.045	6.0950	52.630
0.4755	110.774	6.2755	53.404	0.5003	116.818	6.5711	54.647	0.4795	111.970	6.2003	53.083
0.5762	111.910	6.3536	53.735	0.6003	116.829	6.5996	54.766	0.5801	112.948	6.3120	53.559
0.6790	113.130	6.4465	54.126	0.7002	116.889	6.6389	54.928	0.6825	113.977	6.4304	54.059
0.7838	114.441	6.5556	54.583	0.8002	116.998	6.6898	55.138	0.7865	115.058	6.5559	54.584
0.8908	115.850	6.6825	55.109	0.9001	117.157	6.7530	55.398	0.8924	116.188	6.6888	55.134
1.0000	117.368	6.8295	55.711	1.0000	117.368	6.8295	55.711	1.0000	117.368	6.8295	55.711

Table 5. Excess molar volume ($V_m^E/10^{-6} \text{ m}^3\text{mol}^{-1}$), excess isentropic compressibility ($\kappa_s/10^{-10} \text{ Pa}^{-1}$) and deviation in viscosity ($\Delta\eta/\text{mPa}\cdot\text{s}$) of EL + CHN, CHA and CHO at 303.15, 308.15, 313.15 and 318.15 K

x_1	V_m^E	$\Delta\kappa_s$	$\Delta\eta$	x_1	V_m^E	$\Delta\kappa_s$	$\Delta\eta$	x_1	V_m^E	$\Delta\kappa_s$	$\Delta\eta$
EL (1) + CHN (2)				EL (1) + CHA (2)				EL (1) + CHO (2)			
303.15 K											
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.0915	-0.1429	-0.0216	0.0221	0.1001	-0.0924	-0.0159	0.0174	0.0928	-0.0381	-0.0051	0.0143
0.1847	-0.2516	-0.0379	0.0398	0.2002	-0.1660	-0.0270	0.0307	0.1872	-0.0706	-0.0092	0.0265
0.2798	-0.3274	-0.0492	0.0531	0.3002	-0.2198	-0.0339	0.0401	0.2830	-0.0958	-0.0123	0.0352
0.3767	-0.3711	-0.0558	0.0628	0.4003	-0.2529	-0.0371	0.0465	0.3804	-0.1125	-0.0143	0.0400
0.4755	-0.3837	-0.0576	0.0681	0.5003	-0.2649	-0.0371	0.0489	0.4795	-0.1198	-0.0150	0.0414
0.5762	-0.3659	-0.0548	0.0660	0.6003	-0.2555	-0.0343	0.0473	0.5801	-0.1170	-0.0146	0.0391
0.6790	-0.3181	-0.0477	0.0572	0.7002	-0.2244	-0.0290	0.0407	0.6825	-0.1039	-0.0129	0.0343
0.7838	-0.2410	-0.0361	0.0440	0.8002	-0.1715	-0.0213	0.0311	0.7865	-0.0800	-0.0099	0.0265
0.8908	-0.1349	-0.0202	0.0253	0.9001	-0.0967	-0.0116	0.0176	0.8924	-0.0454	-0.0056	0.0149
1.0000	0.0000	0.0000	0.0000	1.0000	0.0000	0.0000	0.0000	1.0000	0.0000	0.0000	0.0000
308.15 K											
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.0915	-0.1711	-0.0384	0.0158	0.1001	-0.1364	-0.0251	0.0139	0.0928	-0.0855	-0.0151	0.0106
0.1847	-0.3070	-0.0687	0.0313	0.2002	-0.2368	-0.0444	0.0247	0.1872	-0.1504	-0.0269	0.0209
0.2798	-0.4069	-0.0910	0.0424	0.3002	-0.3038	-0.0583	0.0326	0.2830	-0.1955	-0.0354	0.0278

0.3767	-0.4702	-0.1049	0.0512	0.4003	-0.3397	-0.0666	0.0375	0.3804	-0.2213	-0.0406	0.0319
0.4755	-0.4957	-0.1104	0.0556	0.5003	-0.3464	-0.0694	0.0394	0.4795	-0.2284	-0.0423	0.0333
0.5762	-0.4820	-0.1072	0.0517	0.6003	-0.3259	-0.0668	0.0383	0.5801	-0.2173	-0.0408	0.0313
0.6790	-0.4277	-0.0950	0.0433	0.7002	-0.2797	-0.0586	0.0332	0.6825	-0.1885	-0.0358	0.0273
0.7838	-0.3308	-0.0734	0.0316	0.8002	-0.2091	-0.0448	0.0251	0.7865	-0.1424	-0.0273	0.0211
0.8908	-0.1891	-0.0419	0.0175	0.9001	-0.1156	-0.0253	0.0141	0.8924	-0.0795	-0.0154	0.0124
1.0000	0.0000	0.0000	0.0000	1.0000	0.0000	0.0000	0.0000	1.0000	0.0000	0.0000	0.0000
313.15 K											
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.0915	-0.1976	-0.0470	0.0109	0.1001	-0.1697	-0.0352	0.0106	0.0928	-0.1346	-0.0193	0.0077
0.1847	-0.3570	-0.0847	0.0216	0.2002	-0.3031	-0.0626	0.0191	0.1872	-0.2332	-0.0349	0.0151
0.2798	-0.4768	-0.1127	0.0311	0.3002	-0.3999	-0.0823	0.0257	0.2830	-0.2986	-0.0466	0.0217
0.3767	-0.5552	-0.1308	0.0383	0.4003	-0.4597	-0.0943	0.0293	0.3804	-0.3332	-0.0543	0.0260
0.4755	-0.5899	-0.1385	0.0412	0.5003	-0.4821	-0.0985	0.0309	0.4795	-0.3393	-0.0576	0.0280
0.5762	-0.5784	-0.1354	0.0389	0.6003	-0.4662	-0.0951	0.0295	0.5801	-0.3186	-0.0563	0.0263
0.6790	-0.5175	-0.1208	0.0324	0.7002	-0.4113	-0.0837	0.0251	0.6825	-0.2729	-0.0502	0.0227
0.7838	-0.4037	-0.0940	0.0225	0.8002	-0.3162	-0.0643	0.0187	0.7865	-0.2038	-0.0390	0.0172
0.8908	-0.2328	-0.0541	0.0114	0.9001	-0.1796	-0.0365	0.0104	0.8924	-0.1124	-0.0224	0.0096
1.0000	0.0000	0.0000	0.0000	1.0000	0.0000	0.0000	0.0000	1.0000	0.0000	0.0000	0.0000
318.15 K											
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.0915	-0.2296	-0.0583	0.0067	0.1001	-0.2184	-0.0454	0.0086	0.0928	-0.1808	-0.0280	0.0059
0.1847	-0.4186	-0.1056	0.0132	0.2002	-0.3875	-0.0815	0.0152	0.1872	-0.3160	-0.0503	0.0118
0.2798	-0.5643	-0.1415	0.0196	0.3002	-0.5083	-0.1082	0.0198	0.2830	-0.4081	-0.0668	0.0159
0.3767	-0.6633	-0.1654	0.0239	0.4003	-0.5812	-0.1252	0.0223	0.3804	-0.4594	-0.0773	0.0188
0.4755	-0.7117	-0.1765	0.0260	0.5003	-0.6065	-0.1323	0.0229	0.4795	-0.4716	-0.0816	0.0200
0.5762	-0.7048	-0.1739	0.0239	0.6003	-0.5840	-0.1291	0.0215	0.5801	-0.4465	-0.0794	0.0192
0.6790	-0.6373	-0.1565	0.0197	0.7002	-0.5131	-0.1150	0.0182	0.6825	-0.3856	-0.0705	0.0169
0.7838	-0.5026	-0.1229	0.0133	0.8002	-0.3930	-0.0893	0.0138	0.7865	-0.2901	-0.0545	0.0130
0.8908	-0.2932	-0.0714	0.0067	0.9001	-0.2225	-0.0513	0.0074	0.8924	-0.1613	-0.0312	0.0069
1.0000	0.0000	0.0000	0.0000	1.0000	0.0000	0.0000	0.0000	1.0000	0.0000	0.0000	0.0000

Table 6: Redlich–Kister coefficients ($A_j - 1$) and the standard deviations (σ) of excess parameters for the binary mixture of EL and CHN, CHA, CHO at temperatures of 303.15, 308.15, 313.15 and 318.15 K

	V_m^E	$\Delta\kappa_s$	$\Delta\eta$	V_m^E	$\Delta\kappa_s$	$\Delta\eta$	V_m^E	$\Delta\kappa_s$	$\Delta\eta$
	EL (1) + CHN (2)			EL (1) + CHA (2)			EL (1) + CHO (2)		
	303.15 K								
A0	-1.529	-22.933	0.273	-1.060	-14.85	0.196	-0.480	-6.022	0.165
A1	-0.203	-3.168	0.006	0.028	-2.898	-0.005	0.005	-0.146	0.023
A2	-0.031	-0.519	-0.082	0.014	-0.699	-0.025	0.025	0.145	0.006
A3	-0.005	-0.090	-0.006	0.005	-0.143	0.005	0.011	0.061	-0.020
A4	-0.001	-0.024	0.1034	0.001	-0.031	0.035	0.003	0.015	-0.016
σ	0.000001	0.00005	0.00050	0.000003	0.00005	0.00027	0.000005	0.00002	0.00017
	308.15 K								
A0	-1.984	-44.179	0.222	-1.386	-27.77	0.158	-0.910	-16.917	0.133
A1	-0.069	-1.860	0.028	-0.142	0.229	-0.004	-0.116	-1.185	0.019
A2	-0.024	-0.675	-0.130	-0.022	-0.358	-0.006	-0.014	-0.107	-0.008
A3	-0.002	-0.077	-0.035	-0.003	-0.016	0.005	-0.002	-0.012	-0.033
A4	-0.001	-0.025	0.1150	-0.001	0.008	0.003	-0.001	-0.007	0.000
σ	0.000002	0.00007	0.00082	0.000002	0.00011	0.00015	0.000002	0.00004	0.00027
	313.15 K								
A0	-2.366	-55.504	0.165	-1.928	-39.42	0.124	-1.349	-23.083	0.112
A1	0.012	-0.525	0.015	0.070	0.914	0.004	-0.260	0.261	0.009
A2	-0.030	-0.934	-0.095	-0.019	-0.697	-0.018	-0.048	-0.058	-0.042

A3	-0.001	-0.051	-0.008	0.002	0.019	-0.005	-0.009	0.006	-0.022
A4	-0.001	-0.029	0.0494	0.000	-0.019	0.010	-0.002	0.007	0.026
σ	0.000002	0.00009	0.00013	0.000002	0.00006	0.00019	0.000001	0.00005	0.00024
318.15 K									
A0	-2.861	-70.861	0.103	-2.426	-52.92	0.092	-1.878	-32.665	0.080
A1	0.158	2.101	0.016	0.031	4.084	0.010	-0.286	-0.480	0.001
A2	-0.046	-1.484	-0.069	-0.036	-1.225	-0.011	-0.047	-0.263	-0.011
A3	0.002	0.039	-0.012	0.0005	0.131	-0.002	-0.008	-0.028	-0.003
A4	-0.001	-0.044	0.0378	-0.001	-0.017	0.010	-0.002	0.015	-0.004
σ	0.000002	0.00011	0.00023	0.000002	0.00013	0.00016	0.000001	0.00007	0.00020

Table 7(a): Partial molar volumes ($V_{m,i}/10^{-6} \text{ m}^3\text{mol}^{-1}$) and excess partial molar volumes ($V_{m,i}^E/10^{-6}\text{m}^3\text{mol}^{-1}$) of EL + CHN, CHA and CHO mixtures at 303.15 and 308.15 K

x_1	303.15 K				308.15 K			
	$V_{m,1}$	$V_{m,2}$	$V_{m,1}^E$	$V_{m,2}^E$	$V_{m,1}$	$V_{m,2}$	$V_{m,1}^E$	$V_{m,2}^E$
Ethyl lactate + Cyclohexanone								
0.0000	114.151	104.699	-1.353	0.000	114.166	105.167	114.166	0.000
0.0915	114.339	104.690	-1.164	-0.009	114.495	105.152	114.495	-0.016
0.1847	114.524	104.661	-0.980	-0.039	114.797	105.103	114.797	-0.064
0.2798	114.702	104.606	-0.801	-0.093	115.073	105.020	115.073	-0.148
0.3767	114.873	104.523	-0.630	-0.177	115.321	104.898	115.321	-0.269
0.4755	115.033	104.404	-0.470	-0.296	115.540	104.735	115.540	-0.432
0.5762	115.179	104.241	-0.324	-0.458	115.729	104.526	115.729	-0.641
0.6790	115.306	104.027	-0.197	-0.673	115.883	104.266	115.883	-0.902
0.7838	115.408	103.748	-0.095	-0.952	116.001	103.945	116.001	-1.222
0.8908	115.477	103.389	-0.026	-1.311	116.076	103.557	116.076	-1.611
1.0000	115.503	102.930	0.000	-1.769	116.103	103.087	116.103	-2.081
Ethyl lactate + Cyclohexylamine								
0.0000	114.425	115.631	-1.078	0.000	114.839	116.236	-1.264	0.000
0.1001	114.635	115.620	-0.869	-0.011	115.044	116.225	-1.059	-0.011
0.2002	114.821	115.587	-0.682	-0.044	115.236	116.191	-0.867	-0.045
0.3002	114.986	115.532	-0.518	-0.099	115.413	116.131	-0.689	-0.104
0.4003	115.127	115.456	-0.376	-0.175	115.576	116.044	-0.527	-0.192
0.5003	115.246	115.359	-0.258	-0.272	115.721	115.924	-0.382	-0.311
0.6003	115.342	115.242	-0.162	-0.389	115.848	115.769	-0.255	-0.466
0.7002	115.415	115.106	-0.089	-0.525	115.953	115.574	-0.150	-0.662
0.8002	115.465	114.955	-0.038	-0.677	116.033	115.332	-0.070	-0.903
0.9001	115.494	114.790	-0.009	-0.841	116.084	115.038	-0.018	-1.198
1.0000	115.503	114.619	0.000	-1.012	116.103	114.683	0.000	-1.553
Ethyl lactate + Cyclohexanol								
0.0000	115.035	106.391	-0.468	0.000	115.295	106.874	-0.808	0.000
0.0928	115.111	106.388	-0.392	-0.004	115.410	106.868	-0.693	-0.006
0.1872	115.185	106.376	-0.318	-0.016	115.521	106.850	-0.581	-0.024
0.2830	115.254	106.354	-0.249	-0.037	115.629	106.817	-0.474	-0.057
0.3804	115.318	106.323	-0.186	-0.069	115.732	106.766	-0.371	-0.108
0.4795	115.374	106.280	-0.129	-0.111	115.828	106.693	-0.275	-0.181
0.5801	115.422	106.226	-0.081	-0.165	115.914	106.595	-0.188	-0.279
0.6825	115.460	106.162	-0.044	-0.229	115.989	106.467	-0.114	-0.407
0.7865	115.486	106.090	-0.018	-0.301	116.048	106.302	-0.054	-0.572

0.8924	115.500	106.018	-0.004	-0.374	116.088	106.093	-0.015	-0.781
1.0000	115.503	105.956	0.000	-0.436	116.103	105.831	0.000	-1.043

Table 7(b): Partial molar volumes ($V_{m,i}/10^{-6} \text{ m}^3\text{mol}^{-1}$) and excess partial molar volumes ($V_{m,i}^E/10^{-6} \text{ m}^3\text{mol}^{-1}$) of EL + CHN, CHA and CHO mixtures at 313.15 and 318.15 K

x_1	$V_{m,1}$	$V_{m,2}$	$V_{m,1}^E$	$V_{m,2}^E$	$V_{m,1}$	$V_{m,2}$	$V_{m,1}^E$	$V_{m,2}^E$
	313.15 K				318.15 K			
Ethyl lactate + Cyclohexanone								
0.0000	114.328	105.655	-2.408	0.000	114.300	106.152	-3.068	0.000
0.0915	114.768	105.634	-1.968	-0.021	114.910	106.123	-2.459	-0.029
0.1847	115.163	105.571	-1.573	-0.084	115.442	106.038	-1.927	-0.114
0.2798	115.514	105.465	-1.222	-0.190	115.901	105.900	-1.467	-0.253
0.3767	115.823	105.314	-0.913	-0.341	116.293	105.708	-1.075	-0.444
0.4755	116.089	105.117	-0.647	-0.539	116.621	105.465	-0.747	-0.687
0.5762	116.312	104.869	-0.424	-0.786	116.888	105.169	-0.480	-0.983
0.6790	116.491	104.568	-0.245	-1.088	117.096	104.819	-0.272	-1.333
0.7838	116.624	104.206	-0.112	-1.449	117.246	104.412	-0.122	-1.740
0.8908	116.707	103.777	-0.029	-1.878	117.337	103.943	-0.031	-2.209
1.0000	116.736	103.270	0.000	-2.385	117.368	103.404	0.000	-2.748
Ethyl lactate + Cyclohexylamine								
0.0000	114.717	116.845	-2.019	0.000	114.873	117.481	-2.495	0.000
0.1001	115.136	116.823	-1.601	-0.022	115.379	117.454	-1.989	-0.026
0.2002	115.496	116.760	-1.241	-0.085	115.815	117.377	-1.553	-0.103
0.3002	115.802	116.658	-0.934	-0.187	116.189	117.253	-1.179	-0.228
0.4003	116.060	116.519	-0.677	-0.326	116.506	117.082	-0.862	-0.399
0.5003	116.272	116.345	-0.464	-0.500	116.770	116.866	-0.598	-0.615
0.6003	116.442	116.137	-0.294	-0.708	116.985	116.603	-0.384	-0.877
0.7002	116.572	115.896	-0.164	-0.950	117.151	116.294	-0.217	-1.187
0.8002	116.664	115.621	-0.072	-1.224	117.271	115.934	-0.097	-1.547
0.9001	116.718	115.312	-0.018	-1.533	117.344	115.521	-0.025	-1.960
1.0000	116.736	114.969	0.000	-1.876	117.368	115.049	0.000	-2.432
Ethyl lactate + Cyclohexanol								
0.0000	115.607	107.388	-1.129	0.000	115.736	107.903	-1.633	0.000
0.0928	115.748	107.381	-0.988	-0.007	115.958	107.892	-1.410	-0.011
0.1872	115.890	107.358	-0.846	-0.030	116.177	107.856	-1.191	-0.047
0.2830	116.032	107.314	-0.704	-0.074	116.390	107.791	-0.978	-0.113
0.3804	116.172	107.245	-0.564	-0.144	116.595	107.688	-0.773	-0.215
0.4795	116.307	107.142	-0.429	-0.246	116.789	107.542	-0.579	-0.361
0.5801	116.434	106.998	-0.302	-0.390	116.967	107.341	-0.401	-0.563
0.6825	116.549	106.801	-0.187	-0.587	117.123	107.073	-0.245	-0.831
0.7865	116.644	106.537	-0.092	-0.851	117.249	106.722	-0.119	-1.181
0.8924	116.710	106.185	-0.026	-1.203	117.336	106.267	-0.033	-1.636
1.0000	116.736	105.720	0.000	-1.668	117.368	105.683	0.000	-2.220

Table 8(a): Reduced volume ($V/10^{-6} \text{ m}^3\text{mol}^{-1}$), characteristic volume ($V^*/10^{-6} \text{ m}^3\text{mol}^{-1}$) and characteristic pressure (P^*/MPa) of the pure components used in PFP theory

Liquids	303.15 K	308.15 K	313.15 K	318.15 K
Reduced volume (V)				
Ethyl lactate	1.2637	1.2684	1.2731	1.2778
Cyclohexanone	1.2329	1.2370	1.2411	1.2452
Cyclohexylamine	1.2610	1.2657	1.2703	1.2750
Cyclohexanol	1.2377	1.2419	1.2461	1.2504
Characteristic volume (V*)				
Ethyl lactate	91.4013	91.5376	91.6950	91.8505
Cyclohexanone	84.9237	85.0210	85.1311	85.2467
Cyclohexylamine	91.6948	91.8363	91.9801	92.1396
Cyclohexanol	85.9575	86.0571	86.1775	86.2973
Characteristic pressure (P*)				
Ethyl lactate	675.0	672.9	670.2	666.9
Cyclohexanone	599.1	597.9	596.5	594.7
Cyclohexylamine	641.5	640.3	638.8	637.0
Cyclohexanol	678.0	673.2	667.4	661.1

Table 8(b): Interaction parameter, χ_{12} , and the three contributions to the excess molar volume ($V_m^E/10^{-6} \text{ m}^3\text{mol}^{-1}$) at equi-molar mixture ($x = 0.5$) using PFP Theory (PFP) along with experimental V_m^E at different temperatures

Mixture	χ_{12}	V_m^E from PFP				V_m^E Exp
		IC	CC	IP	Total	
303.15 K						
EL + CHN	-33.03	-0.4341	0.0310	0.0807	-0.3844	-0.3821
EL + CHA	-19.05	-0.2672	0.0002	0.0031	-0.2644	-0.2649
EL + CHO	-7.52	-0.0943	0.0223	-0.0025	-0.1192	-0.1201
308.15 K						
EL + CHN	-40.45	-0.5469	0.0322	0.0815	-0.4976	-0.4960
EL + CHA	-24.23	-0.3501	0.0002	0.0030	-0.3473	-0.3465
EL + CHO	-15.82	-0.2048	0.0232	-0.0003	-0.2283	-0.2275
313.15 K						
EL + CHN	-46.08	-0.6417	0.0334	0.0820	-0.5931	-0.5915
EL + CHA	-32.61	-0.4855	0.0003	0.0030	-0.4827	-0.4821
EL + CHO	-23.75	-0.3178	0.0241	0.0025	-0.3393	-0.3371
318.15 K						
EL + CHN	-53.29	-0.7648	0.0347	0.0823	-0.7172	-0.7153
EL + CHA	-39.78	-0.6104	0.0003	0.0029	-0.6078	-0.6065
EL + CHO	-32.69	-0.4522	0.0249	0.0054	-0.4717	-0.4694

Table 9: Experimental saturated vapor pressure (P/kPa) – boiling point temperature (T/K) data of pure components (EL (x_1) + CHN, +CHA and +CHO)

Ethyl Lactate	Cyclohexanone	Cyclohexylamine	Cyclohexanol
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P/ kPa	T/ K	T/ K	T/ K	T/ K
95.32	425.65	426.67	405.49	431.97
89.62	423.65	424.45	403.33	429.94
81.48	420.60	421.07	400.05	426.86
75.33	418.11	418.32	397.39	424.36
68.27	415.03	414.94	394.11	421.29
59.98	411.04	410.57	389.89	417.33
54.05	407.88	407.13	386.57	414.22
48.38	404.57	403.53	383.10	410.97
40.87	399.62	398.19	377.95	406.16
33.92	394.27	392.46	372.43	401.02
27.84	388.74	386.58	366.79	395.76

Table 10: Antoine and Riedel constants of pure liquids obtained from experimental pressure – boiling point data(EL (x₁) + CHN, +CHA and +CHO)

Component	A	B	C	D	E
Ethyl lactate					
Antoine constants	14.6444	3411.9808	-87.4999		
Riedel constants	17.3094	5221.66	-0.1598	0.000003	2.0000
Cyclohexanone					
Antoine constants	13.8245	3163.4352	-85.3763		
Riedel constants	20.1079	6033.11	-0.0172	-0.00001	2.0000
Cyclohexylamine					
Antoine constants	15.7031	4346.7352	-15.4974		
Riedel constants	9.2714	3458.8	0.3729	0.00001	2.0000
Cyclohexanol					
Antoine constants	16.8037	4873.8766	-33.9451		
Riedel constants	8.9000	4001.58	0.4682	0.00001	2.0000

Table 11(a): Data on liquid phase mole fraction (x₁), boiling point temperature (T/K), vapor phase mole fraction (y₁), activity coefficients (γ₁ and γ₂) and excess Gibb's energies (G^E/Jmol⁻¹) at 95.3 kPa of EL (x₁) + CHN liquid mixture

x ₁	T _{cal} /K	y ₁	γ ₁	γ ₂	log (γ ₁ /γ ₂)	G ^E /J.mol ⁻¹
Ethyl lactate + Cyclohexanone						
0.0000	426.73	0.0000	0.8760	1.0000	-0.1323	0.000
0.0455	426.89	0.0418	0.8876	0.9997	-0.1189	-20.283
0.0915	427.02	0.0854	0.8987	0.9988	-0.1056	-38.616
0.1379	427.14	0.1307	0.9092	0.9973	-0.0925	-54.932
0.1847	427.24	0.1775	0.9193	0.9952	-0.0794	-69.209
0.2320	427.31	0.2257	0.9288	0.9925	-0.0664	-81.451
0.2798	427.36	0.2753	0.9377	0.9892	-0.0535	-91.623
0.3280	427.39	0.3259	0.9461	0.9854	-0.0406	-99.678
0.3767	427.40	0.3774	0.9540	0.9810	-0.0279	-105.607
0.4258	427.38	0.4296	0.9612	0.9760	-0.0153	-109.372
0.4755	427.34	0.4825	0.9679	0.9705	-0.0027	-110.958

0.5256	427.28	0.5357	0.9739	0.9645	0.0098	-110.327
0.5762	427.19	0.5890	0.9794	0.9579	0.0222	-107.455
0.6273	427.08	0.6423	0.9842	0.9508	0.0345	-102.313
0.6790	426.95	0.6954	0.9884	0.9432	0.0467	-94.855
0.7311	426.80	0.7481	0.9919	0.9351	0.0589	-85.083
0.7838	426.62	0.8003	0.9948	0.9266	0.0710	-72.930
0.8370	426.43	0.8517	0.9971	0.9176	0.0831	-58.389
0.8908	426.22	0.9022	0.9987	0.9081	0.0951	-41.397
0.9451	425.99	0.9517	0.9997	0.8982	0.1070	-21.957
1.0000	425.75	1.0000	1.0000	0.8879	0.1189	0.0000

Table 11(b): Data on liquid phase mole fraction (x_1), boiling point temperature (T/K), vapor phase mole fraction (y_1), activity coefficients (γ_1 and γ_2) and excess Gibb's energies (G^E/Jmol^{-1}) at 95.3 kPa of EL (x_1) + CHA liquid mixture

x_1	T _{cal} /K	y_1	γ_1	γ_2	log (γ_1/γ_2)	$G^E/\text{J.mol}^{-1}$
Ethyl lactate + Cyclohexylamine						
0.0000	405.48	0.0000	0.9151	1.0000	-0.0888	0.000
0.0501	406.40	0.0251	0.9237	0.9998	-0.0791	-14.187
0.1001	407.34	0.0522	0.9319	0.9991	-0.0696	-26.754
0.1501	408.30	0.0815	0.9396	0.9979	-0.0602	-37.747
0.2002	409.27	0.1131	0.9468	0.9963	-0.0510	-47.204
0.2502	410.25	0.1470	0.9535	0.9943	-0.0419	-55.103
0.3002	411.25	0.1834	0.9598	0.9919	-0.0330	-61.482
0.3503	412.27	0.2225	0.9656	0.9892	-0.0241	-66.367
0.4003	413.29	0.2642	0.9709	0.9860	-0.0155	-69.754
0.4503	414.32	0.3087	0.9757	0.9825	-0.0069	-71.671
0.5003	415.35	0.3561	0.9800	0.9786	0.0015	-72.133
0.5503	416.40	0.4065	0.9840	0.9744	0.0097	-71.156
0.6003	417.45	0.4599	0.9874	0.9699	0.0179	-68.754
0.6503	418.49	0.5163	0.9904	0.9651	0.0259	-64.942
0.7002	419.54	0.5758	0.9930	0.9600	0.0338	-59.745
0.7502	420.59	0.6386	0.9952	0.9547	0.0416	-53.158
0.8002	421.64	0.7046	0.9970	0.9490	0.0493	-45.201
0.8501	422.67	0.7737	0.9983	0.9432	0.0568	-35.909
0.9001	423.71	0.8460	0.9993	0.9371	0.0643	-25.256
0.9501	424.73	0.9215	0.9998	0.9307	0.0716	-13.273
1.0000	425.75	1.0000	1.0000	0.9242	0.0788	0.0000

Table 11(c): Data on liquid phase mole fraction (x_1), boiling point temperature (T/K), vapor phase mole fraction (y_1), activity coefficients (γ_1 and γ_2) and excess Gibb's energies (G^E/Jmol^{-1}) at 95.3 kPa of EL (x_1) + CHO liquid mixture

x_1	T _{cal} /K	y_1	γ_1	γ_2	log (γ_1/γ_2)	$G^E/\text{J.mol}^{-1}$
Ethyl lactate + Cyclohexanol						
0.0000	431.93	0.0000	0.9619	1.0000	-0.0388	0.000
0.0462	431.69	0.0531	0.9654	0.9999	-0.0351	-6.130
0.0928	431.45	0.1063	0.9687	0.9997	-0.0314	-11.691
0.1398	431.20	0.1595	0.9719	0.9992	-0.0277	-16.671
0.1872	430.94	0.2126	0.9750	0.9986	-0.0239	-21.055
0.2349	430.68	0.2655	0.9779	0.9978	-0.0202	-24.825
0.2830	430.40	0.3182	0.9806	0.9968	-0.0164	-27.978
0.3315	430.12	0.3706	0.9832	0.9957	-0.0127	-30.501
0.3804	429.82	0.4227	0.9855	0.9943	-0.0089	-32.381
0.4298	429.52	0.4745	0.9878	0.9928	-0.0051	-33.608
0.4795	429.21	0.5257	0.9898	0.9911	-0.0012	-34.163
0.5296	428.90	0.5764	0.9917	0.9891	0.0026	-34.038

0.5801	428.57	0.6265	0.9934	0.9870	0.0065	-33.220
0.6311	428.24	0.6760	0.9949	0.9847	0.0103	-31.692
0.6825	427.90	0.7248	0.9963	0.9822	0.0142	-29.443
0.7343	427.56	0.7728	0.9974	0.9794	0.0181	-26.459
0.7865	427.21	0.8200	0.9983	0.9765	0.0221	-22.730
0.8392	426.85	0.8664	0.9990	0.9734	0.0260	-18.232
0.8924	426.49	0.9119	0.9996	0.9701	0.0300	-12.949
0.9459	426.12	0.9564	0.9999	0.9665	0.0339	-6.888
1.0000	425.75	1.0000	1.0000	0.9628	0.0380	0.0000

Standard uncertainty in temperature $u(T) = 0.05$ K, combined standard uncertainty in composition $u(x) = 0.0001$, and pressure $u(P) = 0.05$ kPa at a confidence level of 95%

Table 12: Binary interaction parameters for the binary mixtures of EL + CHN, +CHA and +CHO using Wilson, NRTL, Van Laar and Margules models at a pressure of 95.3 kPa

Model	Binary interaction parameters	Ethyl lactate + Cyclohexanone	Ethyl lactate + Cyclohexylamine	Ethyl lactate + Cyclohexanol
Wilson	A_{12}	-167.3042	99.1148	-231.6568
	A_{21}	-248.9590	-376.9231	97.8152
NRTL (1)	Δg_{12}	-2221.09	-2007.69	-1401.23
	Δg_{21}	2514.49	2365.79	1550.09
	α_{12}	0.47	0.47	0.47
NRTL (2)	Δg_{12}	-2372.69	-2149.41	-1457.97
	Δg_{21}	2412.9	2288.25	1505.77
	α_{12}	0.3	0.3	0.3
NRTL (3)	Δg_{12}	-2461.96	-2007.69	-1490.76
	Δg_{21}	2344.76	2365.79	1478
	α_{12}	0.2	0.2	0.2
Van Laar	A	-0.1322	-0.3598	-0.1097
	B	-0.1187	-0.2172	-0.1293
Margules	A	-0.1247	-0.2674	-0.1166
	B	0.0068	0.0691	-0.0116
	D	-0.0012	-0.0179	0.0030

Figures:

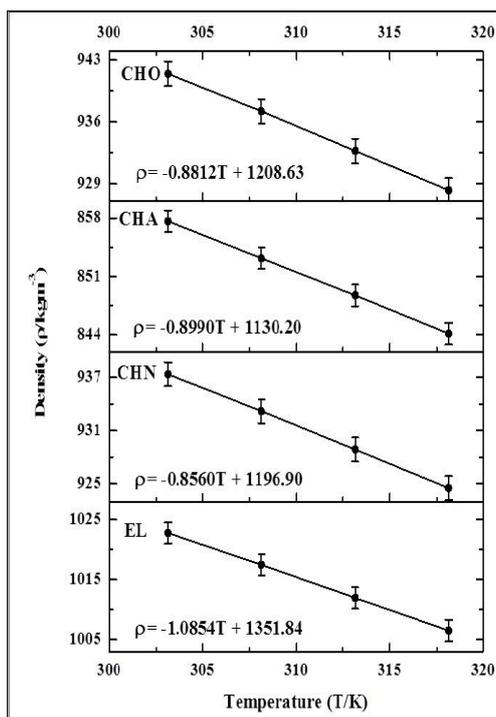
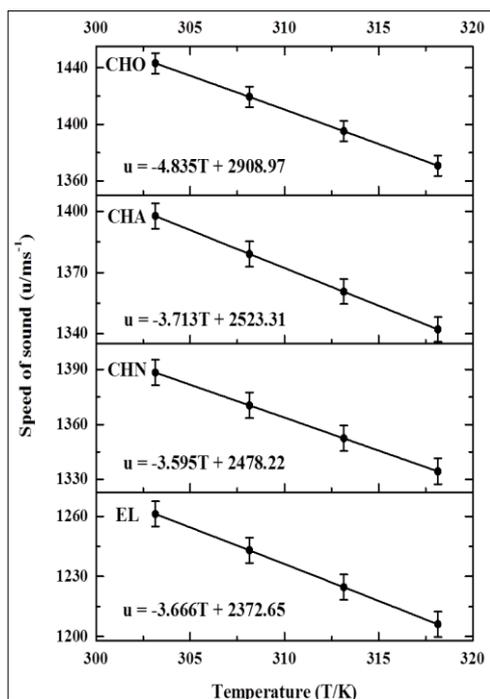


Fig.1 Speed of sound (U/ms⁻¹) of EL, CHN, CHA andCHOvs temperature (T/K)

Fig. 2 Density (ρ/kgm⁻³) of EL, CHN, CHA andCHOvs temperature (T/K)

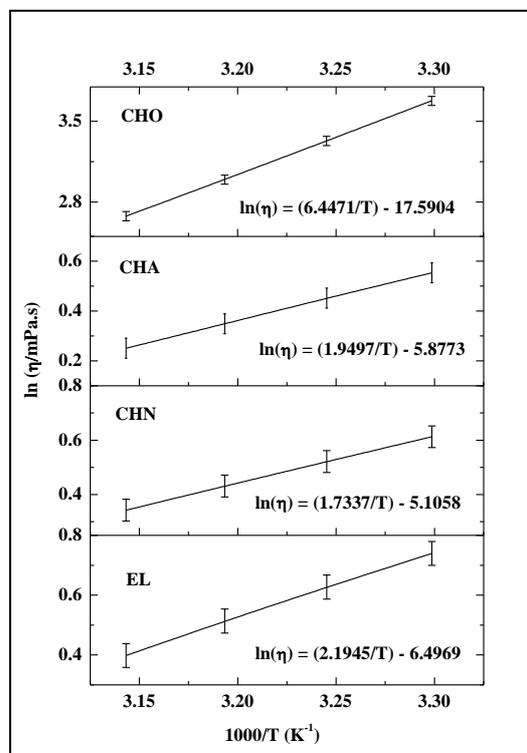


Fig. 3 $\ln(\eta)$ (coefficient of viscosity, η in mPa.s) vs $1000/T$ (T is temperature in K) of EL, CHN, CHA andCHO

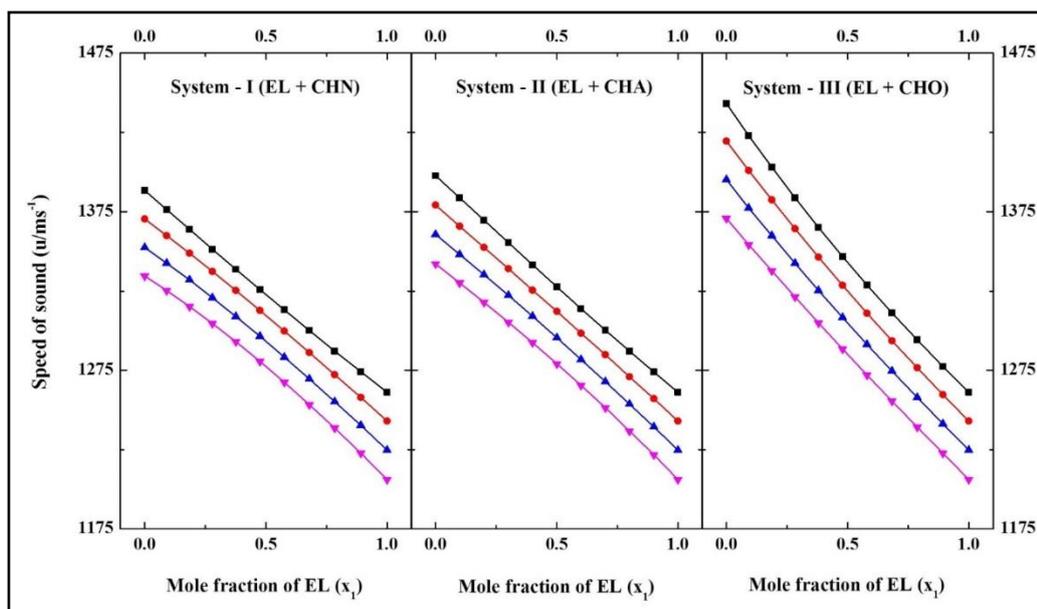


Fig. 4 Variation of speed of sound (U/ms^{-1}) of the binary mixtures of ethyl lactate (EL) + cyclohexanone (CHN), + cyclohexylamine (CHA) and + cyclohexanol (CHO) with the mole fraction of ethyl lactate at 303.15 K (■), 308.15 K (●), 313.15 K (▲) and 318.15 K (▼)

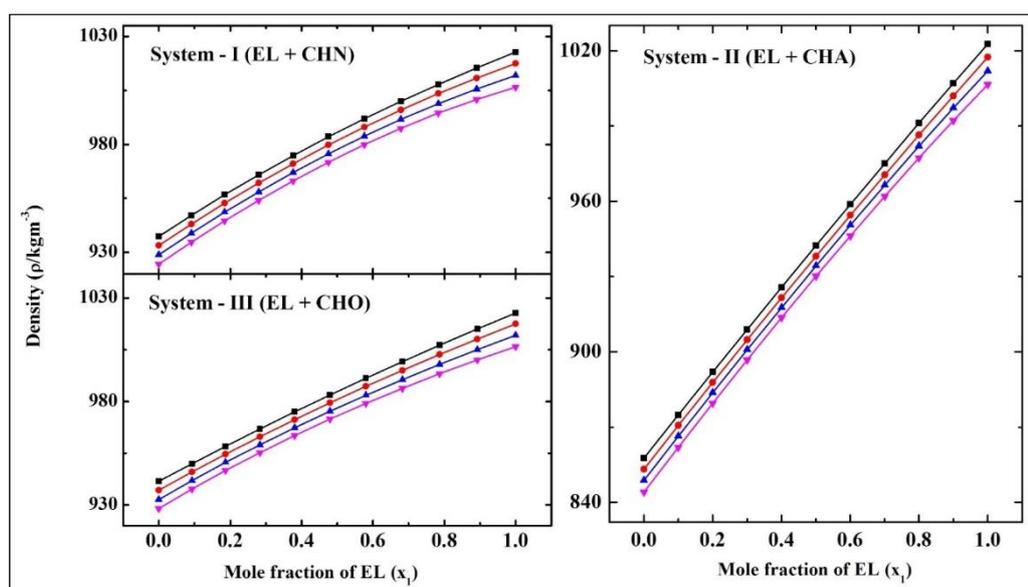


Fig. 5 Variation of density (ρ/kgm^{-3}) of the binary mixtures of ethyl lactate (EL) + cyclohexanone (CHN), + cyclohexylamine (CHA) and + cyclohexanol (CHO) with the mole fraction of ethyl lactate at 303.15 K (■), 308.15 K (●), 313.15 K (▲) and 318.15 K (▼).

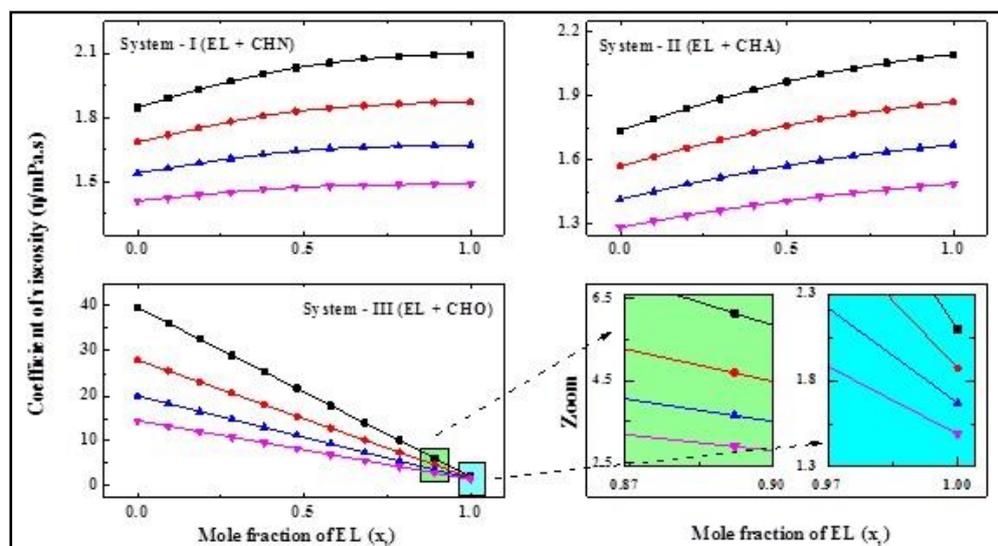


Fig. 6 Variation of coefficient of viscosity ($\eta/\text{mPa.s}$) of the binary mixtures of ethyl lactate (EL) + cyclohexanone (CHN), + cyclohexylamine (CHA) and + cyclohexanol (CHO) with the mole fraction of ethyl lactate at 303.15 K (■), 308.15 K (●), 313.15 K (▲) and 318.15 K (▼).

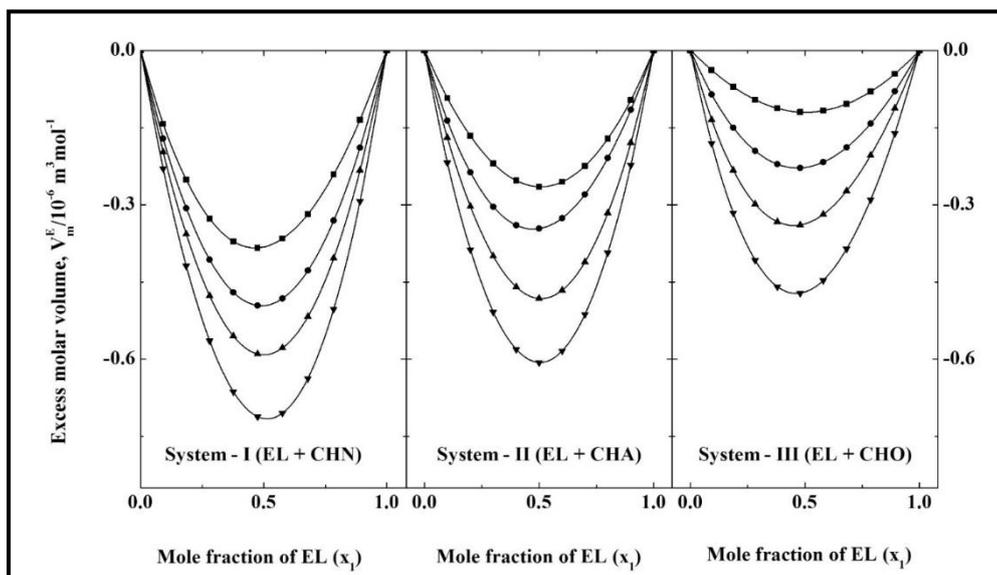


Fig. 7 Variation of excess molar volume ($V_m^E/10^{-6} \text{ m}^3 \text{ mol}^{-1}$) of the binary mixtures of ethyl lactate (EL) + cyclohexanone (CHN), + cyclohexylamine (CHA) and + cyclohexanol (CHO) with the mole fraction of ethyl lactate at 303.15 K (■), 308.15 K (●), 313.15 K (▲) and 318.15 K (▼).

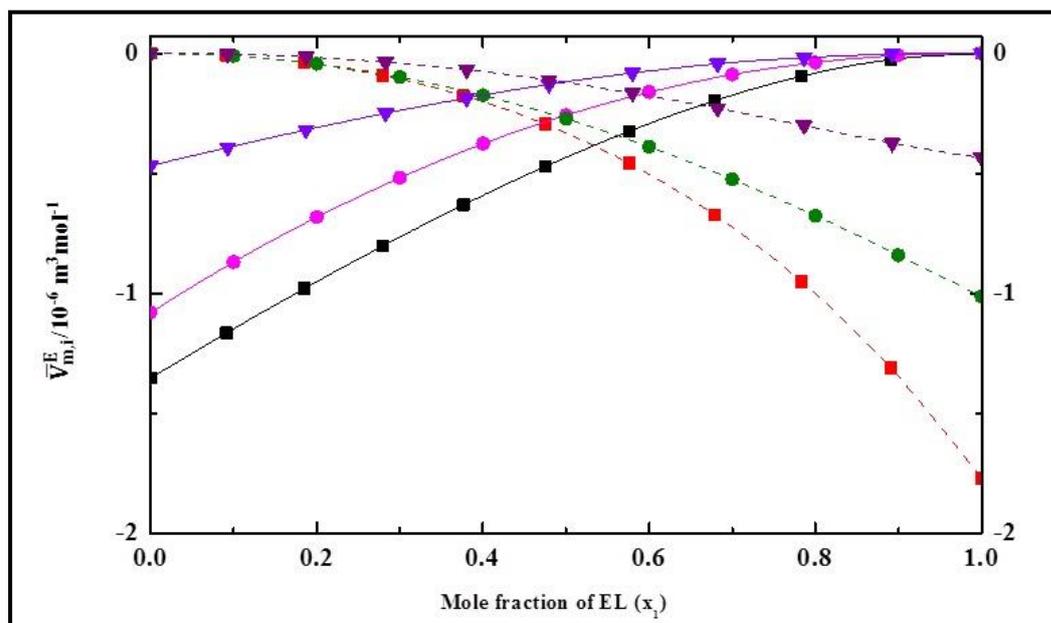


Fig. 8 Excess partial molar volumes ($\bar{V}_{m,1}^E/10^{-6} \text{ m}^3\text{mol}^{-1}$) of ethyl lactate (solid lines), in cyclohexanone (■), cyclohexylamine (●), cyclohexanol (▼), and excess partial molar volumes, $\bar{V}_{m,2}^E$ of cyclohexanone (■), cyclohexylamine (●), cyclohexanol (▼) in ethyl lactate (dotted lines) at 303.15 K against the mole fraction of ethyl lactate (x_1).

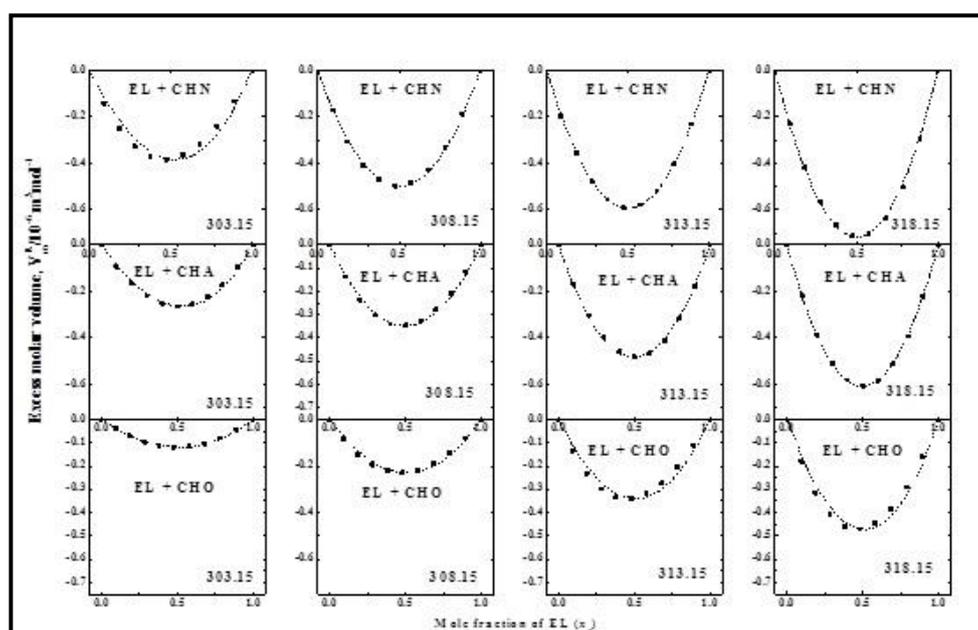


Fig. 9 Comparison of excess molar volume (V_m^E) of the binary mixtures of ethyl lactate + cyclohexanone (a), + cyclohexylamine (b) and + cyclohexanol (c) with the mole fraction of ethyl lactate at 303.15 K, 308.15 K, 313.15 K and 318.15 K. (■) experimental values; (-----), PFP calculations.

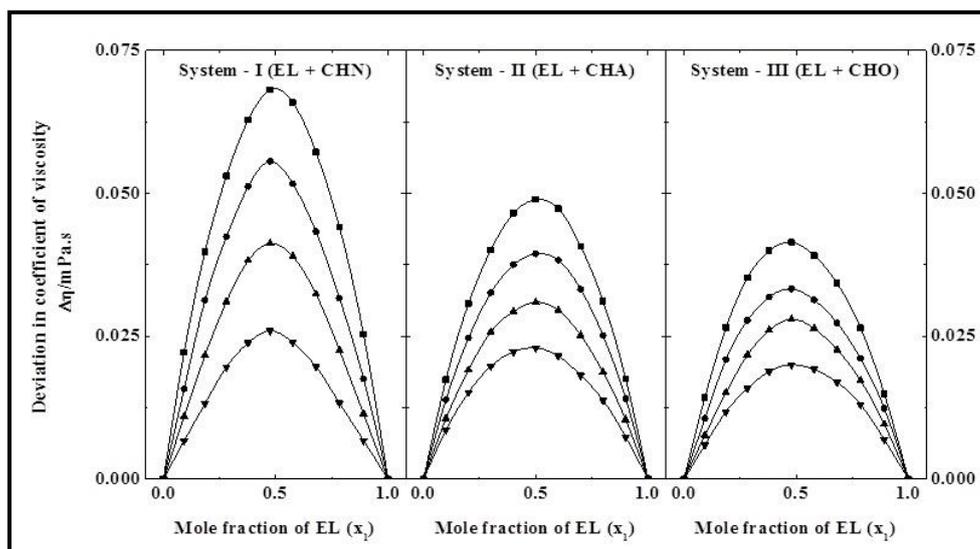


Fig. 10 Variation of deviation in coefficient of viscosity ($\Delta\eta/\text{mPa.s}$) of the binary mixtures of ethyl lactate (EL) + cyclohexanone (CHN), + cyclohexylamine (CHA) and + cyclohexanol (CHO) with the mole fraction of ethyl lactate at 303.15 K (■), 308.15 K (●), 313.15 K (▲) and 318.15 K (▼).

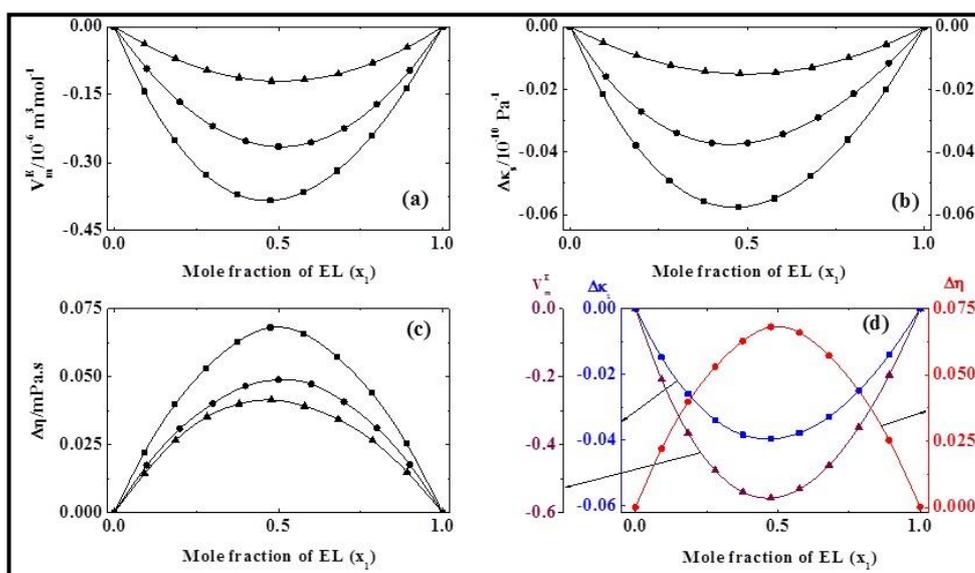


Fig. 11 Variation of (a) excess molar volume (V_m^E), (b) deviation in isentropic compressibility ($\Delta\kappa_s$) and (c) deviation in viscosity ($\Delta\eta$) of the binary mixtures of ethyl lactate + cyclohexanone (■), + cyclohexylamine (●) and + cyclohexanol (▲) with the mole fraction of ethyl lactate at 303.15 K. Fig. (d) represents the variation in these parameters for ethyl lactate + cyclohexanone at 303.15 K.

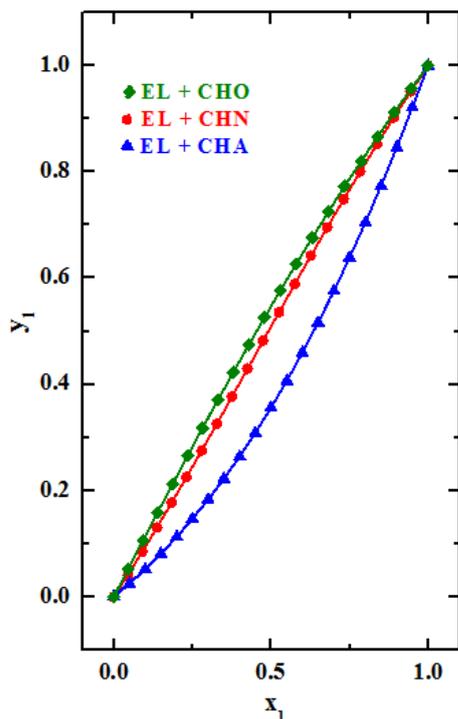


Fig. 12 Liquid phase mole fraction (x_1) vs vapor phase mole fraction (y_1) diagrams at a 95.3 kPa for system –I (EL + CHN, EL + CHA and EL + CHO)

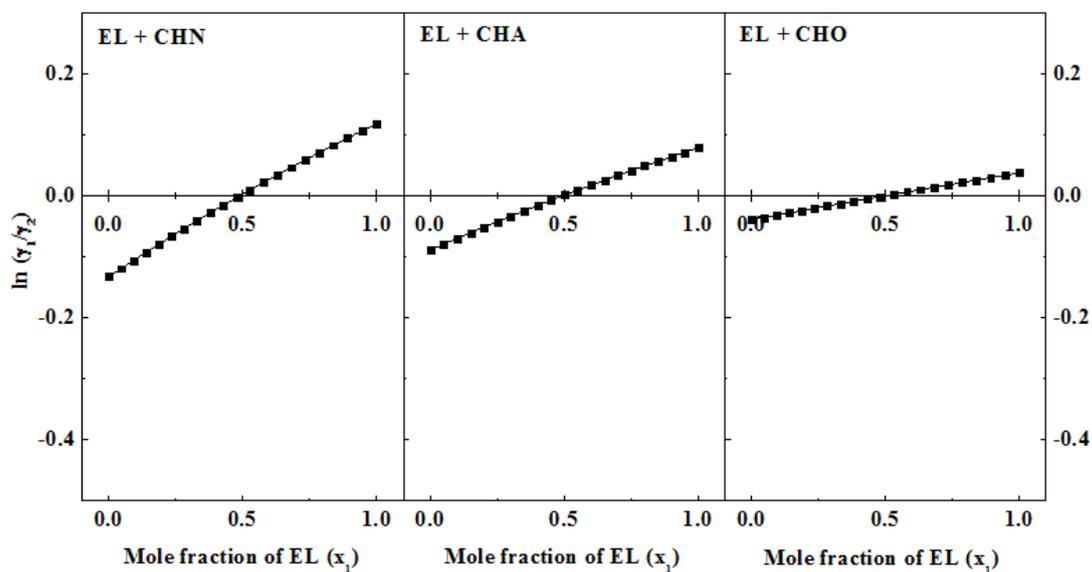


Fig. 13 Plot of $\ln(\gamma_1/\gamma_2)$ against mole fraction (x_1) of EL for EL + CHN, EL + CHA and EL + CHO.

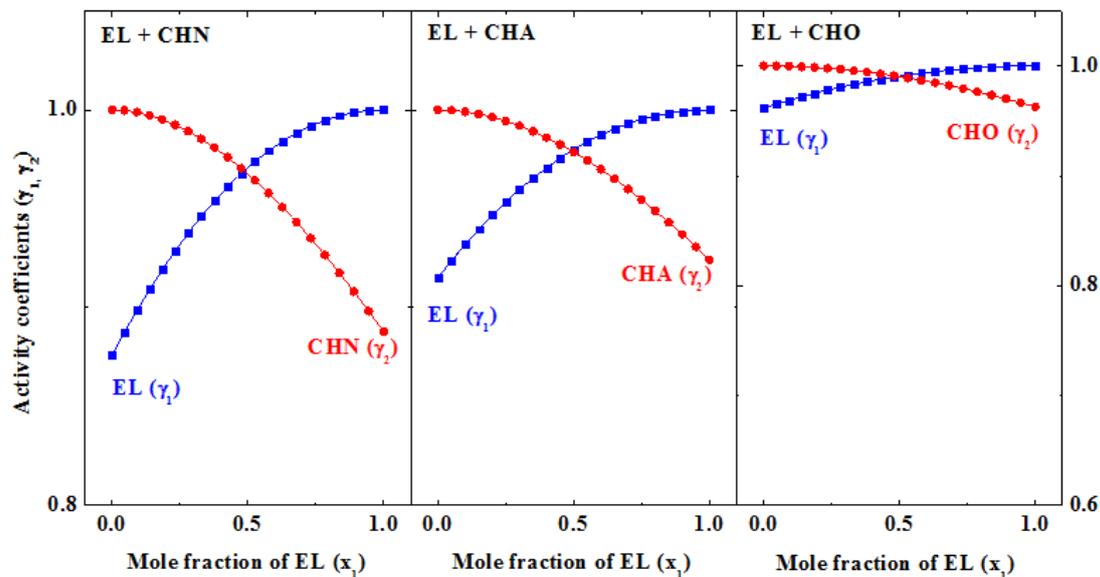


Fig. 14 Variation of Activity coefficients (γ_1, γ_2) with the mole fraction (x_1) of EL for EL + CHN, EL + CHA and EL + CHO.

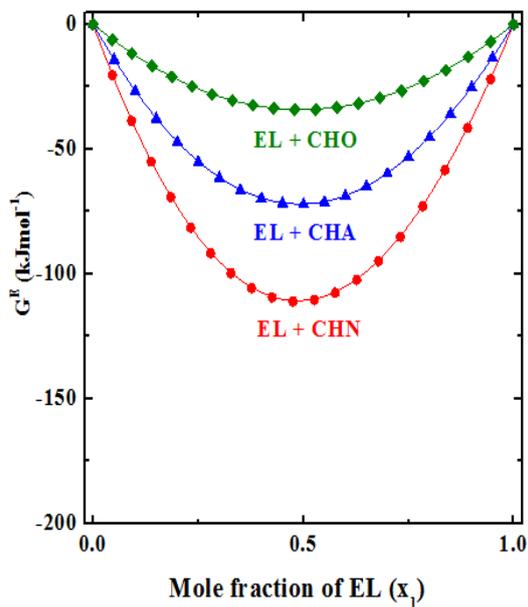


Fig. 15 Variation of excess Gibbs energy with mole fraction (x_1) of ethyl lactate for EL + CHN, EL + CHA and EL + CHO

References:

- [1] P.T. Anastas, J.C. Warner, *Green Chemistry: Theory and Practice*, Oxford University Press, Oxford (England), New York, 1998.
- [2] S.K. Sharma, A. Mudhoo, *Green Chem. for Env. Sustainability*, CRC Press, Boca Raton, 2011.
- [3] R. Hofer, J. Bigorra, *Green Chem.*, 9 (2007) 203.
- [4] J. David N. Cheeke, *Fundamentals and Applications of Ultrasonic Waves*, (CRC Press, New York, USA, 2002).
- [5] Ali A, Nain AK, Chand D, et al. Molecular interactions in binary mixtures of anisole with benzyl chloride, chlorobenzene and nitrobenzene at 303.15 K: An ultrasonic, volumetric, viscometric and refractive index study. *Indian J Chem.* 2005; 44:511–515.
- [6] Das M, Roy MN. Studies on thermodynamic and transport properties of binary mixtures of acetonitrile with some cyclic ethers at different temperatures by volumetric, viscometric, and interferometric techniques. *J. Chem. Eng. Data.* 2006; 51:2225–2232.
- [7] Roy MN, Sinha B, Dakua VK. Excess molar volumes and viscosity deviations of binary liquid mixtures of 1, 3-dioxolane and 1, 4-dioxane with butyl acetate, butyric acid, butyl amine, and 2-butanone at 298.15 K. *J Chem. Eng. Data.* 2006; 51:590–594.
- [8] Shukla RK, Atul Kumar, et al. Density, viscosity and refractive index of binary liquid mixtures at 293.15, 298.15, 303.15, 308.15 and 313.15 K, *Experimental Thermal and Fluid Science*, 2012; 37:1–11.
- [9] Oswal SL, Desai HS, Studies of viscosity and excess molar volume of binary mixtures: 4. 1-Alkanol + tri-n-butyl amine mixtures at 303.15 and 313.15 K, *Fluid Phase Equilib.*, 2003;204:281-294
- [10] Blanco B, Beltran SL, Cabezas JL, Vapor-liquid equilibria of coal-derived liquids. 3. Binary systems with tetralin at 200 mm mercury, *J. Chem. Eng. Data*, 1994;39:23-26.
- [11] Bland WB, Davison RL, *Petroleum Processing Handbook*; McGraw-Hill: New York, 1967.
- [12] Brignole EA, Bottini S, et al. A strategy for the design and selection of solvents for separation processes, *Fluid Phase Equilib.*, 1986; 29:125-132.
- [13] Ramadevi RS, Venkatesu P, Activity coefficients and excess Gibbs free energies for binary mixtures of N, N-dimethylformamide with substituted benzenes, *Thermochimica Acta*, 1996; 277:133-144.
- [14] Weng W, Chen J, et al. Isothermal Vapor–Liquid Equilibria of Binary Mixtures of Nitrogen with Dimethyl Sulfoxide, N-Methyl-2-pyrrolidone and Diethylene Glycol Monobutyl Ether at Elevated Pressures, *J. Chem. Eng. Data*, 2007;52:511-516.
- [15] Sharma SK, Mudhoo A, *Green Chem. for Env. Sustainability*, CRC Press, Boca Raton, 2011.
- [16] Hofer R, Bigorra J, *Green chemistry—a sustainable solution for industrial specialties Applications*, *Green Chem.*, 2007; 9:203.
- [17] Scientists Solve Solvent Production Puzzle, in *Industrial Paint & Powder*, 1998.
- [18] Pereira CSM, Silva VMTM, Rodrigues AE, Ethyl lactate as a solvent: properties, applications and production processes — a review, *Green Chem.*, 2011; 13:2658.
- [19] [19] Carla SM, Pereira M, Viviana MT, Silva M, Ethyl lactate as a solvent: Properties, applications and production processes – a review *Green Chem.*, 2011; 13:2658-2671.
- [20] Jyoti N. Nayak, Mrityunjaya I. Aralaguppi, Density, Viscosity, Refractive Index, and Speed of Sound in the Binary Mixtures of Ethyl Chloroacetate + Cyclohexanone, + Chlorobenzene, + Bromobenzene, or + Benzyl Alcohol at (298.15, 303.15, and

- 308.15) K, J. Chem. Eng. Data. 2003; 48:628-631
- [21] Patnaik P, A Comprehensive Guide to the Hazardous Properties of Chemical Substances, third ed., John Wiley & Sons, New Jersey, USA, 2007
- [22] Rathnam MV, Sayed RT, Bhanushali KR, Density and Viscosity of Binary Mixtures of n-Butyl Acetate with Ketones at (298.15, 303.15, 308.15, and 313.15) K J. Chem. Eng. Data, 2012; 57:1721-1727.
- [23] Laura Lomba, Beatriz Gínera, Thermophysical properties of lactates, *Thermochimica Acta* 2014; 575:305–312.
- [24] María del Carmen Grande, Jorge Alvarez Julia, Insight into the binary mixture of ethyl lactate+ acetonitrile from density, speed of sound and refractive index measurements, *Physics and Chemistry of Liquids*, 2018, <https://doi.org/10.1080/00319104.2018.1432050>
- [25] Emila M, Zivkovi C, Divna M, Volumetric and viscometric behavior of the binary systems ethyl lactate + 1,2-propanediol, +1,3-propanediol, +tetrahydrofuran and +tetraethylene glycol dimethyl ether. New UNIFAC–VISCO and ASOG–VISCO parameters determination, *Fluid Phase Equilibria.*, 2014;373:1–19.
- [26] Nikos G. Tsierkezos, Ioanna E. Molinou, Relative Permittivities, Speeds of Sound, Viscosities, and Densities of Cyclohexanone + cis-Decalin and Cyclohexanone + trans-Decalin Mixtures at 283.15, 293.15, and 303.15 K, *J. Chem. Eng. Data*, 2002;47:1492-1495.
- [27] Rathnam MV, Sayed TS, Density and Viscosity of Binary Mixtures of n-Butyl Acetate with Ketones at (298.15, 303.15, 308.15, and 313.15) K, *J. Chem. Eng. Data*, 2012; 57: 1721–1727.
- [28] Mohammad Almasi, Bahman Sarkoohaki, Densities and viscosities of binary mixtures of cyclohexanone and 2-alkanols, *J. Chem. Eng. Data*, 2012;57:309–316.
- [29] Rayapa Reddy K, Bala Karuna Kumar D, Srinivasa Rao G, Densities, viscosities, sound speed, and IR studies of N-methyl-2-pyrrolidone with cyclohexylamine, cyclohexanol, and cyclohexene at different temperatures, *Thermochimica Acta*, 2014;590:116–126.
- [30] Kijevcanin ML, Radovic IR, Experimental determination and modelling of densities and excess molar volumes of ternary system (1-butanol + cyclohexylamine + n-heptane) and corresponding binaries from 288.15 to 323.15 K, *J. Thermochimica Acta*, 2009;496:71–86.
- [31] Lide DR, Kehiaian HV, *CRC Handbook of Thermophysical and Thermochemical Data*, CRC Press, Boca Ratón, 1994.
- [32] Ali A, Nain AK, Chand D, Lal B, Ultrasonic, volumetric and viscometric studies of molecular interactions in binary mixtures of dimethylsulphoxide with polar substituted cyclohexanes at 30 C, *Physics and Chemistry of Liquids*, 2007;45:79–91.
- [33] Matsuda H, Fukano M, Kikkawa S, Gmehling J, Ebulliometric determination and prediction of (vapor + liquid) equilibria for binary and ternary mixtures containing alcohols (C1–C4) and dimethyl carbonate. *J. Chem. Thermodyn.*, 2012; 44:84-96.
- [34] Nelson SO, *Fundamentals of Dielectric Properties Measurements and Agricultural Applications Journal of Microwave Power and Electromagnetic Energy*, 2010; 44(2):98-113.
- [35] O. Redlich, A.T. Kister, *Industrial and Engineering Chemistry*, 40 (1948) 345-348.
- [36] D. Bala Karuna Kumar, K. Rayapa Reddy, G. Srinivasa Rao, Thermodynamic and spectroscopic study of molecular interactions in the binary liquid mixtures of N-methyl-2-pyrrolidone and some substituted benzenes at different temperatures, *Journal of Molecular Liquids* 174 (2012) 100–111
- [37] Toress RB, Pina CG, Application of PFP theory to excess molar volumes of acetonitrile with 1-alkanols *Journal of Molecular Liquids*, 2009;107:127–139.

- [38] P.J. Flory, J. Am. Chem. Soc. 87 (1965) 1833–1838.
- [39] Reddy VK, Reddy KS, Krishnaiah A, Excess volumes, speeds of sound, and viscosities for mixtures of 1, 2-ethanediol and alkoxy alcohols with water at 308.15 K, J. Chem. Eng. Data. 1994; 39:615-617.
- [40] Reddy GS, Reddy AS, Excess Volumes, Isentropic Compressibilities and Viscosities for Binary Mixtures of tert-Butylamine with Alkyl Acetates at 303.15 K, Journal of Solution Chemistry, 2010;39:399–408.
- [41] R.J. Fort, W.R. Moore, Viscosities of binary liquid mixtures, Transactions of the Faraday Society, 1966; 62:1112–1119.
- [42] Palczewska-Tulinska M, Oracz P, Vapor Pressures of 1-Methyl-2-Pyrrolidone, 1-Methylazepan-2-one, and 1, 2-Epoxy-3-chloropropane, J. Chem. Eng. Data, 2007; 52:2468-2471.
- [43] Alessandro Vetere, The Riedel equation, Ind. Eng. Chem. Res., 1991; 30: 2487-2492.
- [44] G.M. Wilson, Vapor-liquid equilibrium. XI. A new expression for the excess free energy of mixing, J. Am. Chem. Soc., 1964; 86:127-130.
- [45] C.C. Harrison, Vapor-liquid equilibria of nonideal solutions, P.C. Allan, Ind. Eng. Chem., 1942;34: 581-589.
- [46] H. Renon, J.M. Prausnitz, Estimation of parameters for the NRTL equation for excess Gibbs energies of strongly nonideal liquid mixtures, Ind. Eng. Chem. Process, 1969; 8:413-419.
- [47] J.J. van Laar, The vapor pressure of binary mixtures, Z. Phys. Chem., 1910;72:723-751.
- [48] Jaime Wisniak, The Herington test for thermodynamic consistency, Ind. Eng. Chem. Res., 1994;33(1):pp 177–180.