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***Research Article***

# Thermodynamic Properties of Ethanol + Pyridine, Ethanol + Benzene, and Pyridine + Benzene Mixtures at Temperature 298.15 K and Under Atmospheric Pressure

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## Abstract

Experimental densities, viscosities, refractive indices, and sound speeds at temperature 298.15 K and atmospheric pressure are reported for the binary liquid mixtures of ethanol + benzene, ethanol + pyridine, and benzene + pyridine. From these experimental data, various thermodynamic excess and deviation properties were calculated and fitted by the Redlich-Kister polynomial to determine the adjustable coefficients and the standard deviations. The number of Redlich-Kister coefficients for significantly representing each thermodynamic property was optimized by applying the F-test. The variation of thermodynamic excess and deviation properties with composition has been interpreted in terms of molecular interactions between components of the mixture and structural effects. Furthermore, several theoretical and semi-empirical models were used to predict the refractive indices and sound speeds of the investigated mixtures. The predicting ability of each model was ascertained in terms of mean absolute percentage deviation between experimental and calculated data.

***Keywords:*** *Redlich-Kister polynomials; thermodynamic properties; binary mixtures; refractive index; sound speed; F-test.*

## 1. Introduction

The work described in this paper belongs to a systematic study program concerning the measurement and mathematical description of various thermodynamic properties of binary and ternary liquid mixtures containing important compounds [1-3]. The study of thermodynamic properties of binary mixtures of alkanols with aromatics is of great importance both from a practical and theoretical point of view. For example, an increase in the conversion of refined coal and oil yield is observed when raw mined coal is thermally pretreated with a mixture of benzene and ethanol [4]. A mixture of benzene with ethanol is also widely used to extract volatiles in the pulp and paper industry and diesel exhaust particulates [5]. On the other hand, applying pyridine as a fuel additive has improved the coking resistance of SOFCs with Ni cermet anode operating on ethanol fuels [6]. Thorough knowledge of liquid mixtures' thermodynamic properties is also essential for the design and setup of separation processes and process equipment. It will contribute to the fundamental understanding of complex molecular interactions between mixtures' components and, thus, a better understanding of liquid state theory [7-10].

Here we report experimental densities, sound speeds, viscosities, and refractive indices of binary mixtures ethanol + pyridine, ethanol + benzene, and pyridine + benzene at 298.15 K and under atmospheric pressure of 950 hPa. The related thermodynamic properties – excess molar volume, excess Gibbs free energy of activation for viscous flow, isentropic compressibility deviations, and refractive index deviations – have been calculated from the experimental data and interpreted in terms of molecular interactions between components of the mixture and structural effects.

The studied thermodynamic properties were fitted by Redlich-Kister polynomials [11], which is one of the most popular expressions for the mathematical representation of excess thermodynamic properties of binary liquid mixtures. Additionally, various theoretical and semi-empirical models were used to predict the refractive indices [12-17] and sound speeds [18-22] of the investigated liquids mixtures. The predicting ability of each model was ascertained in terms of mean absolute percentage deviation between experimental and calculated data.

A review of literature revealed that some thermodynamic properties of the investigated mixtures had been reported [ 5, 8, 9, 23-25]. However, this work is the first to report a combined study of density, sound speed, viscosity, and refractive index (and their derived thermodynamic excess and deviation properties) for three organic liquids and their binary mixtures of practical importance in various chemical and industrial processes.

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## 2. Materials and Methods

### 2.1 Materials

Ethanol (Carlo Erba) was supplied with purity ≥99.8%, benzene (Lach-Ner) with ≥99.8%, and pyridine (Sigma-Aldrich) with ≥99.5%. Densities ($kg\cdot m^{-3}$), sound speeds ($m\cdot s^{-1}$), viscosities (mPa· s), and refractive indices of pure liquids are within 0.05%, 0.08%, 0.8%, and 0.008%, respectively, with the corresponding literature values [8, 10, 26-32]. Since the agreement with the literature is very good, all the chemicals were used without further purification.

### 2.2 Methods

Mixtures were prepared by syringing known masses of the pure liquids into airtight stoppered amber glass bottles. Preferential evaporation during the preparation of mixtures was minimized by always charging the higher-boiling component first. Precautions were also taken to avoid losses by evaporation during manipulation. A KERN & Sohn ABS220-4N type electronic balance with a precision of ±0.1 mg was used for mass measurements. Conversion from mass to molar quantities was based on IUPAC's relative atomic mass Table of 2011 [33]. The uncertainty in the mole fraction of the studied mixtures was estimated to be better than ±0.0001. All mixtures were prepared just before use for measurements of density ($\rho$), speed of sound ($c$), viscosity ($\eta$), and refractive index ($n$) at temperature 298.15 K and ambient pressure of ~95.0 kPa.

This work used a pycnometer made of borosilicate glass to determine the densities of pure liquids and liquid mixtures. The pycnometer volume was calibrated at 298.15 K with in-house triple distilled and bubble-free water. Utmost care was taken while filling the pycnometer with sample liquid such that no air bubbles were trapped in the bulb or capillary of the pycnometer. The pycnometer with sample liquid was immersed for 30 minutes in a water bath maintained at 298.15 ± 0.04 K to minimize temperature fluctuations. After temperature equilibration, the pycnometer was dried with filter paper before recording its mass in an electronic balance. The density of the sample liquid was then calculated using the values of its mass and volume. The reported densities represent averages over three measurements.

A variable path single-crystal ultrasonic interferometer operating at 2 MHz (Mittal model SE-02) was used to measure sound speed ($c$). In-house triple-distilled and bubble-free water was used to check the performance of the interferometer. The speed of sound for water at 298.15 K was 1497 ± 1 $m\cdot s^{-1}$, which agrees very well with values reported in the literature [30, 32]. Thermal control of the sample liquids was performed by circulating water from a bath maintained at 298.15 ± 0.04 K through the inner walls of the measuring cell of the interferometer. The reported sound speeds are average values taken over ten measurements.

The dynamic viscosities were determined with calibrated Cannon-Fenske capillary viscometer. Much effort was put into ensuring that the capillary was vertical while mounting the viscometer in a water bath controlled at 298.15 ± 0.04 K. The viscometer with the sample liquid was kept for 30 minutes in the water bath before making the flow-time measurements. A digital stopwatch with a readability of 0.01 s was used for flow-time measurements. Measurements were repeated at least five times, and average values were considered in all calculations.

Refractive indices of pure liquids and binary mixtures were measured with an Abbe refractometer operated with a low-pressure sodium vapor lamp ($\lambda$ = 589 nm). The refractometer was thermostatically controlled at 298.15 ± 0.04 K. Regular calibration checks were performed with in-house triple distilled water to ensure the accuracy of the measurements. At least three independent measurements were performed for each sample, and the average value was considered in all calculations.

The combined expanded uncertainties at a 95% confidence level for $\rho$, $c$, $\eta$, and $n$ measurements are 0.2 $kg\cdot m^{-3}$, 2 $m\cdot s^{-1}$, 0.003 mPa·s, and 0.0002, respectively. The corresponding uncertainties were calculated following the NIST guidelines for evaluating and expressing uncertainties of measurement results [34].

## 3. Results and Discussion

The measured physical properties ($\rho$, $c$, $\eta$, and $n$) at temperature 298.15 K and ambient pressure ~95.0 kPa of the studied mixtures appear in Tables 1 to 3. The experimental results reveal that in the mixtures of pyridine or benzene with ethanol, the density, sound speed, and refractive index decrease with the mole fraction of ethanol ($x_1$). A second-order degree polynomial on $x_1$ can satisfactorily represent these properties. On contrary, dynamic viscosity data show a minimum around $x_1$ = 0.35 and 0.10 for ethanol (1) + pyridine (2) and ethanol (1) + benzene (2) mixtures, respectively. For the pyridine (1) + benzene (2) system, the $\rho$, $c$, and $\eta$ data exhibit a nearly linear relationship with composition, while the $n$ data show a second-order degree variation.

The excess molar volumes, $V^E$, excess Gibbs free energies of activation for viscous flow, $G^{*E}$, refractive index deviations, $\Delta n$, and isentropic compressibility deviations, $\Delta\kappa_S$, were derived from $\rho$, $c$, $\eta$, and $n$ values by using the following equations [2 ,9, 10, 35]:

$$V^E = \sum_{i=1}^{2} x_i M_i (\rho^{-1} - \rho_i^{-1}), \tag{1}$$

$$G^{*E} = RT\left[\ln(\eta V_m) - \sum_{i=1}^{2} x_i \ln(\eta_i V_{m,i})\right], \tag{2}$$

$$\Delta\kappa_S = \kappa_S - \sum_{i=1}^{2} \varphi_i \kappa_{S,i}, \tag{3}$$

$$\Delta n = n - \sum_{i=1}^{2} \varphi_i n_i, \tag{4}$$

$$\varphi_i = \left(\frac{x_i M_i \rho_i^{-1}}{\sum_j x_j M_j \rho_j^{-1}}\right). \tag{5}$$

where $\kappa_S = \rho^{-1}c^{-2}$ is the isentropic compressibility of the mixture; $x_i$, $M_i$, $\rho_i$, $\eta_i$, $\kappa_{S,i} = \rho_i^{-1}c_i^{-2}$, $n_i$, and $\varphi_i$, are the mole fraction, molar mass, density, dynamic viscosity, isentropic compressibility, refractive index, and volume fraction of pure component $i$, respectively. $R$ is the universal gas constant. Other symbols have the usual meaning. The combined expanded uncertainties at a 95% confidence level are $U_c(V^E) = 0.006\ cm^3\cdot mol^{-1}$, $U_c(G^{*E}) = 11\ J\cdot mol^{-1}$, $U_c(\Delta\kappa_s) = 1.6\ TPa^{-1}$, and $U_c(\Delta n) = 0.0002$. The $V^E$, $G^{E*}$, $\Delta n$, and $\Delta\kappa_S$ results of the studied mixtures are graphically shown in Figures 1, 2, 3, and 4, respectively. The literature values are also shown [5, 8, 23-25, 36, 37] for comparison purposes.

We can observe that the $V^E$ results of this work for ethanol + benzene agree well with those reported by Han et al. [8] and Šerbanović et al. [5] over the entire composition range. A small discrepancy is observed between the $V^E$ of Garrett and Pollock [23] and the results of this work for pyridine + benzene at the middle mole fraction region. The data of Findlay and Copp [25] present good agreement for ethanol + pyridine over the entire composition range. However, the results of Singh et al. [36] are lower in the middle fraction region, probably because of the higher measurement temperature. From Figure 2 it can be seen that for ethanol + benzene the $G^{*E}$ of this work agrees well with those reported by Kouris and Panayiotou [37] over the whole composition range. We can observe from Figure 3 that our $\Delta\kappa_S$ data for ethanol + benzene show good agreement up to ~0.7 mole fraction of ethanol but deviate with those of Gonzales-Olmos et al. [24] at higher compositions.

Because of the different natures of benzene, pyridine, and ethanol—in terms of polarity and geometrical shape—the resulting values of thermodynamic properties of their mixtures will reflect the opposite contributions that are dominant in certain regions of the concentrations. When these compounds are mixed, then the observed changes in thermodynamic properties are clearly due to: (*i*) stretching and breaking of H bonded structures in pure ethanol, (*ii*) N•••HO interactions between the lone pair of electrons of N in pyridine and the OH group of ethanol, (*iii*) π•••HO interactions between the π electrons of the aromatic rings (of pyridine and benzene) and the OH group of ethanol, (*iv*) π•••H interactions between the partial positive charge of H – in the position *para* with N - of pyridine with π electrons of aromatic rings, (*v*) geometrical interstitial accommodation of molecules into each other's structure due to differences in size and shape of the component molecules of the mixtures; (*vi*) in all cases weak London dispersion interactions are also present [5, 9, 38].

When considering $V^E$ and $\Delta\kappa_S$, then it is known that contributions (*i*) and (*vi*) give positive values, while (*ii*) - (*v*) contribute negatively to the values of $V^E$ and $\Delta\kappa_S$ [35, 38, 39]. Having in mind the various contributions operating in the studied systems, then the positive values of $\Delta\kappa_S$ and $V^E$ in the benzene-rich region of the ethanol + benzene system (Figures 1 and 3) can be attributed mainly to the disruption of the H-bonded ethanol structures as the ethanol molecules are added to a large amount of benzene. The negative $\Delta\kappa_S$ and $V^E$ values in the ethanol-rich region indicate that complex formation occurred through $\pi\cdots$HO bonding between the π-electron cloud of the aromatic ring of benzene and the hydroxyl group of ethanol. A further negative contribution may occur from the interstitial accommodation of benzene molecules into the remaining H-bonded ethanol structure [35]. The negative $V^E$ and $\Delta\kappa_S$ values for the ethanol + pyridine system can be attributed mainly to the formation of complexes by strong cross-associated N$\cdots$HO interactions. Contributions (*iii*) and (*v*) may also play a role. Similar results are also obtained by Anwar et al. [38] for binary mixtures of pyridine with alkanols ($C_6$-$C_{10}$) and by Kijevčanin et al. [39] for mixtures of pyridine with 1-propanol and 1,2-propanediol.

Figure 2 shows that excess Gibbs free energy of activation for viscous flow $G^{*E}$ is negative for mixtures involving ethanol but is positive for the system pyridine + benzene. Positive $G^{*E}$ is generally observed in systems with strong specific interactions between mixture components. In contrast, negative values can be seen in binary mixtures where weak dispersion forces are primarily responsible for interaction but may also occur where components are known to interact more strongly [40, 41], as in our case of the ethanol + pyridine system. Similar results are observed for binary mixtures of alkanols with pyridine [35, 38] and N-methyl pyrrolidine [42].

*Table 1. Densities ρ, speeds of sound c, dynamic viscosities η, and refractive indices n of ethanol (1) + pyridine (2) mixtures at 298.15 K and ~95.0 kPa.*

| $x_1$ | ρ (kg·m$^{-3}$) | $c$ (m·s$^{-1}$) | η (mPa·s) | $n$ |
|---|---|---|---|---|
| 0.0000 | 978.3 | 1417 | 0.879 | 1.5071 |
| 0.0229 | 975.2 | 1414 | 0.873 | 1.5047 |
| 0.0498 | 971.6 | 1410 | 0.866 | 1.5019 |
| 0.1000 | 964.7 | 1402 | 0.856 | 1.4966 |
| 0.1493 | 957.8 | 1394 | 0.850 | 1.4911 |
| 0.2000 | 950.6 | 1385 | 0.846 | 1.4854 |
| 0.2488 | 943.5 | 1376 | 0.843 | 1.4797 |
| 0.2999 | 935.7 | 1366 | 0.842 | 1.4735 |
| 0.3552 | 926.9 | 1355 | 0.841 | 1.4666 |
| 0.4000 | 919.4 | 1345 | 0.841 | 1.4608 |
| 0.5000 | 901.7 | 1321 | 0.848 | 1.4471 |
| 0.6000 | 882.5 | 1294 | 0.866 | 1.4324 |
| 0.7000 | 861.6 | 1264 | 0.897 | 1.4165 |
| 0.7454 | 851.5 | 1249 | 0.915 | 1.4089 |
| 0.8000 | 838.7 | 1229 | 0.940 | 1.3993 |
| 0.8349 | 830.0 | 1216 | 0.956 | 1.3929 |
| 0.9000 | 813.1 | 1190 | 0.992 | 1.3804 |
| 0.9258 | 806.2 | 1179 | 1.012 | 1.3753 |
| 0.9500 | 799.6 | 1168 | 1.032 | 1.3703 |
| 0.9778 | 791.7 | 1155 | 1.059 | 1.3644 |
| 1.0000 | 785.1 | 1145 | 1.082 | 1.3594 |

*Table 2. Densities ρ, speeds of sound c, dynamic viscosities η, and refractive indices n of pyridine (1) + benzene (2) mixtures at 298.15 K and ~95.0 kPa.*

| $x_1$ | ρ (kg·m$^{-3}$) | $c$ (m·s$^{-1}$) | η (mPa·s) | $n$ |
|---|---|---|---|---|
| 0.0522 | 972.6 | 1411 | 0.865 | 1.5067 |
| 0.1000 | 967.4 | 1406 | 0.852 | 1.5063 |
| 0.1439 | 962.7 | 1402 | 0.841 | 1.5060 |
| 0.1999 | 956.8 | 1395 | 0.827 | 1.5056 |
| 0.2601 | 950.5 | 1389 | 0.810 | 1.5052 |
| 0.3001 | 946.3 | 1385 | 0.800 | 1.5049 |
| 0.3504 | 941.1 | 1379 | 0.786 | 1.5045 |
| 0.4001 | 935.9 | 1374 | 0.772 | 1.5042 |
| 0.4492 | 930.8 | 1368 | 0.759 | 1.5038 |
| 0.5001 | 925.5 | 1363 | 0.745 | 1.5034 |
| 0.5502 | 920.3 | 1357 | 0.731 | 1.5030 |
| 0.6000 | 915.1 | 1351 | 0.717 | 1.5025 |
| 0.6439 | 910.6 | 1346 | 0.705 | 1.5021 |
| 0.7000 | 904.8 | 1339 | 0.689 | 1.5015 |
| 0.7691 | 897.6 | 1330 | 0.669 | 1.5007 |
| 0.8000 | 894.4 | 1326 | 0.660 | 1.5004 |
| 0.8495 | 889.3 | 1319 | 0.646 | 1.4998 |
| 0.9000 | 884.0 | 1313 | 0.630 | 1.4991 |
| 0.9601 | 877.7 | 1305 | 0.613 | 1.4982 |
| 1.0000 | 873.4 | 1299 | 0.602 | 1.4976 |

*Table 3. Densities ρ, speeds of sound c, dynamic viscosities η, and refractive indices n of ethanol (1) + benzene (2) mixtures at 298.15 K and ~95.0 kPa.*

| $x_1$ | ρ (kg·m$^{-3}$) | $c$ (m·s$^{-1}$) | η (mPa·s) | $n$ |
|---|---|---|---|---|
| 0.0227 | 871.8 | 1292 | 0.592 | 1.4954 |
| 0.0500 | 869.9 | 1285 | 0.584 | 1.4928 |
| 0.1000 | 866.6 | 1275 | 0.577 | 1.4878 |
| 0.1557 | 863.0 | 1265 | 0.581 | 1.4821 |
| 0.1999 | 860.0 | 1258 | 0.587 | 1.4774 |
| 0.2508 | 856.6 | 1251 | 0.594 | 1.4719 |
| 0.2998 | 853.2 | 1244 | 0.602 | 1.4664 |
| 0.3451 | 850.0 | 1238 | 0.614 | 1.4612 |
| 0.3998 | 846.0 | 1232 | 0.632 | 1.4546 |
| 0.4561 | 841.7 | 1225 | 0.651 | 1.4475 |
| 0.4998 | 838.2 | 1220 | 0.669 | 1.4418 |
| 0.5509 | 834.0 | 1214 | 0.694 | 1.4349 |
| 0.5998 | 829.7 | 1208 | 0.722 | 1.4280 |
| 0.6404 | 826.1 | 1203 | 0.746 | 1.4221 |
| 0.7000 | 820.4 | 1196 | 0.785 | 1.4130 |
| 0.7511 | 815.2 | 1189 | 0.825 | 1.4049 |
| 0.8000 | 810.0 | 1182 | 0.866 | 1.3968 |
| 0.8599 | 803.2 | 1173 | 0.920 | 1.3863 |
| 0.9000 | 798.4 | 1166 | 0.962 | 1.3790 |
| 0.9500 | 792.0 | 1156 | 1.025 | 1.3694 |
| 0.9778 | 788.2 | 1150 | 1.059 | 1.3639 |

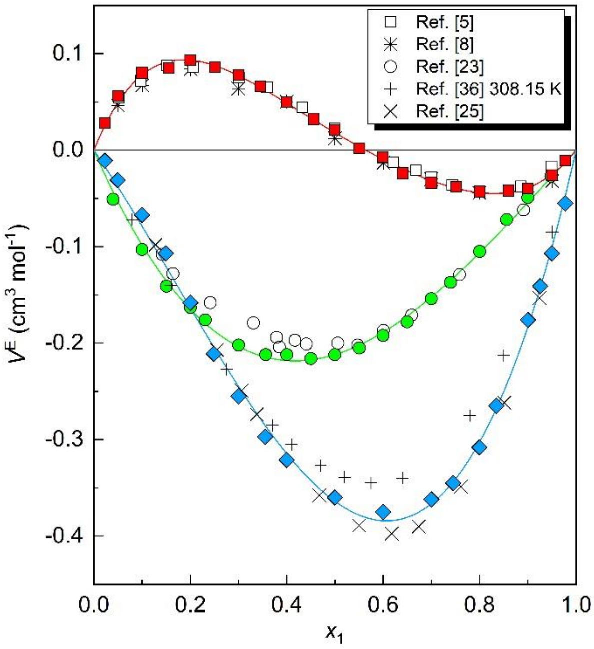

*Figure 1. Excess molar volumes, $V^E$, for the □ ethanol (1) + benzene (2), □ pyridine (1) + benzene (2), and ◆ ethanol (1) + pyridine (2) binary mixtures. Solid lines are the results calculated from the Redlich-Kister polynomial [11]. (Figure is in color in the online version of the paper).*

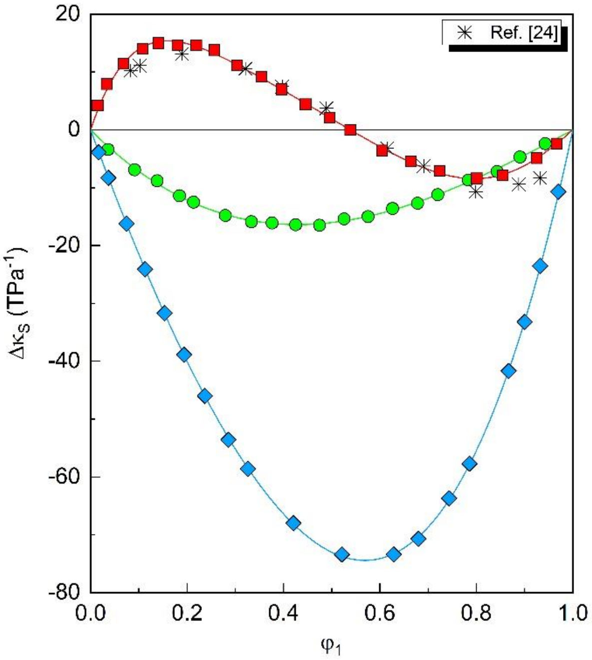

*Figure 3. Isentropic compressibility deviation, $\Delta\kappa_S$, for the □ ethanol (1) + benzene (2), □ pyridine (1) + benzene (2), and ◆ ethanol (1) + pyridine (2) binary mixtures. Solid lines are the results calculated from the Redlich-Kister polynomial [11]. (Figure is in color in the online version of the paper).*

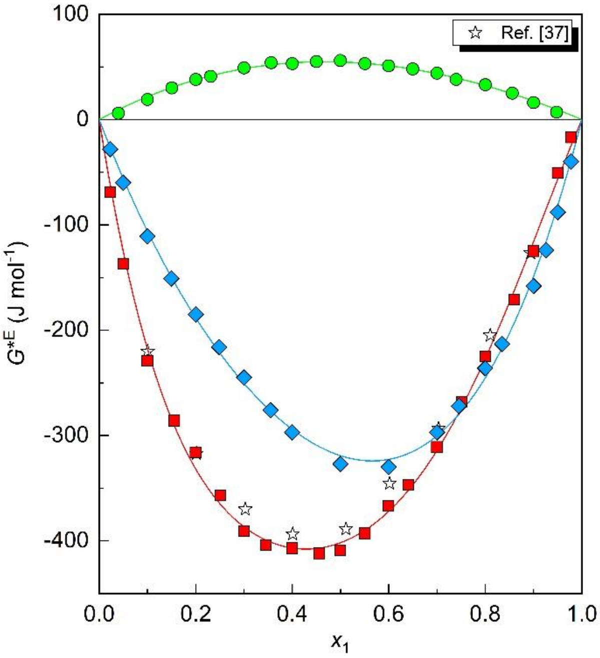

*Figure 2. Excess Gibbs free energy of activation for viscous flow, $G^{*E}$, for the □ ethanol (1) + benzene (2), □ pyridine (1) + benzene (2), and ◆ ethanol (1) + pyridine (2) binary mixtures. Solid lines are the results calculated from the Redlich-Kister polynomial [11]. (Figure is in color in the online version of the paper).*

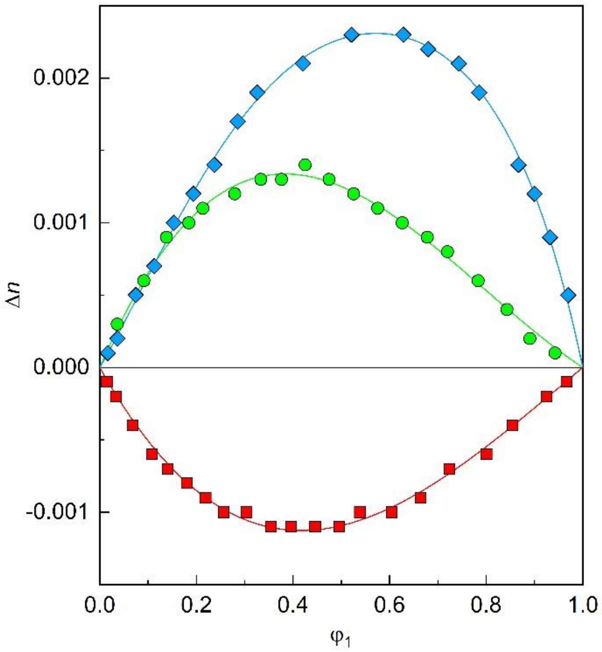

*Figure 4. Refractive index deviation, $\Delta n$, for the □ ethanol (1) + benzene (2), □ pyridine (1) + benzene (2), and ◆ ethanol (1) + pyridine (2) binary mixtures. Solid lines are the results calculated from the Redlich-Kister polynomial [11]. (Figure is in color in the online version of the paper).*

The variations of $\Delta n$ with the volume fraction of the first component in the mixture are shown in Figure 4. The $\Delta n$ shows negative dependence for the system ethanol (1) + benzene (2) but is positive for ethanol (1) + pyridine (2) and pyridine (1) + benzene (2). The data seem to support the finding that $\Delta n$ tends to increase as the strength of interaction between the components of the mixture increases, thereby showing an opposite trend to that of $V^E$ values. This negative correlation of $\Delta n$ with $V^E$ is a widely valid rule [3, 7, 38, 43], and it may be used as a quick check on the consistency of the data pertaining to $V^E$ [43].

*Table 4. Adjustable coefficients $B_j$ and standard deviations of the fitting σ for mathematical representation with Redlich-*

*Kister polynomial, Eqn. (6), of excess molar volumes* $V^E$ *(*$cm^3 \cdot mol^{-1}$*), isentropic compressibility deviations* $\Delta\kappa_S$ *(*$TPa^{-1}$*), deviations in refractive indices* $\Delta n$*, and excess Gibbs free energy of activation for viscous flow* $G^{*E}$ *(*$J \cdot mol^{-1}$*) at 298.15 K.*

| Property $Y$ | $B_1$ | $B_2$ | $B_3$ | $B_4$ | $B_5$ | σ ($Y$) |
|---|---|---|---|---|---|---|
| ethanol + pyridine | | | | | | |
| $V^E$ | -1.456 | 0.723 | | | | 0.008 |
| $\Delta\kappa_s$ | -292.0 | 80.4 | -17.6 | | | 0.2 |
| $\Delta n$ | 0.0091 | -0.0021 | 0.0017 | -0.0028 | | 0.00003 |
| $G^{*E}$ | -1276 | 297 | -218 | | | 6 |
| ethanol + benzene | | | | | | |
| $V^E$ | 0.073 | 0.592 | 0.226 | 0.342 | | 0.003 |
| $\Delta\kappa_s$ | 7.6 | 98.4 | 8.5 | 64.4 | 73.5 | 0.4 |
| $\Delta n$ | -0.0044 | -0.0016 | | | | 0.00003 |
| $G^{*E}$ | -1607 | -339 | -386 | -577 | | 8 |
| pyridine + benzene | | | | | | |
| $V^E$ | -0.847 | -0.306 | | | | 0.004 |
| $\Delta\kappa_s$ | -64.1 | -19.4 | | | | 0.3 |
| $\Delta n$ | 0.0050 | 0.0028 | | | | 0.00004 |
| $G^{*E}$ | 219 | 28 | | | | 1 |

### 3.1 Correlation of $V^E$, $\Delta\kappa_S$, $G^{*E}$ and $\Delta n$

The thermodynamic excess and deviation properties ($V^E$, $\Delta\kappa_S$, $G^{*E,}$ and $\Delta n$) of the studied mixtures were correlated by polynomials due to Redlich and Kister [11]:

$$Y = X_1 X_2 \sum_{j=0}^{k} B_j \, (X_2 - X_1)^j, \tag{6}$$

where $k$ is the polynomial order optimized by applying the $F$-test [44] at a 0.01 significance level. The polynomial coefficients $B_j$ were fitted by the unweighted least squares method and are recorded in Table 4 along with the standard deviations. $X = x$ (mole fraction) when fitting $Y = V^E$ and $G^{*E}$; $X = \phi$ (volume fraction) for $Y = \Delta\kappa_S$ and $\Delta n$. The subscripts 1 and 2 refer to the first and second components in the corresponding binary mixture.

The solid lines in Figures 1 to 4 refer to the values calculated with Eq. (6) using the corresponding coefficients $B_j$ in Table 4. We can observe a good agreement between the experimental data and the solid lines generated with an optimal number of coefficients. Generally, the number of fitting coefficients depends on the shape of data across the graph, the number of data points, the experimental data quality, and the significance level [35]. E.g., more parameters were needed to significantly fit the $\Delta\kappa_S$ and $V^E$ data of the ethanol + benzene system as they exhibited sine-like behavior. When data show a parabolic-like dependence, fewer parameters are needed to fit them significantly.

### 3.2 Predictive Models for $n$ and $c$

Information on refractive index and speed of sound is essential for designing and optimizing multi-component liquid mixtures. The invaluable information provided by these properties has considerably increased the interest in applying different models for predicting them. In this work, Lorentz and Lorenz (L-L) [12], Eykman (EYK) [13], Oster (OST) [14], Dale and Gladstone (D-G) [13, 15, 17], and Newton (NEW) [16] mixing rules were used to predict the refractive indices of the studied systems:

Lorentz-Lorenz (L-L):

$$\frac{n^2-1}{n^2+2} = \sum_{i=1}^{2} \phi_i \frac{n_i^2-1}{n_i^2+2} \tag{7}$$

Eykman (EYK):

$$\frac{n^2-1}{n+0.4} = \sum_{i=1}^{2} \phi_i \frac{n_i^2-1}{n_i+0.4} \tag{8}$$

Oster (OST):

$$\frac{(n^2-1)(2n^2+1)}{n^2} = \sum_{i=1}^{2} \phi_i \frac{(n_i^2-1)(2n_i^2+1)}{n_i^2} \tag{9}$$

Dale-Gladstone (D-G):

$$n - 1 = \sum_{i=1}^{2} \phi_i (n - 1) \tag{10}$$

Newton (NEW):

$$n^2 - 1 = \sum_{i=1}^{2} \phi_i (n_i^2 - 1) \tag{11}$$

In Eqs. (7)-(11), $n$ and $n_i$ are the refractive indices of the liquid mixture and pure component $i$, respectively; $\phi_i$ is the volume fraction of component $i$ in the mixture.

For predicting sound speeds, the relations of Nomoto (NOM) [18], van Dael (VAN) [19], Ernst et al. (ERN) [20], Junjie (JUN) [21], and Rao [22] were used. The formulae pertaining to these relations, which were subjected to proper rearrangement, are given in the following:

Nomoto's relation:

$$V^{id} c^{1/3} = \sum_{i=1}^{2} x_i V_i c_i^{1/3} \quad \therefore \quad c = \left[ (V^{id})^{-1} \sum_{i=1}^{2} x_i V_i c_i^{1/3} \right]^3 \tag{12}$$

where $c$ is the speed of sound in the mixture, $V^{id} = \sum_{i=1}^{2} x_i V_i$; $x_i$, $V_i$, and $c_i$, are the mole fractions, molar volumes, and sound speeds of component $i$ in the mixture.

van Dael's ideal mixing relation:

$$(Mc^2)^{-1} = \sum_{i=1}^{2} x_i (M_i c_i^2)^{-1} \quad \therefore \quad c = \left[ M \sum_{i=1}^{2} x_i (M_i c_i^2)^{-1} \right]^{-1/2} \tag{13}$$

where $c$ and $M$ are the speed of sound and molar mass, respectively, of liquid mixture; $x_i$, $M_i$, and $c_i$, are the mole fractions, molar masses, and sound speeds of component $i$ in the mixture.

Ernst et al. relation:

$$(c)^{-1} = \sum_{i=1}^{2} \phi_i (c_i)^{-1} \quad \therefore \quad c = \left[ \sum_{i=1}^{2} \phi_i (c_i)^{-1} \right]^{-1} \tag{14}$$

where $c$ is the speed of sound of liquid mixture; $\phi_i$, and $c_i$, are the volume fractions and speeds of sound, respectively, of component $i$ in the mixture.

Junjie's relation:

$$\left( V^{id} M^{-1/2} c^{-1} \right)^2 = \sum_{i=1}^{2} x_i \left( V_i M_i^{-1/2} c_i^{-1} \right)^2 \quad \therefore \quad c = \left[ (V^{id})^{-2} M \sum_{i=1}^{2} x_i \left( V_i M_i^{-1/2} c_i^{-1} \right)^2 \right]^{-1/2} \tag{15}$$

where $c$ and $M$ are the speed of sound and molar mass, respectively, of the liquid mixture, and $V^{id} = \sum_{i=1}^{2} x_i V_i$; $x_i$, $M_i$, $V_i$, and $c_i$, are the mole fractions, molar masses, molar volumes, and sound speeds of component $i$ in the mixture.

Rao's relation:

$$\rho^{-1} c^{1/3} = \sum_{i=1}^{2} x_i \rho_i^{-1} c_i^{1/3} \quad \therefore \quad c = \left[ \rho \sum_{i=1}^{2} x_i \rho_i^{-1} c_i^{1/3} \right]^3 \tag{16}$$

where $c$ and $\rho$ are the speed of sound and density, respectively, of liquid mixture; $x_i$, $\rho_i$, and $c_i$, are the mole fractions, density, and sound speeds, respectively, of components $i$ in the mixture.

The ability of the models to predict refractive indices and sound speeds of investigated systems was tested by calculating the mean absolute percentage deviation (MAPD) [45] between experimental and predicted values. The MAPD results are summarized in Tables 5 and 6 for refractive indices and speeds of sound, respectively.

*Table 5. Mean absolute percentage deviation (MAPD) for the Lorentz–Lorenz (L–L), Eykman (EYK), Newton (NEW), Oster (OST), and Dale–Gladstone (D–G) mixing rules for ethanol + pyridine, pyridine + benzene, and ethanol + benzene mixtures at 298.15 K*

| System | L-L | EYK | NEW | D-G | OST |
|---|---|---|---|---|---|
| ethanol + pyridine | 0.172 | 0.118 | 0.019 | 0.094 | 0.051 |
| pyridine + benzene | 0.059 | 0.059 | 0.058 | 0.058 | 0.058 |
| ethanol + benzene | 0.026 | 0.026 | 0.123 | 0.049 | 0.091 |

*Table 6. Mean absolute percentage deviation (MAPD) for the Nomoto (NOM), Van Dael (VAN), Ernst et al. (ERN), Rao, and Junjie (JUN) relations for ethanol + pyridine, pyridine + benzene, and ethanol + benzene mixtures at 298.15 K*

| System | NOM | VAN | ERN | Rao | JUN |
|---|---|---|---|---|---|
| ethanol + pyridine | 1.05 | 6.26 | 2.43 | 3.39 | 2.78 |
| pyridine + benzene | 0.43 | 0.45 | 0.36 | 0.15 | 0.86 |
| ethanol + benzene | 0.90 | 3.45 | 0.45 | 2.50 | 0.49 |

Table 5 shows that all the mixing rules performed well for the systems under study. The NEW mixing rule shows the best agreement with experimental values for the ethanol + pyridine system but the worst agreement for ethanol + benzene. The observed deviations are expected and can be accounted for, to some degree, if the excess volume is taken into consideration in the various mixing rules [7, 46]. Based on MAPD data, the predicting ability of the mixing rules follows this sequence: EYK ≈ L-L > D-G > OST > NEW for ethanol + benzene; NEW > OST > D-G > EYK > L-L for ethanol + pyridine. All the mixing rules obviously performed equally well for the pyridine + benzene system.

From a perusal of Table 6, it is obvious that some relations did not present good agreement with experimental data. The VAN relation resulted in the highest disagreement with experimental data for ethanol + pyridine, whereas the Rao relation showed the best performance for pyridine + benzene. Based on the results of Table 6, the predicting ability of the speed of sound relations follows the sequence: NOM > ERN > JUN > Rao > VAN for ethanol + pyridine; Rao > ERN > NOM > VAN > JUN for pyridine + benzene; ERN > JUN > NOM > Rao > VAN for ethanol + benzene.

## 4. Conclusions

This paper reports a combined experimental study of density, sound speed, viscosity, and refractive index (and their derived thermodynamic excess and deviation properties $V^E$, $G^{E*}$, $\Delta n$, and $\Delta\kappa_S$) for pure liquids - ethanol, benzene, and pyridine - and their binary mixtures essential for various chemical and industrial processes.

Redlich-Kister polynomial provided a statistically significant mathematical representation of $V^E$, $G^{E*}$, $\Delta n$, and $\Delta\kappa_S$ data with an optimal number of coefficients and standard deviations comparable to or better than experimental uncertainties.

The composition dependence of thermodynamic excess and deviation properties has been successfully interpreted in terms of molecular interactions between components of the mixture and structural effects.

The application of various models for predicting the refractive indices and sound speeds showed that the considered refractive index models worked well for all investigated systems. In contrast, some speed of sound models did not present good agreement with experimental data.

## Nomenclature

$\rho$ – density of the mixture ($\text{kg·m}^{-3}$)
$c$ – sound speed of the mixture ($\text{m·s}^{-1}$)
$n$ – refractive index of the mixture
$\eta$ - dynamic viscosity of the mixture ($10^{-3}$ Pa·s)
$\rho_j$ – density of the component $i$ ($\text{g·cm}^{-3}$)
$c_i$ – sound speed of the component $i$ ($\text{m·s}^{-1}$)
$n_i$ – refractive index of the component $i$
$\eta_i$ – dynamic viscosity of the component $i$ ($10^{-3}$ Pa·s)
$x_i$ – mole fraction of component $i$
$\varphi_i$ – volume fraction of component $i$
$V^E$ – excess molar volume ($\text{cm}^3\text{·mol}^{-1}$)
$G^{*E}$ – excess Gibbs free energy of activation for viscous flow ($\text{J·mol}^{-1}$)
$\Delta\kappa_S$ – deviation i isentropic compressibility ($10^{12}$ $\text{Pa}^{-1}$)
$\Delta n$ – deviation in refractive index
ERN – Ernst et al. speed of sound predictive relation
EYK – Eykman refractive index mixing rule
D-G – Dale and Gladstone refractive index mixing rule
JUN – Junjie speed of sound predictive model
L-L – Lorentz-Lorenz refractive index mixing rule
MAPD – Mean Absolute Percentage Deviation
NEW – Newton refractive index mixing rule
NOM – Nomoto speed of sound predictive relation
OST – Oster refractive index mixing rule
VAN – Van Dael speed of sound predictive relation

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