# Volumetric and Transport Properties of Binary Liquid Mixtures of Phenylacetonitrile with Aliphatic Esters at Temperatures of (303.15 to 313.15) K

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# Volumetric and Transport Properties of Binary Liquid Mixtures of Phenylacetonitrile with Aliphatic Esters at Temperatures of (303.15 to 313.15) K

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The present paper reports the experimental data for density, $\rho$, viscosity, $\eta$, and speed of sound, $u$, for the binary mixtures of phenylacetonitrile (PAN) with aliphatic esters [ethyl acetate (EA), ethyl chloroacetate (ECA), and ethyl cyanoacetate (ECNA)] over the miscibility region ($0 < x_1 < 1$) at temperatures of (303.15, 308.15, and 313.15) K. The experimental data have been used to calculate various properties like the excess molar volume $V^E$ and deviation in isentropic compressibility $\Delta\kappa_s$. These properties are used to interpret the molecular interactions in the binary mixtures. The Redlich−Kister polynomial equation was fitted to the experimental data to derive binary coefficients and standard deviations.

## 1. Introduction

Thermodynamic behavior of mixtures containing phenylacetonitrile (PAN) and aliphatic esters are of considerable interest because of their industrial importance. PAN and esters are good industrial solvents having various applications in the synthesis of dyes, pesticides, pharmaceuticals, insecticides and agrochemicals. Thus, correlation of the molecular structures with thermodynamic properties of such mixtures is necessary to obtain systematic information on the behavior of components in the binary mixtures of (PAN + ethyl acetate (EA)), (PAN + ethyl chloroacetate (ECA)), and (PAN + ethyl cyanoacetate (ECNA)). It is easy to understand the importance of the availability of the solvent thermodynamic parameters, such as density, $\rho$, viscosity, $\eta$, and speed of sound, $u$, which are three important physical properties of solvent systems and are often used to explain the medium effects of solvent on transport phenomena, electrolyte behavior, and reaction mechanisms in solutions.[1] As is well-known, these properties are functionally dependent on the temperature and at least for binary mixtures on the composition of the solvent systems.[2]

To the best of our knowledge, for the mixtures of PAN with aliphatic esters (+ EA, + ECA, and + ECNA) studied in this paper, no experimental data on density, viscosity, and speed of sound as a function of temperature are available in the accessible literature.

The aim of the present work is to analyze the changes in the thermodynamic properties, as a function of temperature and composition of the mixture. For that purpose, density, $\rho$, viscosity, $\eta$, and speed of sound, $u$, are measured within the temperature range from (303.15 to 313.15) K. The measured values are used to calculate the various properties such as excess molar volumes $V^E$ and deviations in isentropic compressibility $\Delta\kappa_s$.

As a continuation of our research work,[3−8] now we report the experimental data for density, $\rho$, viscosity, $\eta$, and speed of sound, $u$, for the binary mixtures of PAN with aliphatic esters (+ EA, + ECA, and + ECNA) over the entire range of composition at the temperatures of (303.15, 308.15, and 313.15) K. The results are enlightened in terms of molecular interactions present in the mixtures.

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**Table 1. Experimental Density ($\rho$), Viscosity ($\eta$), and Speed of Sound ($u$) of Pure Liquids at $T$ = 303.15 K**

| | $10^{-3}\cdot\rho/(\mathrm{kg\cdot m^{-3}})$ | | $10^{3}\cdot\eta/(\mathrm{mPa\cdot s})$ | | $u/(\mathrm{m\cdot s^{-1}})$ | |
|---|---|---|---|---|---|---|
| component | exptl | lit. | exptl | lit. | exptl | lit. |
| PAN | 1.0088 | | 1.761 | | 1519.2 | |
| EA | 0.8889 | 0.8885[9] | 0.379 | 0.403[10] | 1118.5 | 1118[9] |
| ECA | 1.1393 | 1.1393[11] | 0.969 | 1.007[11] | 1249.0 | 1249[11] |
| ECNA | 1.0564[a] | 1.0564[12] | 2.501[a] | 2.500[12] | 1396.9 | |

[a] At $T$ = 298.15 K.

## 2. Experimental Section

***2.1. Materials.*** All of the component liquids are of analytical grade. The PAN and EA were procured from SD Fine Chemicals, India; ECA and ECNA were supplied by Aldrich Chemicals, U.S. The stated mass fraction purities of these are as follows: PAN (0.99), EA (0.995), ECA (0.99), and ECNA (0.98). These solvents were used without further purification. The densities, viscosities, and speeds of sound of pure substances and their comparison with literature values are shown in Table 1.[9−12]

***2.2. Apparatus and Procedure.*** Binary mixtures were prepared by mass in airtight bottles. The mass measurements were performed on a Dhona 100 DS, India, single-pan analytical balance with a resolution of $0.01\cdot10^{-6}$ kg. The required properties of the mixture were measured on the same day of preparing the mixtures. The uncertainty in mole fraction was estimated to be less than $\pm 1\cdot10^{-4}$.

Densities of pure liquids and their mixtures were determined by using a $1\cdot10^{-5}$ m$^3$ double arm pycnometer.[13] The uncertainties in density and excess molar volume values were found to be $\pm 4\cdot10^{-5}$ g·cm$^{-3}$ and $\pm 1\cdot10^{-3}$ cm$^3$·mol$^{-1}$, respectively.

A suspended level viscometer[14,15] was used to measure the flow times of pure liquids and liquid mixtures, and it was calibrated with benzene and doubly distilled water [water conductivity less than $1\cdot10^{-6}$ $\Omega^{-1}\cdot$cm$^{-1}$ with (0.9970 and 0.9940) g·cm$^{-3}$ as its density at (298.15 and 308.15) K,

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respectively, and the density of benzene (0.87381 and 0.87341) $g\cdot cm^{-3}$ at (298.15 and 308.15) K, respectively]. Viscosity values ($\eta$) of pure liquids and mixtures were calculated using the flow times by relation

$$\eta = (at - b/t)\rho \qquad (1)$$

where $a$ and $b$ are the characteristic constants of the viscometer, $\rho$ is the density, and $t$ represents the flow time. The flow times of pure liquids and liquid mixtures were determined by the

**Table 2. Values of Density ($\rho$), Viscosity ($\eta$), Speed of Sound ($U$), Excess Molar Volume ($V^E$), and Deviation in Isentropic Compressibility ($\Delta\kappa_s$) for All Binary Liquid Mixtures at Various Temperatures**

| $x_1$ | $10^{-3}\cdot\rho$/(kg·m$^{-3}$) | $10^3\cdot\eta$/(mPa·s) | $u$/(m·s$^{-1}$) | $10^6\cdot V^E$/(m$^3$·mol$^{-1}$) | $10^{11}\cdot\Delta\kappa_s$/(m$^2$·N$^{-1}$) | $x_1$ | $10^{-3}\cdot\rho$/(kg·m$^{-3}$) | $10^3\cdot\eta$/(mPa·s) | $u$/(m·s$^{-1}$) | $10^6\cdot V^E$/(m$^3$·mol$^{-1}$) | $10^{11}\cdot\Delta\kappa_s$/(m$^2$·N$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | PAN (1) + EA (2) | | | | | | |
| | | | | | $T$ = 303.15 K | | | | | | |
| 0.0000 | 0.8889 | 0.379 | 1118.5 | 0.0000 | 0.000 | 0.4610 | 0.9553 | 0.839 | 1326.1 | –0.7138 | –6.887 |
| 0.0198 | 0.8924 | 0.396 | 1125.1 | –0.0800 | –0.314 | 0.5665 | 0.9675 | 0.984 | 1366.7 | –0.6807 | –6.173 |
| 0.1279 | 0.9104 | 0.483 | 1173.8 | –0.4379 | –3.316 | 0.6978 | 0.9815 | 1.180 | 1417.8 | –0.5698 | –4.942 |
| 0.2425 | 0.9268 | 0.591 | 1230.8 | –0.5736 | –5.883 | 0.8328 | 0.9949 | 1.416 | 1464.3 | –0.4151 | –2.946 |
| 0.3589 | 0.9423 | 0.714 | 1286.7 | –0.6553 | –7.216 | 0.9745 | 1.0065 | 1.695 | 1508.3 | –0.0380 | –0.304 |
| | | | | | | 1.0000 | 1.0088 | 1.761 | 1519.2 | 0.0000 | 0.000 |
| | | | | | $T$ = 308.15 K | | | | | | |
| 0.0000 | 0.8826 | 0.361 | 1097.8 | 0.0000 | 0.000 | 0.4610 | 0.9509 | 0.781 | 1312.5 | –0.8501 | –7.717 |
| 0.0198 | 0.8874 | 0.376 | 1109.3 | –0.2232 | –1.270 | 0.5665 | 0.9633 | 0.914 | 1355.1 | –0.8272 | –6.963 |
| 0.1279 | 0.9054 | 0.458 | 1164.8 | –0.5646 | –5.217 | 0.6978 | 0.9781 | 1.092 | 1410.8 | –0.7781 | –5.797 |
| 0.2425 | 0.9227 | 0.556 | 1218.2 | –0.7860 | –7.230 | 0.8328 | 0.9918 | 1.307 | 1461.3 | –0.6316 | –3.698 |
| 0.3589 | 0.9380 | 0.668 | 1278.4 | –0.8292 | –8.807 | 0.9745 | 1.0026 | 1.554 | 1500.5 | –0.1381 | –0.319 |
| | | | | | | 1.0000 | 1.0041 | 1.602 | 1512.9 | 0.0000 | 0.000 |
| | | | | | $T$ = 313.15 K | | | | | | |
| 0.0000 | 0.8759 | 0.344 | 1081.2 | 0.0000 | 0.000 | 0.4610 | 0.9465 | 0.733 | 1303.1 | –1.0243 | –8.663 |
| 0.0198 | 0.8808 | 0.357 | 1104.3 | –0.2301 | –3.331 | 0.5665 | 0.9585 | 0.854 | 1344.9 | –0.9202 | –7.742 |
| 0.1279 | 0.8996 | 0.431 | 1159.7 | –0.6502 | –7.220 | 0.6978 | 0.9724 | 1.017 | 1400.0 | –0.7391 | –6.303 |
| 0.2425 | 0.9169 | 0.524 | 1209.3 | –0.8440 | –8.577 | 0.8328 | 0.9852 | 1.209 | 1446.8 | –0.4557 | –3.626 |
| 0.3589 | 0.9334 | 0.627 | 1263.6 | –0.9890 | –9.481 | 0.9745 | 0.9981 | 1.430 | 1490.0 | –0.1526 | –0.314 |
| | | | | | | 1.0000 | 0.9995 | 1.489 | 1503.4 | 0.0000 | 0.000 |
| | | | | | PAN (1) + ECA (2) | | | | | | |
| | | | | | $T$ = 303.15 K | | | | | | |
| 0.0000 | 1.1393 | 0.969 | 1229.4 | 0.0000 | 0.000 | 0.4843 | 1.0726 | 1.336 | 1370.5 | 0.1059 | –0.822 |
| 0.0205 | 1.1358 | 0.982 | 1235.7 | 0.0586 | –0.079 | 0.5875 | 1.0593 | 1.419 | 1400.6 | 0.1005 | –0.786 |
| 0.1376 | 1.1192 | 1.069 | 1268.8 | 0.0902 | –0.349 | 0.7152 | 1.0432 | 1.524 | 1438.2 | 0.0858 | –0.680 |
| 0.2585 | 1.1026 | 1.161 | 1303.2 | 0.1019 | –0.535 | 0.8434 | 1.0275 | 1.628 | 1476.9 | 0.0533 | –0.550 |
| 0.3793 | 1.0864 | 1.254 | 1338.7 | 0.1082 | –0.698 | 0.9764 | 1.0116 | 1.740 | 1516.0 | 0.0134 | –0.267 |
| | | | | | | 1.0000 | 1.0088 | 1.761 | 1519.2 | 0.0000 | 0.000 |
| | | | | | $T$ = 308.15 K | | | | | | |
| 0.0000 | 1.1325 | 0.898 | 1212.4 | 0.0000 | 0.000 | 0.5875 | 1.0564 | 1.302 | 1388.9 | –0.1801 | –0.972 |
| 0.0205 | 1.1298 | 0.912 | 1218.9 | –0.0128 | –0.132 | 0.7152 | 1.0400 | 1.394 | 1426.3 | –0.1415 | –0.713 |
| 0.1376 | 1.1143 | 0.991 | 1254.0 | –0.0605 | –0.570 | 0.8434 | 1.0237 | 1.488 | 1466.0 | –0.0785 | –0.490 |
| 0.2585 | 1.0985 | 1.072 | 1291.5 | –0.1101 | –0.971 | 0.9764 | 1.0070 | 1.584 | 1505.6 | –0.0075 | –0.066 |
| 0.3793 | 1.0833 | 1.156 | 1328.4 | –0.1838 | –1.183 | 1.0000 | 1.0041 | 1.602 | 1512.9 | 0.0000 | 0.000 |
| | | | | | $T$ = 313.15 K | | | | | | |
| 0.0000 | 1.1259 | 0.834 | 1197.6 | 0.0000 | 0.000 | 0.4843 | 1.0628 | 1.139 | 1348.5 | –0.0536 | –1.362 |
| 0.0205 | 1.1232 | 0.846 | 1204.0 | –0.0045 | –0.078 | 0.5875 | 1.0498 | 1.207 | 1381.0 | –0.0492 | –1.291 |
| 0.1376 | 1.1076 | 0.916 | 1240.4 | –0.0185 | –0.654 | 0.7152 | 1.0340 | 1.292 | 1419.9 | –0.0412 | –1.110 |
| 0.2585 | 1.0917 | 0.993 | 1279.0 | –0.0331 | –1.112 | 0.8434 | 1.0183 | 1.379 | 1457.4 | –0.0305 | –0.636 |
| 0.3793 | 1.0762 | 1.070 | 1316.6 | –0.0472 | –1.327 | 0.9764 | 1.0023 | 1.471 | 1495.8 | –0.0052 | –0.040 |
| | | | | | | 1.0000 | 0.9995 | 1.489 | 1503.4 | 0.0000 | 0.000 |
| | | | | | PAN (1) + ECNA (2) | | | | | | |
| | | | | | $T$ = 303.15 K | | | | | | |
| 0.0000 | 1.0514 | 2.186 | 1396.9 | 0.0000 | 0.000 | 0.4842 | 1.0289 | 1.995 | 1448.0 | 0.1222 | 0.530 |
| 0.0223 | 1.0501 | 2.179 | 1399.6 | 0.0285 | 0.011 | 0.5882 | 1.0246 | 1.950 | 1461.3 | 0.1109 | 0.479 |
| 0.1383 | 1.0444 | 2.135 | 1412.3 | 0.0775 | 0.119 | 0.7172 | 1.0194 | 1.893 | 1479.4 | 0.0916 | 0.322 |
| 0.2569 | 1.0388 | 2.088 | 1424.4 | 0.1069 | 0.278 | 0.8426 | 1.0146 | 1.835 | 1496.9 | 0.0634 | 0.185 |
| 0.3778 | 1.0334 | 2.040 | 1436.0 | 0.1197 | 0.477 | 0.9759 | 1.0097 | 1.773 | 1515.5 | 0.0152 | 0.045 |
| | | | | | | 1.0000 | 1.0088 | 1.761 | 1519.2 | 0.0000 | 0.000 |
| | | | | | $T$ = 308.15 K | | | | | | |
| 0.0000 | 1.0465 | 1.962 | 1384.8 | 0.0000 | 0.000 | 0.4842 | 1.0263 | 1.799 | 1436.3 | –0.1268 | 0.581 |
| 0.0233 | 1.0456 | 1.955 | 1386.5 | –0.0170 | 0.073 | 0.5882 | 1.0218 | 1.761 | 1450.4 | –0.1139 | 0.524 |
| 0.1383 | 1.0409 | 1.917 | 1397.7 | –0.0652 | 0.282 | 0.7172 | 1.0162 | 1.713 | 1468.5 | –0.0860 | 0.430 |
| 0.2569 | 1.0359 | 1.877 | 1410.0 | –0.1024 | 0.442 | 0.8426 | 1.0109 | 1.664 | 1487.6 | –0.0598 | 0.259 |
| 0.3778 | 1.0308 | 1.836 | 1423.7 | –0.1184 | 0.533 | 0.9759 | 1.0052 | 1.612 | 1508.7 | –0.0222 | 0.052 |
| | | | | | | 1.0000 | 1.0041 | 1.602 | 1512.9 | 0.0000 | 0.000 |
| | | | | | $T$ = 313.15 K | | | | | | |
| 0.0000 | 1.0408 | 1.770 | 1367.7 | 0.0000 | 0.000 | 0.4842 | 1.0211 | 1.644 | 1429.2 | –0.1168 | 0.138 |
| 0.0223 | 1.0398 | 1.764 | 1370.4 | –0.0023 | 0.026 | 0.5882 | 1.0168 | 1.612 | 1442.0 | –0.1146 | 0.126 |
| 0.1383 | 1.0348 | 1.733 | 1384.6 | –0.0124 | 0.079 | 0.7172 | 1.0114 | 1.572 | 1459.4 | –0.0973 | 0.099 |
| 0.2569 | 1.0299 | 1.701 | 1399.1 | –0.0379 | 0.109 | 0.8426 | 1.0058 | 1.535 | 1478.0 | –0.0253 | 0.049 |
| 0.3778 | 1.0253 | 1.671 | 1414.2 | –0.0961 | 0.128 | 0.9759 | 1.0004 | 1.496 | 1495.9 | –0.0029 | 0.009 |
| | | | | | | 1.0000 | 0.9995 | 1.489 | 1503.4 | 0.0000 | 0.000 |

average of five measurements. The uncertainty of viscosity was found to be ± 0.005 mPa·s.

Speeds of sound was determined by using an ultrasonic interferometer (model M-82, Mittal Enterprises, India), working at a 2 MHz frequency. The working principle used in the measurement of the speed of sound through a medium was based on the accurate determination of the wavelength of ultrasonic waves of known frequency produced by a quartz crystal in the measuring cell.[3,16] The temperature of the solution was controlled by circulating water at a desired temperature through the jacket of the double-walled cell. The speed of sound was measured with relative uncertainty of 0.3 %.

In all of the property measurements, the temperature was controlled within ± 0.01 K using a constant temperature bath (INSREF model IRI-016 C, India), and the temperature was monitored with a platinum resistance thermometer with an accuracy of ± 0.001 K and an uncertainty of ± 0.004 K.

## 3. Results and Discussion

Table 2 reports the experimental data of density, $\rho$, viscosity, $\rho$, ultrasonic speed, $u$, excess molar volume, $V^E$, and deviation in isentropic compressibility, $\Delta\kappa_s$, for the binary mixtures of (PAN + EA), (PAN + ECA), and (PAN + ECNA) at $T$ = (303.15, 308.15, and 313.15) K along with the mole fraction.

The excess molar volumes ($V^E$) have been evaluated from density using

$$V^E/(\mathrm{cm^3\cdot mol^{-1}}) = (x_1M_1 + x_2M_2)/\rho_m - (x_1M_1/\rho_1 + x_2M_2/\rho_2) \quad (2)$$

where $\rho_m$ is the density of the mixture; $x_1$, $M_1$, and $\rho_1$ and $x_2$, $M_2$, and $\rho_2$ are the mole fraction, molar mass, and density of pure components, respectively.

The deviations in isentropic compressibility ($\Delta\kappa_s$) have been evaluated using the equation

$$\Delta\kappa_s/(\mathrm{m^2\cdot N^{-1}}) = \kappa_s - (\Phi_1\kappa_{s1} + \Phi_2\kappa_{s2}) \quad (3)$$

where $\Phi_i$ is the volume fraction of pure components and is calculated from the individual pure molar volumes, $V_i$, using the relation

$$\Phi_i = x_iV_i/(\sum x_iV_i) \quad (4)$$

and $\kappa_{s1}$, $\kappa_{s2}$, and $\kappa_s$ are the isentropic compressibility of the pure components and observed isentropic compressibility of the liquid mixture, respectively.

The excess or deviation properties $\Delta Y$ are fitted by the method of nonlinear least-squares to the fourth-order Redlich−Kister type polynomial equation.[17]

$$\Delta Y = x_1x_2\sum A_i(x_1 - x_2)^i \quad (5)$$

where $A_0$, $A_1$, $A_2$, $A_3$, and $A_4$ are adjustable binary coefficients. The coefficients $A_i$ were estimated using multiparametric regression analysis based on a nonlinear least-squares method. The number of $A_i$ parameters was optimized using the $F$-test and is found to be five ($m$ = 5). In each case, the optimum number of coefficients $A_i$ is determined from an examination of the variation of standard deviation ($\sigma$) as calculated by

$$\sigma(Y^E) = [\sum(\Delta Y_{obs} - \Delta Y_{cal})^2/(n - m)]^{1/2} \quad (6)$$

where $n$ represents the number of experimental points and $m$ is the number of coefficients used in fitting the data. The coefficients $A_i$ and standard deviations ($\sigma$) $V^E$, ($\sigma$) $\Delta\eta$, and ($\sigma$) $\Delta\kappa_s$ of the fit are summarized in Table 3.

***3.1. Excess Molar Volume ($V^E$).*** Figure 1 depicts the graphical representation of excess molar volumes ($V^E$) for PAN with EA, ECA, and ECNA at 303.15 K. The strength of unlike molecular interactions in the solution is better estimated by the sign and magnitude of $V^E$. The values of $V^E$ are negative for the PAN + EA system, whereas they are positive for PAN + ECA and PAN + ECNA systems. The positive contributions are thought to be arising from the disruption of dipolar association of PAN. However, it is observed that the EA show considerable larger negative $V^E$ values compared to other esters. This observation supports the interstitial accommodation of EA molecules due to the smaller size in dipolar network of the PAN.[6,16] The fact that $V^E$ values become more negative with the temperature further supports the interstitial accommodation of EA molecules (Figure 4). The observed negative $V^E$ values for ECA and ECNA systems (Figures 2, 3, and 4) at higher temperatures show the existence of weaker dipolar interaction between unlike molecules.

**Table 3. Binary Coefficients $A_i$ and Corresponding Standard Deviations ($\sigma$) of Equation 6**

| property | $T$/K | $A_0$ | $A_1$ | $A_2$ | $A_3$ | $A_4$ | $\sigma$ |
|---|---|---|---|---|---|---|---|
| | | | | PAN (1) + EA (2) | | | |
| $10^6\cdot V^E/(\mathrm{m^3\cdot mol^{-1}})$ | 303.15 | −2.780 | 0.07 | −0.70 | 1.1 | −0.4 | 0.022 |
| | 308.15 | −3.39 | 0.08 | −1.9 | 1 | −2.2 | 0.037 |
| | 313.15 | −4.048 | 1.08 | 2.35 | 0.86 | −6.9 | 0.028 |
| $10^{11}\cdot\Delta\kappa_s/(\mathrm{m^2\cdot N^{1-}})$ | 303.15 | −27.73 | 9 | −2.9 | −13.1 | 17.6 | 0.1 |
| | 308.15 | −31.84 | 11.1 | −8 | −3.9 | 2 | 0.35 |
| | 313.15 | −35.7 | 7.4 | 4 | 32 | −45 | 0.57 |
| | | | | PAN (1) + ECA (2) | | | |
| $10^6\cdot V^E/(\mathrm{m^3\cdot mol^{-1}})$ | 303.15 | 0.441 | 0.02 | −0.26 | −0.60 | 1.23 | 0.012 |
| | 308.15 | −0.80 | −0.03 | 0.82 | −0.05 | −0.61 | 0.0069 |
| | 313.15 | −0.2101 | −0.012 | 0.130 | −0.073 | −0.187 | 0.0014 |
| $10^{11}\cdot\Delta\kappa_s/(\mathrm{m^2\cdot N^{1-}})$ | 303.15 | −3.26 | −0.44 | 3.0 | −2 | −7.9 | 0.039 |
| | 308.15 | −4.94 | 1.87 | 4.6 | −2.4 | −6.0 | 0.058 |
| | 313.15 | −5.41 | 0.01 | −2.08 | 0.27 | 5.30 | 0.014 |
| | | | | PAN (1) + ECNA (2) | | | |
| $10^6\cdot V^E/(\mathrm{m^3\cdot mol^{-1}})$ | 303.15 | 0.4857 | −0.093 | −0.08 | −0.069 | 0.53 | 0.0035 |
| | 308.15 | −0.5005 | 0.149 | 0.291 | −0.193 | −0.65 | 0.0028 |
| | 313.15 | −0.48 | −0.272 | 0.76 | 0.38 | −0.2 | 0.0071 |
| $10^{11}\cdot\Delta\kappa_s/(\mathrm{m^2\cdot N^{-1}})$ | 303.15 | 2.130 | 0.089 | −3.37 | 0.65 | 2.91 | 0.0067 |
| | 308.15 | 2.283 | 0.003 | −0.73 | −0.29 | 1.10 | 0.0094 |
| | 313.15 | 0.5478 | 0.02 | −0.216 | −0.391 | 0.35 | 0.014 |

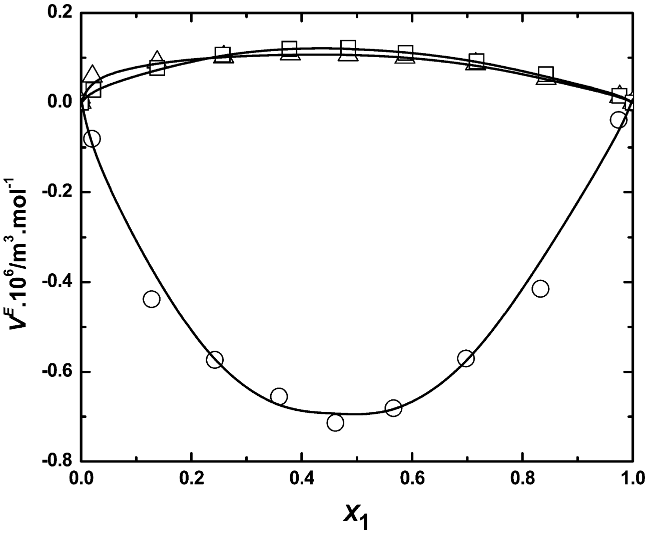


**Figure 1.** Plots of excess molar volumes, $V^E$, as a function of mole fraction $x$ at $T$ = 303.15 K: ○, {PAN (1) + EA (2)}; △, {PAN (1) + ECA (2)}; □, {PAN (1) + ECNA (2)}; the symbols represent experimental values and solid curves represent the smoothed data of this work.

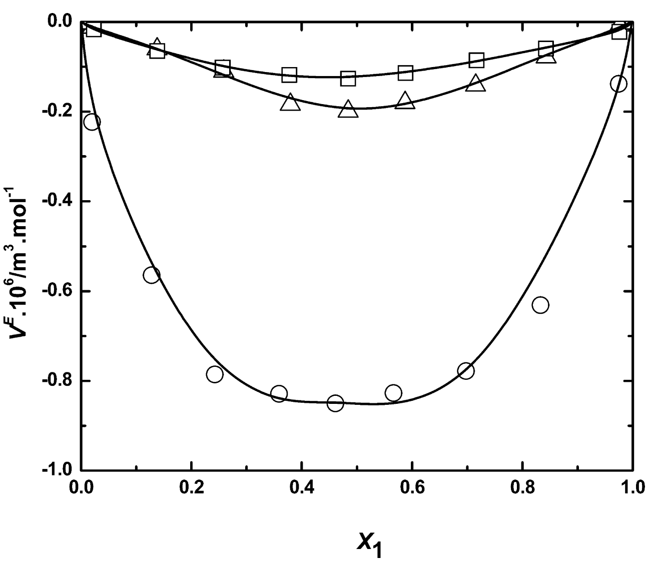


**Figure 2.** Plots of excess molar volumes, $V^E$, as a function of mole fraction $x$ at $T$ = 308.15 K: ○, {PAN (1) + EA (2)}; △, {PAN (1) + ECA (2)}; □, {PAN (1) + ECNA (2)}; the symbols represent experimental values and solid curves represent the smoothed data of this work.

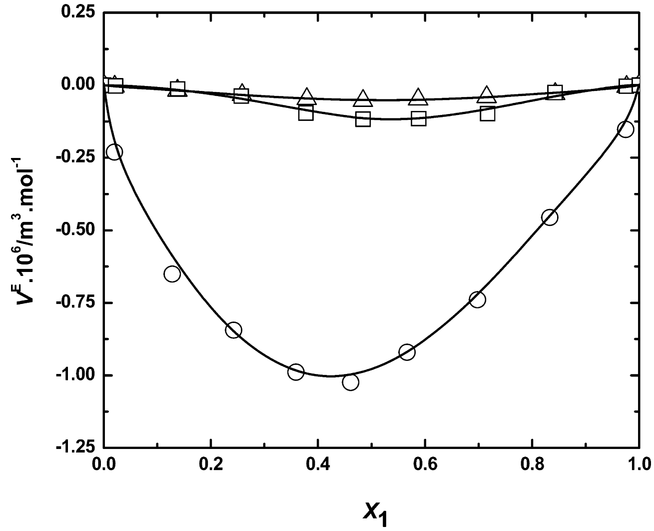


**Figure 3.** Plots of excess molar volumes, $V^E$, as a function of mole fraction $x$ at $T$ = 313.15 K: ○, {PAN (1) + EA (2)}; △, {PAN (1) + ECA (2)}; □, {PAN (1) + ECNA (2)}; the symbols represent experimental values and solid curves represent the smoothed data of this work.

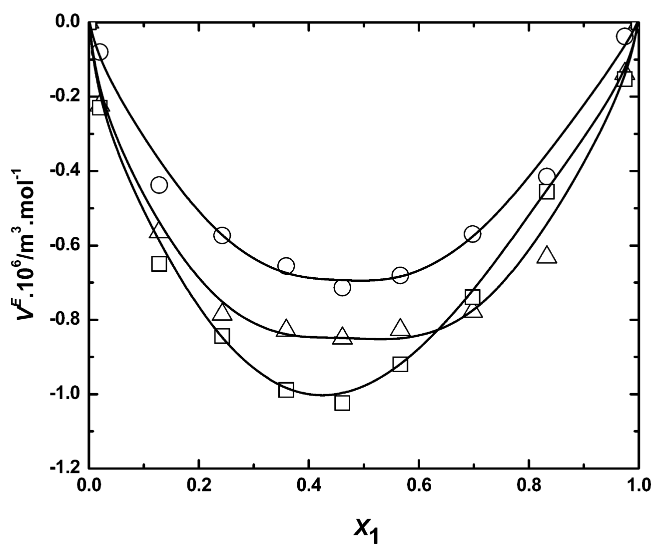


**Figure 4.** Plots of excess molar volumes, $V^E$, as a function of mole fraction $x$ of PAN (1) + EA (2) at ○, 303.15; △, 308.15; □, 313.15 K; the symbols represent experimental values and solid curves represent the smoothed data of this work.

The algebraic values of $V^E$ of PAN with aliphatic esters fall in the order at 303.15 K,

$$\mathrm{EA} < 0 < \mathrm{ECA} < \mathrm{ECNA}$$

whereas at 308.15 and 313.15 K

$$\mathrm{EA} < \mathrm{ECA} < \mathrm{ECNA} < 0$$

***3.2. Deviation in Isentropic Compressibility ($\Delta\kappa_s$).*** Generally $V^E$ and $\Delta\kappa_s$ have the same sign as observed in the case of PAN + EA and + ECA binary mixtures, while the PAN + ECNA system does not follow the general rule. The $\Delta\kappa_s$ value increases become more negative with the temperature, which further fortified the observation about interstitial accommodation of EA molecules.

The values of $\Delta\kappa_s$ may be attributed to the effects of relative strength that influence the free space defined by Jacobson.[18] In the present investigation the negative $\Delta\kappa_s$ values obtained over a range of temperatures studied for all mixtures are attributed to chemical forces operating between unlike molecules of binary mixtures.[19,20] The positive $\Delta\kappa_s$ values for PAN + ECNA system may be attributed to mutual loss of dipolar association.

The algebraic values of $\Delta\kappa_s$ vary in the following order at 303.15 K.

$$\mathrm{EA} < \mathrm{ECA} < 0 < \mathrm{ECNA}$$

## 4. Conclusion

In this paper, we present the experimental data on density, viscosity, and speeds of sound for three binary mixtures of PAN + EA, ECA, and ECNA at $T$ = (303.15 to 313.15) K. It may also be concluded from the interpretation of derived properties, excess molar volume ($V^E$) and isentropic compressibility ($\Delta\kappa_s$), that mixing the liquids creates the structure through interstitial accommodation and dipolar−dipolar association in the binary mixtures.

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## Literature Cited


(1) Muhuri, P. K.; Hazra, D. K. Density and Viscosity of Propylene Carbonate + 2-Methoxyethanol at 298.15, 308.15, and 318.15 K. *J. Chem. Eng. Data* **1995**, *40*, 582–585.

(2) Marchetti, A.; Preti, C.; Tagliazucchi, M.; Tassi, L.; Tosi, G. The *N*, *N*-Dimethylformamide/Ethane-1,2-Diol Solvent System. Density, Viscosity, and Excess Molar Volume at Various Temperatures. *J. Chem. Eng. Data* **1991**, *36*, 360–365.

(3) Boodida, S.; Tangeda, S. J.; Nallani, S. Acoustic Studies of Binary Mixtures of *N*-Methyl acetamide with Some Chloroethanes and Chloroethenes at 308.15 K. *Indian J. Pure Appl. Phys.* **2006**, *44*, 587–591.

(4) Bachu, R. K.; Patwari, M. K.; Boodida, S.; Tangeda, S. J.; Nallani, S. Densities, Viscosities and Speeds of Sound of Binary Liquid Mixtures of Phenylacetonitrile with Some Aliphatic Alcohols at 308.15 K. *Indian J. Chem.* **2008**, *47A*, 1026–1031.

(5) Boodida, S.; Bachu, R. K.; Patwari, M. K.; Nallani, S. Volumetric and Transport Properties of Binary Liquid Mixtures of *N*-Methylacetamide with Lactones at Temperatures (303.15 to 318.15) K. *J. Chem. Thermodyn.* **2008**, *40*, 1422–1427.

(6) Boodida, S.; Bachu, R. K.; Tangeda, S. J.; Nallani, S. Excess Molar Volumes and Viscosity Deviations of Binary Liquid Mixtures of *N*-methylacetamide with Ethyl Acetate, Ethyl Chloroacetatae and Ethyl Cyanoacetate. *Indian J. Chem.* **2008**, *47A*, 66–70.

(7) Tangeda, S. J.; Nallani, S. Density and Viscosity of Binary Liquid Systems of *N*-Methyl acetamide with Aromatic Ketones at 308.15 K. *J. Chem. Thermodyn.* **2006**, *38*, 272–277.

(8) Tangeda, S. J.; Nallani, S. Ultrasonic Studies of Binary Mixtures of Some Aromatic Ketones with *N*-Methylacetamide at 308.15 K. *J. Chem. Eng. Data* **2005**, *50*, 89–91.

(9) Oswal, S. L.; Oswal, P.; Modi, P. S.; Dave, J. P.; Gardas, R. L. Acoustic, Volumetric, Compressibility and Refractivity Properties and Flory's Reduction Parameters of Some Homologous Series of Alkyl alkanoates from 298.15 to 333.15 K. *Thermochim. Acta* **2004**, *410*, 1–14.

(10) González, B.; Domínguez, A.; Tojo, J. Dynamic Viscosities, Densities, and Speed of Sound and Derived Properties of the Binary Systems Acetic Acid with Water, Methanol, Ethanol, Ethyl Acetate and Methyl Acetate at $T$ = (293.15, 298.15, and 303.15) K at Atmospheric Pressure. *J. Chem. Eng. Data* **2004**, *49*, 1590–1596.

(11) Nayak, J. N.; Aralaguppi, M. I.; Aminabhavi, T. M. Density, Viscosity, Refractive Index, and Speed of Sound for the Binary Mixtures of Ethyl Chloroacetate with n-Alkanes ($C_6$ to $C_{12}$) at (298.15, 303.15, and 308.15) K. *J. Chem. Eng. Data* **2001**, *46*, 891–896.

(12) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. Techniques of Chemistry, Organic Solvents. In *Physical Properties and Methods of Purifications*, Vol. 2; John Wiley & Sons: New York, 1986.

(13) Tangeda, S. J.; Boodida, S.; Nallani, S. Ultrasonic Studies on Binary Mixtures of Some Aromatic Ketones with Acetonitrile at $T$ = 308.15 K. *J. Chem. Thermodyn.* **2006**, *38*, 1438–1442.

(14) Nikam, P. S.; Shrisat, L. N.; Hasan, M. B. Density and Viscosity Studies of Binary Mixtures of Acetonitrile with Methanol, Ethanol, Propan-1-ol, Butan-1-ol, 2-Methylpropan-1-ol, and 2-Methylpropan-2-ol at (298.15, 303.15, 308.15, and 313.15) K. *J. Chem. Eng. Data* **1998**, *43*, 732–737.

(15) Boodida, S.; Bachu, R. K.; Tangeda, S. J.; Nallani, S. Densities and Viscosities of Binary Liquid Mixtures of N-Methylacetamide with Some Chloroethanes and Chloroethenes at $T$ = 308.15 K. *J. Chem. Thermodyn.* **2007**, *39*, 16–21.

(16) Nallani, S.; Boodida, S.; Tangeda, S. J. Density and Speed of Sound of Binary Mixtures of N-Methylacetamide with Ethyl Acetate, Ethyl Chloroacetate and Ethyl Cyanoacetate in the Temperature Interval (303.15 to 318.15) K. *J. Chem. Eng. Data* **2007**, *52*, 405–409.

(17) Redlich, O.; Kister, A. T. Algebriac Representation of Thermodynamic Properties and the Classification of Solutions. *Ind. Eng. Chem.* **1948**, *40*, 345–348.

(18) Jacobson, B. Ultrasonic Velocity of Liquids and Liquid Mixtures. *J. Chem. Phys.* **1952**, *20*, 927–928.

(19) Jose, M. R.; Jose, M. G.; Ana, I. S. Density, Refractive Index, Speed of Sound at 298.15 K, and Vapor-Liquid Equilibria at 101.3 kPa for Binary Mixtures of Ethyl Acetate + Ethyl Lactate and Methyl Acetate + Ethyl Lactate. *J. Chem. Eng. Data* **2006**, *51*, 1294–1299.

(20) Shanti, L. O.; Navin, B. P. Speeds of Sound, Isentropic Compressibilities, and Excess Volumes of Binary Mixtures of Acrylonitrile with Organic Solvents. *J. Chem. Eng. Data* **2000**, *45*, 225–230.


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