Densities and viscosities for binary mixtures of *n*-heptane with alcohols at different temperatures

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Abstract: Densities (ρ) and viscosities (η) of the binary systems *n*-heptane with alcohols (ethanol, propan-1-ol and propan-2-ol) were measured at temperatures between 288.15 and 308.15 K and at atmospheric pressure, over the whole composition range. The excess values of molar volume (V^E) and viscosity (η^E) were calculated from experimental measurements. The excess functions of the binary systems were fitted to Redlich–Kister Equation. Comparison between experimental excess molar volume and the one calculated from Flory and Prigogine–Flory–Patterson theories, has also been done. The viscosity results were fitted to the equations of Grunberg–Nissan, Heric–Brewer, Jouyban––Acree and McAllister. Also, the activation energies of viscous flow have been obtained and their variations with compositions have been discussed.

Keywords: *n*-heptane; ethanol; propan-1-ol; propan-2-ol; Flory theory; Prigogine–Flory–Patterson theory.

INTRODUCTION

Experimental liquid densities and viscosities of pure hydrocarbons and their mixtures are useful in the design and the simulation of processes. The physico-chemical properties play an important role in the understanding of several industrial processes.[1] Therefore, experimental measurements are needed to understand the fundamental behaviour of these properties and then to develop new models.[2] The obtained properties (excess molar volumes and excess viscosities) in combinations with other mixing properties provide valuable information for the qualitative analysis of the interactions between molecules.[3]

In this work, the densities and viscosities of three binary systems of *n*-heptane + ethanol or + propan-1-ol or propan-2-ol were measured at temperatures between 288.15 and 308.15 K, over the entire composition range and at atmospheric pressure. The investigations into the literature have shown that these systems have been studied, but not quite in the same conditions.

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Jimenez *et al.*[4] reported the values of viscosities and densities for propan-1--ol + *n*-heptane at 293.15, 298.15, 303.15 and 308.15 K. Keller *et al.*[5] investigated the excess molar volumes of propan-1-ol + *n*-heptane at 298.15 K and Tanaka *et al.*[6] studied excess molar volumes of propan-2-ol + *n*-heptane at the temperature 298.15 K. Pereiro *et al.*[7] reported densities for ethanol + *n*-heptane at 293.15, 298.15, 303.15 K and Orge *et al.*[8] studied densities and viscosities for ethanol + *n*-heptane and propan-1-ol + *n*-heptane at 298.15 K. Papaioannou *et al.*[9] presented densities for *n*-heptane + ethanol at 298.15 K and Zeberg-Mikkelsen *et al.*[10] investigated dynamic viscosities for ethanol + *n*-heptane at 293.15, 313.15, 333.15 and 353.15 K. Zielkiewicz[11] reported excess volumes of heptane + propan-2-ol at 313.15 K and Rajendran[12] studied density and viscosity of binary liquid mixtures of *n*-heptane with propan-2-ol at 298.15 K.

From our experimental data, the excess molar volumes and the excess viscosities were calculated and correlated by the Redlich–Kister Equation. The experimental data of excess volumes of the binary mixtures were used to test to applicability of Flory[13–16] and Prigogine–Flory–Patterson[17,18] theories, which has not previously been employed for the study of excess molar volume of binary mixtures of ethanol, propan-1-ol and propan-2-ol with *n*-heptane. The thermodynamic functions of activation of viscous flow have been estimated from the experimental data. The purpose of this paper is also to test five semiempirical equations with one to four parameters to correlate viscosity of binary mixtures.

EXPERIMENTAL

Materials

n-Heptane (mole fraction purity > 0.990) was supplied by Sigma–Aldrich, propan-1-ol (mole fraction purity > 0.999) was obtained from Merck, ethanol (mole fraction purity > 0.993) and propan-2-ol (mole fraction purity > 0.997) were supplied by Chemical Company. The chemicals were dried over molecular sieves (Fluka type 4 Å). The purity was checked through chromatographic analysis. Samples were determined by weighing at atmospheric pressure and ambient temperature using a Adventurer Pro AV 264CM balance with an uncertainty of and precision of $\pm 10^{-4}$ g. The error in the final mole fraction is estimated to be less than ± 0.0001. Conversion to molar quantities was based on the relative atomic mass table of 2006 issued by IUPAC.[19]

Measurements

The densities were determined by the hydrostatic weighing method of Kohlrausch[20] with the precision of ± 0.05 kg m^{-3}. The estimated uncertainty for density was ± 0.15 kg m^{-3}. The experimental technique has been previously described,[21] an ultra-thermostat type U10 (Freital) has been used to maintain a constant temperature (± 0.05 K). The uncertainty in the excess molar volume was estimated to be $\pm 5.5 \times 10^{-8}$ m^3·mol^{-1}. Viscosities of the pure compounds and of the binary mixtures were determined with an Ubbelohde kinematic viscometer,[22] viscosity measuring unit ViscoClock (Schott-Gerate GmbH), that was kept in a vertical position in a water thermostat. A thermostatically controlled bath (U10 constant to ± 0.05 K) was used. The kinematic viscosity was calculated using the relation (1):

$$v = At - B/t \qquad (1)$$

where t, in s, is the flowing time of a constant volume liquid through the viscometer capillary. Accuracy of time measurement for the viscosity measuring unit ViscoClock is ±0.01 s. A and B are characteristic constants of the used viscometer, which were determined by taking bidistilled water and benzene (Merck, mole fraction purity > 0.995) as the calibrating liquids for correction of kinetic energy deviations. The dynamic viscosity was determined from the Eq. (2):

$$\eta = v\rho \qquad (2)$$

where ρ is the density of the liquid. The precision of the viscosity was estimated to be ±0.001 mPa·s. In all determinations, triplicate experiments were performed at each composition and temperature, and the arithmetic mean was taken for the calculations of the viscosity. The uncertainty in the excess viscosity is estimated to be $\pm 4\times10^{-3}$ mPa·s.

RESULTS AND DISCUSSION

The measured densities and viscosities of the pure component liquids present good agreement with the literature values, as seen in Table S-I of the Supplementary material to this paper. Densities and viscosities of the binary mixtures of *n*-heptane + ethanol, *n*-heptane + propan-1-ol and *n*-heptane + propan-2-ol are reported in Table S-II of the Supplementary material. The results of this study are in close agreement with the values reported in the literature.

n-Heptane and ethanol densities values reported in the literature differ from our experimental data with a maximum of 0.09 %. For propan-1-ol, densities values published in the literature differ by less than 0.08 % and for propan-2-ol differ by less than 0.2 %.

Viscosity values reported in the literature differ than our results with a maximum 0.8 % for *n*-heptane, with maximum 2 % for ethanol, with maximum 1.5 % for propan-1-ol and with 0.6 % for propan-2-ol.

The excess molar volumes were calculated from the densities of the pure liquids and their mixtures using the following Eq. (3):

$$V^{E} = (xM_1+(1-x)M_2)/\rho - (xM_1/\rho_1+(1-x)M_2/\rho_2) \qquad (3)$$

where x is the mole fraction of a component 1, M_1 and M_2 are the molar masses of the components 1 and 2, and ρ, ρ_1 and ρ_2 are the respective densities of the solution and of the pure components.

The experimental values of the dynamic viscosity are used to calculate the excess viscosity (η^{E}) defined by the Eq. (4):

$$\eta^{E} = \eta - (x\eta_1+(1-x)\eta_2) \qquad (4)$$

where η_1 and η_2 are the viscosities of pure components.

The results of V^{E} and η^{E} are reported in Tables S-III and S-IV of the Supplementary material. The values of the excess molar volumes and the excess viscosities for the investigated binary mixtures in this work at 298.15 K show good agreement with the literature data.[4,8]

For the solution *n*-heptane + ethanol with $x \approx 0.4$, the deviation between calculated excess molar volume value and literature value[8] is 1.8 %, while for excess viscosity the corresponding deviation is 0.4 %. For the solution *n*-heptane + propan-1-olwith $x \approx 0.5$, the excess molar volume value reported in the literature[4] differs from our experimental data with 2.2 % and the excess viscosity value differs with 0.7 %.

The deviation between our excess molar volume value and the literature[12] value for the solution *n*-heptane + propan-2-ol with $x \approx 0.5$ is 10 % and for the excess viscosity is 5.0 %. These differences may be due to different purity of the components used and the differences in concentrations of solutions.

Figures S-1–S-6 of the Supplementary material present comparisons of our experimental excess molar volume and excess viscosity of *n*-heptane + ethanol, *n*-heptane + propan-1-ol and *n*-heptane + propan-2-ol at 298.15 K with data available in the literature.

The excess functions of the binary systems can be represented by a Redlich––Kister type equation:

$$X^{\mathrm{E}} = x_i x_j \sum_{k=0}^{3} A_{\mathrm{k}} \left(2x_i - 1\right)^k \tag{5}$$

where X^{E} represents any of the following properties: V^{E}, η^{E} and x_i and x_j are the mole fractions of the components *i* and *j*, respectively, and *k* is the number of the polynomial coefficient, A_k.

The values of these coefficients are indicated in Tables S-V and S-VI along with the standard deviation, σ, defined by relation:

$$\sigma = \left[\sum \left(X_{\mathrm{exp}} - X_{\mathrm{calc}}\right)^2 / \left(m - k\right) \right]^{1/2} \tag{6}$$

where X_{exp} is the experimental excess function, X_{calc} is the calculated excess function with Eq. (5), *m* is the number of data points and *k* is the number of the polynomial coefficient.

Several effects may contribute to the values of excess molar volumes, such as breaking of liquid order on mixing, unfavourable interactions between groups, differences in molecular volumes and differences in free volumes between liquids components.[23]

Fig. 1 shows experimental (Eq. (3)) and calculated values (Eq. (5)) of V^{E} at 298.15 K constant temperature.

The experimental excess molar volumes for all the binary mixtures studied in this work are positive in the whole composition range and at all temperatures. The positive values are due to the expansion of solution volume due to the mixing caused by the hydrogen bond rupture and the dispersive interactions between unlike molecules. In this sense, the addition of non-polar solvent causes the disruption of alcohol aggregates through the breaking of hydrogen bonds, making

V^{E} positive, since aggregates have higher volumes than the sum of their components.[24]
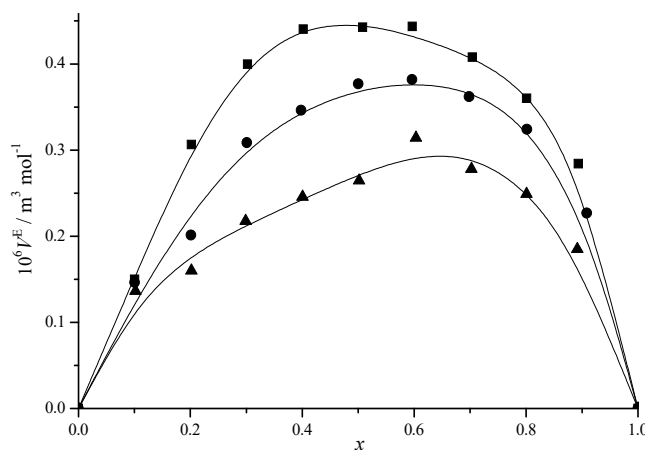

Fig. 1. Experimental excess molar volumes versus *n*-heptane mole fraction, *x*, at 298.15 K for the mixtures: ■) *n*-heptane + ethanol; ▲) *n*-heptane + propan-1-ol; ●) *n*-heptane + propan-2-ol. Continuous curve was calculated from Eq. (5) for experimental data.

The curves for *n*-heptane + propan-1-ol and *n*-heptane + propan-2-ol systems are asymmetric, with its maximum shift toward a high mole fraction of *n*-heptane; this behaviour agrees with the literature.[25–27] The excess molar volumes decreases with the increasing alkyl chain length of the alcohol. The excess molar volumes of *n*-heptane + propan-2-ol solutions is greater than the excess molar volumes of *n*-heptane + propan-1-ol mixtures. These behaviour is in accordance with the results of Ortega *et al.*[28] that showed that V^{E} values are greater when alkanes are mixed with secondary or tertiary alcohols than when they are mixed with primary alcohols. Breaking the hydrogen bonds by adding a non-polar solvent is more pronounced for propan-2-ol compared with propan-1-ol. This may explain the higher values of the excess molar volumes in propan-2-ol solutions than in propan-1-ol solutions. The effect of temperature on the V^{E} shows a systematic decrease with temperature for all the mixtures.

The excess viscosities values may be generally explained by considering the difference in size and shape of the component molecules and specific interactions between unlike molecules, such as H-bond formation and charge transfer complexes. These interactions may cause an increase in viscosity in mixtures, rather than in a pure component.[29] Positive values of excess viscosities indicate strong interactions, while negative values indicate weaker interactions.[30]

Fig. 2 shows experimental (Eq. (4)) and calculated values (Eq. (5)) of η^{E} at 303.15 K constant temperature.
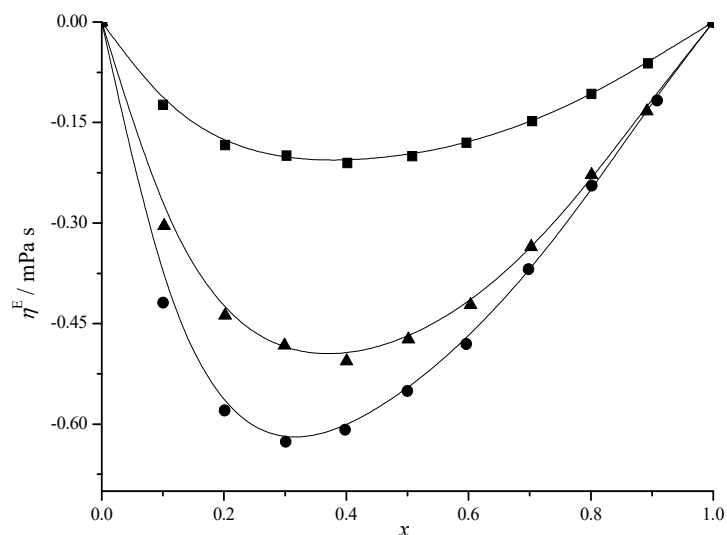
Fig. 2. Experimental excess viscosities versus *n*-heptane mole fraction, *x*, at 303.15 K for the mixtures: ■) *n*-heptane + ethanol; ▲) *n*-heptane + propan-1-ol; ●) *n*-heptane + propan-2-ol. Continuous curve was calculated from Eq. (5) for experimental data.

The excess viscosities are negative over the entire range of mole fractions at all the temperatures. The negative excess viscosity was explained by many authors through different forms.[31–34] The negative values support the main factor of breaking of the self-associated alcohols and weak interactions between unlike molecules.[35] The minimum of η^{E}–*x* curves occurs at low mole fractions of *n*-heptane. This behaviour is characteristic of binary mixtures formed by a component that presents a molecular association and the other component does not have this characteristic.[4] If the temperature increases the negative values of excess viscosity decrease. This can be explained by breaking the hydrogen bonds and increasing mobility of molecules due to the increase of thermal energy.[36]

Flory and Prigogine–Flory–Patterson (PFP) theories

Experimental results of the molar excess volume have been used to test the applicability of the Flory[13–16] and PFP theories.[17,18]

In the Flory theory, the excess molar volume is related to the reduced volume, $\widetilde{v}$, the reduced temperature, $\widetilde{T}$, and the adjustable interactional parameter χ_{12}. The PFP theory includes three contributions in order to explain the thermodynamic behaviour of the liquid mixtures: an interactional contribution ($V_{\mathrm{int}}^{\mathrm{E}}$), which is proportional to the interactional parameter χ_{12}, the free volume contribution ($V_{\mathrm{FV}}^{\mathrm{E}}$), which arises from the dependence of the reduced volume, upon the reduced temperature, as a result of the difference between the degree of expansion of the two components and the internal pressure contribution ($V_{p^{*}}^{\mathrm{E}}$),

which depends on both the difference of characteristic pressures and the reduced volumes of the components.

The excess molar volume given by the Flory theory is:

$$V^{E} = \frac{\left(x_1 V_1^* + x_2 V_2^*\right)\left(\phi_1 \tilde{v}_1 + \phi_2 \tilde{v}_2\right)^{7/3}\left(\tilde{T} - \tilde{T}^0\right)}{\left(4/3\right) - \left(\phi_1 \tilde{v}_1 + \phi_2 \tilde{v}_2\right)^{1/3}} \tag{7}$$

The PFP Equation is:

$$\frac{V^{E}}{x_1 V_1^* + x_2 V_2^*} = \frac{\left(\tilde{v}^{1/3} - 1\right)\tilde{v}^{2/3}}{\left[\left(4/3\right)\tilde{v}^{-1/3} - 1\right]}\psi_1\theta_2\frac{\chi_{12}}{p_1^*} -$$

$$- \frac{\left(\tilde{v}_1 - \tilde{v}_2\right)^2\left[\left(14/9\right)\tilde{v}^{-1/3} - 1\right]}{\left[\left(4/3\right)\tilde{v}^{-1/3} - 1\right]\tilde{v}}\psi_1\psi_2 +$$

$$\frac{\left(\tilde{v}_1 - \tilde{v}_2\right)\left(p_1^* - p_2^*\right)}{\psi_1 p_2^* + \psi_2 p_1^*}\psi_1\psi_2 = \frac{V_{\text{int}}^{E}}{x_1 V_1^* + x_2 V_2^*} + \tag{8}$$

$$+ \frac{V_{\text{FV}}^{E}}{x_1 V_1^* + x_2 V_2^*} + \frac{V_{p^*}^{E}}{x_1 V_1^* + x_2 V_2^*}$$

where $\tilde{v}$ is the reduced volume:

$$\tilde{v} = \left(\frac{\alpha T}{3\left(1 + \alpha T\right)} + 1\right)^3 \tag{9}$$

V^* – characteristic volume; p^* – characteristic pressure; $\tilde{T}$ – reduced temperature:

$$\tilde{T} = \frac{\phi_1 p_1^* \tilde{T}_1 + \phi_2 p_2^* \tilde{T}_2}{\phi_1 p_1^* + \phi_2 p_2^* - \phi_1 \theta_2 \chi_{12}} \tag{10}$$

$\tilde{T}^0$ – "ideal" reduced temperature for the mixture; ψ_i – contact energy fraction:

$$\psi_1 = 1 - \psi_2 = \phi_1 p_1^* \Big/ \left(\phi_1 p_1^* + \phi_2 p_2^*\right) \tag{11}$$

φ_i – hard core volume fraction:

$$\phi_2 = 1 - \phi_1 = x_2 V_2^* \Big/ \left(x_1 V_1^* + x_2 V_2^*\right) \tag{12}$$

θ_i – surface site fraction:

$$\theta_2 = 1 - \theta_1 = \phi_2 V_2^{*1/3} \Big/ \left(\phi_1 V_1^{*1/3} + \phi_2 V_2^{*1/3}\right) \tag{13}$$

The coefficient of thermal expansion, α, was obtained from the following equation:[37]

$$\alpha = (1/V)(\partial V/\partial T)_p \tag{14}$$

where V is the molar volume of the solution; T – temperature.

The various parameters involved in Eqs. (7) and (8) for the pure components and the mixture are obtained from Flory's theory[13,14] and are shown in Tables S-VII and S-VIII of the Supplementary material.

The values of the interaction parameter χ_{12}, were derived by fitting the theory to experimental values of the excess molar volume for equimolar solutions. The results of V^E calculated from Eqs. (7) and (8) are reported in Table S-IX of the Supplementary material. These results were compared by means of the percentage absolute average deviation (ADD), with the following equation:

$$ADD = \frac{100}{n} \sum_{i=1}^{n} \frac{\left|Q_{\text{exp}} - Q_{\text{calc}}\right|}{Q_{\text{exp}}} \tag{15}$$

where n is the number of experimental data and Q represents V^E.

The results in Table S-IX reveal that ADD values in the predictions of the excess molar volume for n-heptane + ethanol mixtures are less than 0.9 % using the Flory theory and less than 1.2 % using PFP theory. For n-heptane + propan-1--ol system the ADD value is 0.7 % using the Flory theory and less than 2.2 % using PFP theory. For n-heptane + propan-2-ol system the ADD values are less than 0.7 % for Flory theory and less than 1.4 % using PFP theory. These low values of percentage absolute average deviation obtained, suggest the validity of these theories. An analysis of each of the three contributions to excess molar volume shows that the interaction contribution is positive, being the most important contribution. The volume contribution is positive, while the internal pressure contribution is negative.

The viscosity data correlation

Several empirical and semiempirical relations have been used to represent the dependence of viscosity on the concentration of components in binary systems. These relations are classified according to the number of the adjustable parameters used to account for the deviation from some average.[38,39]

Grunberg-Nissan[40] proposed the following equation based on one parameter:

$$\ln\eta = x_1\ln\eta_1 + x_2\ln\eta_2 + x_1 x_2 d \tag{16}$$

Heric-Brewer[41] expression with two parameters is:

$$\ln\eta = x_1\ln\eta_1 + x_2\ln\eta_2 + x_1\ln M_1 + x_2\ln M_2 - \ln(x_1 M_1 + x_2 M_2) + x_1 x_2 [\alpha_{12} + \alpha_{21}(x_1 - x_2)] \tag{17}$$

The three-body McAllister[42] Equation with two parameters is:

$$\ln \eta = x_1^3 \ln \eta_1 + 3x_1^2 x_2 \ln \eta_{12} + 3x_1 x_2^2 \ln \eta_{21} + x_2^3 \ln \eta_2 -$$
$$-\ln\left[x_1 + x_2 M_2 / M_1\right] + 3x_1^2 x_2 \ln\left[\left(2 + M_2 / M_1\right) / 3\right] + \qquad (18)$$
$$+3x_1 x_2^2 \ln\left[\left(1 + 2M_2 / M_1\right) / 3\right] + x_2^3 \ln\left[M_2 / M_1\right]$$

We tested also the four-body McAllister Equation with three parameters:

$$\ln \eta = x_1^4 \ln \eta_1 + 4x_1^3 x_2 \ln \eta_{1112} + 6x_1^2 x_2^2 \ln \eta_{1122} + 4x_1 x_2^3 \ln \eta_{2221} +$$
$$x_2^4 \ln \eta_2 - \ln\left[x_1 + x_2 M_2 / M_1\right] + 4x_1^3 x_2 \ln\left[\left(3 + M_2 / M_1\right) / 4\right] +$$
$$6x_1^2 x_2^2 \ln\left[\left(1 + M_2 / M_1\right) / 2\right] + 4x_1 x_2^3 \ln\left[\left(1 + 3M_2 / M_1\right) / 4\right] + \qquad (19)$$
$$+x_2^4 \ln\left[M_2 / M_1\right]$$

and Jouyban Acree[43,44] Equation with four parameters:

$$\ln \eta = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 \sum_{j=0}^{n}\left(A_j \left(x_1 - x_2\right)^j / T\right), \; n = 3 \qquad (20)$$

In the Eqs. (16)–(20) the dynamic viscosity of the liquid mixture is designated by η and η_1 and η_2 are the dynamic viscosities, x_1 and x_2 are the mole fractions of the pure components 1 and 2 constituting the liquid mixture, M_1 and M_2 are the molecular masses, T is the temperature; d, α_{12}, α_{21} and A_j are interaction parameters (viscosity coefficients) and reflect the non-ideality of the system and the McAllister model adjustable parameters are given by η_{12}, η_{21}, η_{1112}, η_{1122} and η_{2221}. The parameters that appear in Eqs. (16)–(20) were estimated using the experimental viscosity data and a non-linear regression analysis employing the Levenberg–Marquardt algorithm.[45]

Table S-X of the Supplementary material shows the parameters calculated, the standard deviations (σ) and the *ADD* values between experimental values and those obtained using the semiempirical relations. The standard deviation was calculated using the Eq. (6), were X_{exp} is the experimental viscosity, X_{calc} is the calculated viscosity with Eqs. (16)–(20) and k is the number of adjustable parameters. The *ADD* values were determined for all equations with the Eq. (15), were Q represents the values of viscosity.

The interactional parameter, d, is negative for binary systems. Nigam and Mahl[46] concluded from the study of binary mixtures that if $\eta^E < 0$, $d < 0$ and magnitude of both are large then the dispersion force would be dominant. Applying the model with one parameter (Grunberg–Nissan model) gives the highest values of standard deviation. Models with two parameters (Heric–Brewer and three body McAllister model) lead to the identical result of standard deviation and their application leads to a poor estimate of viscosities solutions. These models are not suitable to estimate viscosities of the systems studied in this work.

Use of three and four parameter equations reduces the σ values. The data show that the Jouyban–Acree model is suitable for 288.15, 298.15 and 303.15 K, while the four body McAllister model is adequate at 293.15 and 308.15 K for *n*-heptane and ethanol system. The Jouyban–Acree model shows the best agreement with experimental data for *n*-heptane + propan-1-ol system at all temperatures. A comparison of the calculated and the experimental viscosities for the *n*-heptane + propan-2-ol mixtures shows that the Jouyban–Acree model produces accurate results for 288.15, 293.15, 303.15 and 308.15 K, while for 298.15 K the four-body McAllister model is able to describe viscosities. It can be concluded from this study that the correlating ability significantly improves for these non-ideal systems, as the number of adjustable parameters is increased.

Thermodynamic functions of activation

The energies of activation of viscous flow for the binaries studied were calculated using the following Eq. (21):[47]

$$\eta = \frac{hN}{V}\exp\left(\frac{\Delta G^{\neq}}{RT}\right) \tag{21}$$

where η is viscosity of a liquid mixtures, h is Planck's constant, N is Avogadro's number, V is the molar volume of the solution, R is universal gas constant, T is temperature and $\Delta G^{\neq}$ is Gibbs energy change of activation for viscous flow process. The combination yields the equation:

$$\ln\left(\frac{\eta V}{hN}\right) = \frac{\Delta H^{\neq}}{RT} - \frac{\Delta S^{\neq}}{R} \tag{22}$$

where $\Delta H^{\neq}$ and $\Delta S^{\neq}$ are enthalpy and entropy changes of activation of viscous flow.

The plots of $\ln(\eta V/hN)$ *vs.* $1/T$ were found to be linear in the temperature range 288.15 to 308.15 K, as such the values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ were obtained by the corresponding slopes and the intercepts. With $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values as input in Eq. (22), the corresponding values of $\Delta G^{\neq}$ were also calculated. The values of thermodynamic functions of activation of viscous flow and of correlation coefficient (r) are listed in Table S-XI of the Supplementary material as a function of composition. The experimental values of $\Delta G^{\neq}$ against mole fraction are presented in Figs. S-7–S-9 of the Supplementary material.

The values of $\Delta H^{\neq}$ are more than two times higher for ethanol and propan-1-ol than for *n*-heptane, while for propan-2-ol the values are more than three times higher than that for *n*-heptane, indicating that the association and the dipole–dipole interactions increase the value of $\Delta H^{\neq}$.

The value of $\Delta S^{\neq}$ is negative for *n*-heptane and positive for ethanol, propan-1-ol and propan-2-ol and shows that the overall molecular order increases for *n*-heptane (non-associating component) due to activated complex formation, but

decreases in the case of ethanol, propan-1-ol and propan-2-ol. The positive $\Delta S^{\neq}$ for all alcohols indicated that probably the rupturing of hydrogen bonds formed through OH groups of alcohols in the activation process for viscous flow occurs, resulting in the structural disorder.[48] The values of $\Delta H^{\neq}$ and $\Delta G^{\neq}$ are positive for all the binary mixtures and at all temperatures used. These values of Gibbs energy and enthalpy change of activation of viscous flow increase with the alcohol concentration of solution at constant temperature. The values of $\Delta G^{\neq}$ at constant concentration decrease if the temperature increases, in accord with the viscosity variation, except for the mixtures concentrated in alcohols. The values of $\Delta S^{\neq}$ are negative for all binary mixtures except for the mixtures concentrated in alcohols. These values show that overall molecular order due to activated complex formation increases for all binary mixtures except for the mixtures concentrated in alcohols.[49]

The excess Gibbs energy change of activation of viscous flow, $\Delta G^{\neq E}$, were obtained from following equation:

$$\Delta G^{\neq E} = RT[\ln \eta V - (x \ln \eta_1 V_1 + (1-x) \ln \eta_2 V_2))] \tag{23}$$

where V is the molar volume of the mixture and V_1 and V_2 are the respective molar volumes of the pure components. The $\Delta G^{\neq E}$ parameter may be considered as a valid measure to detect the presence of an interaction between molecules.[50,51] Negative values were observed for the excess Gibbs energy change of activation of viscous flow of the all the binary mixtures and at all temperatures studied. These values lead us to conclude that dispersion forces are the predominant in these systems. The experimental values of $\Delta G^{\neq E}$ against mole fraction are presented in Figs. S-10–S-12 of the Supplementary material.

CONCLUSIONS

The densities and viscosities of binary mixtures of *n*-heptane with alcohols (ethanol, propan-1-ol and propan-2-ol) were measured experimentally at temperatures between 288.15 and 308.15 K over the entire composition range. From these results, the excess values of molar volume and viscosity have been determined and fitted into the Redlich–Kister equation. Positive deviations were observed for the excess molar volumes and negative deviations for the excess dynamic viscosity, at all of the temperatures and in the whole concentration range. The experimental results of the molar excess volume have been used to test the applicability of the Flory and Prigogine–Flory–Patterson theories. The values of the percentage absolute average deviation obtained suggest the validity of these theories. Grunberg–Nissan, Heric–Brewer, Jouyban–Acree, three-body and four--body McAlister models have been used to calculate viscosity coefficients and these were compared with the experimental data for the mixtures. The results of these correlations showed that Jouyban–Acree and four-body McAllister models are suitable to describe viscosities of the binary mixtures studied in this work.

The energies of activation of viscous flow and the excess molar Gibbs energies of activation of viscous for these binary mixtures were also calculated. The values of $\Delta H^{\neq}$ and $\Delta G^{\neq}$ are positive for all the binary mixtures at all of the temperatures and in the whole concentration range. The values of $\Delta S^{\neq}$ are negative for all binary mixtures, except for the mixtures concentrated in alcohols. The negative deviations were observed for $\Delta G^{\neq E}$ of the all systems and at all of the temperatures.

ИЗВОД

ГУСТИНЕ И ВИСКОЗНОСТИ БИНАРНИХ СМЕША *n*-ХЕПТАНА СА АЛКОХОЛИМА НА РАЗЛИЧИТИМ ТЕМПЕРАТУРАМА

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Густине (ρ) и вискозности (η) бинарних система *n*-хептана са алкохолима (етанол, пропан-1-ол и пропан-2-ол) су измерене на температурама између 288,15 и 308,15 K и на атмосферском притиску. При мерењу је покривен цео концентрациони опсег испитиваних смеша. Допунске вредности моларне запремине (V^{E}) и вискозности (η^{E}) израчунате су из експерименталних података. Допунске функције бинарних система корелисане су Redlich–Kister једначином. Урађено је поређење између експерименталних допунских функција бинарних система и израчунатих помоћу Flory и Prigogine–Flory––Patterson теорија. Експериментални резултати вискозности корелисани су помоћу једначина Grunberg–Nissan, Heric–Brewer, Jouyban–Acree и McAllister. Такође, израчунате су активационе енергије вискозног тока бинарних система и дискутован је утицај састава смеше на њих.

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