Molecular interactions of α,ω-alkanediols in pyrrolidin-2-one: Thermophysical and spectroscopic measurements

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Abstract
The thermodynamic parameters viz. excess molar volume \( V^E \) and speed of sound \( u \), transport parameter viscosity \( \eta \), and spectroscopic parameters viz. i.r., \(^1\)H and \(^{13}\)C n.m.r. have been determined for the mixtures of α,ω-alkanediols (1,2-ethanediol, 1,3-propanediol, and 1,5-pentanediol) and pyrrolidin-2-one over the whole composition range at \( T = 308.15 \) K. The partial molar quantities \( f^E \), isentropic compressibility \( K_s \), viscosity deviation \( \Delta \eta \), deviation in Gibbs free energies of activation for viscous flow \( \Delta G_r \) and excess n.m.r. chemical shift \( \delta_e \) have been estimated and analyzed. The results reveal distinctly that the interaction between unlike molecules takes place through hydroxyl groups of α,ω-alkanediols and CO group of pyrrolidin-2-one. An excellent correlation between thermodynamic and spectroscopic measurements has been observed.

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Keywords: Thermodynamic characterization; Spectroscopic measurements; α,ω-Alkanediols; Pyrrolidin-2-one

1. Introduction
Alkanediols and amides are used in a wide variety of end-use practical and theoretical applications [1–15]. In recent papers, we have reported thermophysical and spectroscopic studies for the mixtures of alkanediols (isomeric butanediols and α,ω-alkanediols) with amides (N,N-dimethylformamide and pyrrolidin-2-one) [16–18]. As a continuation of our earlier communications, the excess molar volumes \( V^E \), speed of sound \( u \), viscosity \( \eta \), i.r. spectra, \(^1\)H and \(^{13}\)C n.m.r. for liquid binary mixtures of α,ω-alkanediols [1,2-ethanediol (ED), 1,3-propanediol (PPD), and 1,5-pentanediol (PTD)] and pyrrolidin-2-one (PY) have been determined in the present report. Several related parameters were estimated and are discussed in comparison with (α,ω-alkanediols – N,N-dimethylformamide) (DMF) mixtures reported earlier [18]. The aim of this work is to obtain information about structural and interactional studies of progressive addition of methylene groups in the series of α,ω-alkanediols in pyrrolidin-2-one.

2. Experimental
2.1. Materials
The pyrrolidin-2-one (PY; mass fraction purity >0.99 g.c.), 1,2-ethanediol (1,2-ED; mass fraction purity >0.995 g.c.), 1,3-propanediol (1,3-PPD; mass fraction purity >0.99 g.c.) and 1,5-pentanediol (1,5-PTD; mass fraction purity >0.96 g.c.) were obtained from Fluka. Pyrrolidin-2-one was dried with CaO and fractionally distilled as described elsewhere [19]. The 1,5-pentanediol was fractionally distilled in an 45 cm Stedman column and then distilled in vacuo over sodium hydroxide pellets [19]. Prior to use, all the chemicals were stored over molecular sieves to remove any traces of water. The water impurity in the chemicals was as low as mass fraction <0.005%. The purity of all the chemicals was checked by comparing their densities (measured using Anton Paar digital precision densimeter DMA 60) with the literature values [6,10,19,20] (table 1).
The uncertainty in density measurements was ±1 \( \cdot 10^{-2} \) kg \( \cdot \) cm\(^{-3}\).

2.2. Methods

The measurement of excess molar volume was carried out in a continuous dilution dilatometer. The dilatometer was immersed in a water bath controlled to better than ±0.01 K. Temperature control was achieved using a circulating water bath, regulated to ±0.01 K, using a proportional temperature controller. The temperature was calibrated to (308.15 ± 0.01) K with a precision platinum resistance thermometer. Details of the experimental setup and the measuring procedure have been described elsewhere [21]. The results for \( P^E \) are estimated to be accurate to ±0.002 cm\(^3\) \cdot mol\(^{-1}\).

An ultrasonic time intervalometer (UTI-101) from Innovative Instruments based on the pulse-echo-overlap technique (PET) coupled with an oscilloscope was used for the speed of sound measurements. The frequency of sound was 2.0 MHz. The cell for the speed of sound measurements was calibrated with water [22] as a reference. The uncertainty in the measurement of speed of sound lay within ±2 \( \cdot 10^{-2} \) m \( \cdot \) s\(^{-1}\).

Viscosity measurements were made using the modified form of Ubbelohde viscometer placed in a water thermostat, the temperature of which was controlled to (308.15 ± 0.01) K. The flow time of a definite volume of liquid through the capillary was measured with an accurate stopwatch with a resolution of 1 \( \cdot 10^{-2} \) s. Viscosity values are uncertain to within the range 0.001 mPa \( \cdot \) s.

The \(^1\)H and \(^13\)C n.m.r. chemical shifts were observed with the help of a JEOL AL FT-NMR spectrometer operating at 300 MHz. In order to determine the chemical shift, \( \delta \), for liquid mixtures of PY and \( \alpha,\omega\)-alkanediols over the entire composition range, CDC\(_3\) was used as an external solvent for all the n.m.r. measurements. A Perkin-Elmer (RX1) FT-IR spectrometer in the frequency range (4400 to 350) cm\(^{-1}\) was utilized to record the FT-IR spectra.

3. Results and discussion

3.1. Thermodynamic properties

The experimentally measured values of the excess molar volume, \( P^E \) (cm\(^3\) \cdot mol\(^{-1}\)) for mixtures of PY and \( \alpha,\omega\)-alkanediols at \( T = 308.15 \) K are listed in table 2 and graphically presented in figure 1. The \( P^E \) values are positive for 1,2-ED and 1,5-PTD and both negative and positive for 1,3-PDD and 1,4-BTD. The data of 1,4-BTD system have been taken from our previous paper [16]. The \( P^E \) values for the present systems vary in the order 1,4-BTD ~ 1,3-PDD < 1,5-PTD < 1,2-ED. The breaking of self-associated diols, particularly in the case of 1,2-ED and non-specific physical interactions of 1,5-PTD with PY (with longer-chain \( \alpha,\omega\)-alkanediols, attractive interactions between unlike species decrease) dominate, making the \( P^E \) positive. Negative \( P^E \) values at lower mole fraction regions of PY are indicative of the strong interactions between PY and 1,3-PDD and 1,4-BTD. In these mixtures, interaction occurs mainly because of strong hydrogen bonding between \( \alpha,\omega\) group of PY and -OH groups of diols.

The \( \alpha,\omega\)-alkanediols in DMF are negative for all the mixtures except for the binary mixtures of the same diols with DMF [18]. The \( P^E \) values of \( \alpha,\omega\)-alkanediols in DMF are indicative of the strong interactions between \( \alpha,\omega\)-alkanediols in aqueous media [1,3] is larger than that in PY and this reverse trend in aqueous medium is explained on the basis of occupation of free volume, or cavity in the open ice-like structure of water by diol molecules.

The speed of sound \( u \) (m \( \cdot \) s\(^{-1}\)) for the (\( \alpha,\omega\)-alkanediols + PY) have been summarized in table 3. Combining speed of sound with excess volume \( P^E \) data, one can calculate the isentropic compressibility \( \kappa_s \) as

<table>
<thead>
<tr>
<th>Component</th>
<th>( \rho_{\text{m,exp}} ) kg ( \cdot ) m(^{-3})</th>
<th>( \rho_{\text{m,cal}} ) kg ( \cdot ) m(^{-3})</th>
<th>( u ) m ( \cdot ) s(^{-1})</th>
<th>( \eta ) mPa ( \cdot ) s</th>
<th>( \alpha^\prime ) ( \cdot ) 10(^{-5} )</th>
<th>( C_p^\prime ) J ( \cdot ) K(^{-1} \cdot ) mol(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>PY</td>
<td>1097.14</td>
<td>1099.13(^*)</td>
<td>1599.97</td>
<td>8.922</td>
<td>9.775(^*)</td>
<td>169.4(^{**})</td>
</tr>
<tr>
<td>1,2-ED</td>
<td>1102.90</td>
<td>1102.50(^*)</td>
<td>1633.36</td>
<td>11.354</td>
<td>6.77(^*)</td>
<td>149.7(^{**})</td>
</tr>
<tr>
<td>1,3-PDD</td>
<td>1042.70</td>
<td>1043.71(^*)</td>
<td>1604.47</td>
<td>26.438</td>
<td>7.0(^*)</td>
<td>176.4(^{**})</td>
</tr>
<tr>
<td>1,5-PTD</td>
<td>974.30</td>
<td>974.30(^*)</td>
<td>1566.12</td>
<td>63.997</td>
<td>11.28(^*)</td>
<td>233.2(^{**})</td>
</tr>
</tbody>
</table>

\(^*\) Reference [20];
\(^*\) Reference [6];
\(^*\) Reference [19];
\(^*\) Reference [20];
\(^*\) Reference [9];
\(^*\) Reference [10];
\(^*\) Reference [19];
\(^*\) Reference [16].
FIGURE 1. Plot of excess volumes \( V^E \) against mole fraction for \( x, x,\alpha\)-alkanediols: 0, 1,2-ED; o, 1,3-PPD; -----, 1,4-BTD; □, 1,5-PTD; and ---, fitting with equation (5) + (1 - \( x \)) \( \rho \).

TABLE 3

<table>
<thead>
<tr>
<th>Speed of sound ( u ) values for ( x, x,\alpha)-alkanediols + (1 - ( x )) ( \rho ) at ( T=308.15 ) K</th>
</tr>
</thead>
<tbody>
<tr>
<td>( x )</td>
</tr>
<tr>
<td>------</td>
</tr>
<tr>
<td>0.038 0.094 0.3232 0.029 0.2239 0.059</td>
</tr>
<tr>
<td>0.0505 0.116 0.4784 0.025 0.3769 0.070</td>
</tr>
<tr>
<td>0.0512 0.122 0.5180 0.022 0.5091 0.070</td>
</tr>
<tr>
<td>0.0607 0.120 0.5751 0.018 0.6010 0.061</td>
</tr>
<tr>
<td>0.0694 0.115 0.6505 0.010 0.7035 0.047</td>
</tr>
<tr>
<td>0.0743 0.102 0.7028 0.004 0.8220 0.028</td>
</tr>
<tr>
<td>0.0828 0.087 0.7719 0.000 0.8947 0.018</td>
</tr>
<tr>
<td>0.0868 0.070 0.8237 0.010 0.9538 0.007</td>
</tr>
<tr>
<td>0.0924 0.052 0.8712 0.019</td>
</tr>
<tr>
<td>0.0960 0.027 0.9116 0.024</td>
</tr>
<tr>
<td>0.0976 0.004 0.9476 0.022</td>
</tr>
<tr>
<td>0.1057 0.002 0.9758 0.008</td>
</tr>
</tbody>
</table>

The corresponding molar quantity is given by

\[
K_s = -\frac{1}{\rho} \left( \frac{\partial \rho}{\partial x} \right)_s = V_s - \rho \frac{\partial V}{\partial \rho}.
\]

where \( M \) is the molar mass of the mixture. Since the \( u \) and \( V^E \) measurements have not been made on the same samples, the \( V^E \) data were extrapolated to the mole fractions of the speed of sound using least square method.

The excess molar isentropic compressibility, \( K_s^E \), was determined using the following equation:

\[
K_s^E = K_s - K_s^F,
\]

where \( K_s^F \) can be expressed as follows:

\[
K_s^{id} = \sum \frac{[K_s^F + T(A_{s}^F)^2/C_s^F] - T \left( \sum \frac{A_{s}^F}{C_s^F} \right)}{C_s^F},
\]
FIGURE 2. Plot of excess isentropic compressibility $K^E$ against mole fraction for $\alpha, \omega$-alkanediols: •, 1,2-ED; ○, 1,3-PPD; ……, 1,4-BTD; □, 1,5-PTD; and ——, fitting with equation (5) + ($1 - x$) $\rho$.

where $C^{*pi}$ is the isobaric molar heat capacity, $K^{*Si}$ is the isentropic compressibility, $x_i$ is the mole fraction and $A^{*pi}$ is the product of molar volume $V^{*}$ and thermal expansivity $\alpha^{*}$ for the pure component $i$.

The uncertainty in calculated excess molar isentropic compressibility $A^E$ data are same as that of the speed of sound measurement. Figure 2 depicts the graphical representation of the excess molar isentropic compressibility, $A^E$. The $K^E$ values are negative for all the mixtures except for ($\rho$ + 1,5-PTD) for which it shows S-shaped behaviour and vary in the sequence 1,3-PPD < 1,4-BTD < 1,2-ED < 1,5-PTD. These results show that 1,3-PPD and 1,4-BTD form more compressible species with $\rho$ than 1,2-ED and 1,5-PTD. The $K^E$ values of the same diols in DMF [18] are more negative in comparison with $\rho$. A comparative analysis of $K^E$ values shows that DMF forms more compressible species with $\alpha, \omega$-alkanediols than with $\rho$. The $K^E$ values for aqueous mixtures of $\alpha, \omega$-alkanediols are larger and more negative than in $\rho$ and DMF, which show that compression effects are maximum in aqueous medium, thereby facilitating the strong hetero-atomic hydrogen bonding between water and $\alpha, \omega$-alkanediols [6].

The excess values of $\rho^E$ and $K^E$ have been fitted by the conventional curve fitting strategy for the excess properties of binary mixtures by using the Redlich–Kister type equation in the following form:

$$y^E = x(1 - x) \sum A_i(2x - 1)^i,$$

where $y^E$ represents the excess properties. The values for the coefficient $A_i$ and the standard deviation of the fit for each system are given in table 4.

The partial molar excess quantities viz. volume $V^E$ and isentropic compressibility were calculated from the following equations:

$$\Delta V^E = \Delta V^{(\rho)} + (1 - x) \frac{\partial (\rho x)}{\partial x},$$

$$\Delta K^E = K^E_x + (1 - x) \frac{\partial K^E_x}{\partial x}.$$
FIGURE 3. Plot of partial molar excess volume against mole fraction for \( x_\text{o,co-alkanediols} \): -0- 1,2-ED; ~0-, 1,3-PPD; ......, 1,4-BTD; and -O-, 1,5-PTD + (1 - \( x \)) PY.

for 1,3-PPD and 1,4-BTD and positive for 1,2-ED and 1,5-PTD. The negative value of the partial molar volumes may be taken as sign of strong interaction between diols and PY indicating strong interactions of 1,3-PPD and 1,4-BTD with PY through C=O - H-O hydrogen bonding. Dispersion forces and non-specific physical interaction of 1,2-ED and 1,5-PTD with PY are dominating in these systems. However, \( V_f^0 \) values are large and negative for all the mixtures of (diols + DMF) and vary as 1,2-ED < 1,3-PPD < 1,4-BTD < 1,5-PTD [18]. A competitive study of \( V_f^0 \) values reveals that for short-chain diols, the existence of strong hydrogen bonding through C=O - H-O between the more polar DMF and the two hydroxy groups on the diols causes a decrease in volume. The \( V_f^0 \) values of \( \alpha,\omega \)-alkanediols in DMF increase with the extension of hydrophobic chain. The estimated values of partial molar quantities for (\( \alpha,\omega \)-alkanediols + PY) mixtures at infinite dilution are listed in table 5.

Figure 4 shows the variation of partial molar excess compressibility \( K_f^0 \) for the given systems. The estimated values of partial molar excess compressibility at infinite dilution are also given in table 5. Negative \( K_f^0 \) values for all the mixtures except for (1,5-PTD + PY) (figure 4) infer that hydroxyl groups in diols facilitate hydrogen bonding with the carbonyl group of PY and these compression effects are maximum for 1,3-PPD and the magnitude of these compression effects decreases as 1,3-PPD > 1,4-BTD > 1,5-PTD ~ 1,2-ED.

### 3.2. Transport properties

Experimental viscosity \( \eta \) (mPa·s) data for mixtures of (\( \alpha,\omega \)-alkanediols + PY) are given in table 6 and plotted in figure 5. The viscosity deviations \( \Delta \eta \) of the measured values were calculated using the following equation:

\[
\Delta \eta \eta = \eta - \exp \left( \sum x_i \ln \eta_i \right), \tag{8}
\]

where \( \eta \) and \( \eta_i \) are the viscosities of mixture and of pure component \( i \), respectively. Viscosity deviation \( \Delta \eta \) determined at different mole fractions, represent a measure of the type of intermolecular interactions. The variation of viscosity deviation \( \Delta \eta \) values for the binary mixtures of PY with diols over the whole composition range at \( T = 308.15 \text{ K} \) are presented in figure 5. The \( \Delta \eta \) values follow the order 1,5-PTD < 1,2-ED < 1,3-PPD. Figure 5 shows that \( \Delta \eta \) values are large and negative for (1,5-PTD + PY) and positive for 1,3-PPD. Negative \( \Delta \eta \) values are common in which dispersion forces are dominant and the increase in \( \Delta \eta \) values may consistently be ascribed to an increase in specific interactions and to a decrease in dispersion forces [11,12,25]. These

<table>
<thead>
<tr>
<th>PY</th>
<th>( \eta_f^{\infty} ) cm(^3) mol(^{-1})</th>
<th>( \eta_f^{\infty} ) cm(^3) mol(^{-1})</th>
<th>( K_f^{\infty} ) Pa(^{-1}) m(^3) mol(^{-1})</th>
<th>( K_f^{\infty} ) m(^3) mol(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,2-ED</td>
<td>0.399</td>
<td>0.390</td>
<td>-0.54</td>
<td>-0.26</td>
</tr>
<tr>
<td>1,3-PPD</td>
<td>-0.491</td>
<td>0.281</td>
<td>-2.41</td>
<td>-2.09</td>
</tr>
<tr>
<td>1,5-PTD</td>
<td>0.213</td>
<td>0.471</td>
<td>0.79</td>
<td>-1.42</td>
</tr>
</tbody>
</table>
results show that the magnitude of these dispersion forces are more for 1,5-PTD than 1,3-PPD. The results obtained from viscosity measurement are in good agreement with the measured thermodynamic properties.

Deviation in Gibbs free energies of activation for viscous flow $g(x)$ values may also be considered a reliable measure to detect the presence of interactions between molecules [11,12,25] are calculated using the following equation:

$$ g(x) = RT \left[ \ln \eta V - \left( \sum x_i \ln \eta_i V_i^* \right) \right], $$  \hspace{1cm} (9)

where $R$ is the gas constant, $T$ is the absolute temperature, $\eta$ and $V_i^*$ are the molar volume of the mixture and that of the pure components. Figure 6 depicts the graphical representation of the deviation in Gibbs free energies of activation for viscous flow $g(x)$ values and its values decrease from (1,3-PPD + PY) to 1,5-PTD. The values of $g(x)$ decrease as the strength of intermolecular interactions decreases, which support our above assumption of strong interactions between (1,3-PPD + PY) than (1,5-PTD + PY). Both $\Delta \eta$ and $g(x)$ values were fitted to equation (5) and parameters are listed in table 4.

### 3.3. Spectroscopic properties

We have recently shown [16–18] that the combined use of i.r. and n.m.r. spectroscopy can yield valuable information about the intermolecular interactions. I.r. measurements have also been carried out for mixtures of (a,ω-alkanediols + PY) over the entire composition range. The shift in wave number $v$ appears for hydroxyl groups of a,ω-alkanediols and >CO group of PY. The results indicate that the interactions are taking place through both –OH and >CO groups. Table 7 depicts the wave number $v$ values at maximum absorbance of –OH and >CO stretching frequencies for mixtures of diols in PY over the whole composition range.

The $^1$H and $^{13}$C n.m.r. chemical shifts, $\delta$, for the mixtures of (a,ω-alkanediols + PY) have been measured over the entire composition range. It is observed that there is an appreciable change in $\delta$ values for the –OH protons of diols, –NH proton of PY and >CO carbon of PY as a function of mole fraction of diol. However, not much change in $\delta$ values is seen for the –CH of PY and diols. The n.m.r. chemical shift, $\delta$, data of $^1$H and $^{13}$C n.m.r. are tabulated in tables 8 and 9, respectively.
The excess n.m.r. chemical shift, $\delta^E$, has been estimated from the additivity rule i.e.:

$$\delta^E = \delta - x_1\delta_1^p - x_2\delta_2^p,$$

where $\delta_1^p$ and $\delta_2^p$ are the chemical shifts of diols and PY at infinite dilution concentration, respectively.

### 3.3.1. Chemical shift of –OH groups

The $\delta$ values of hydroxyl protons are shown graphically as a function of mole fraction of diol in figure 7. The

<table>
<thead>
<tr>
<th>x</th>
<th>$v$ cm$^{-1}$</th>
<th>x</th>
<th>$v$ cm$^{-1}$</th>
<th>x</th>
<th>$v$ cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,2-ED</td>
<td>3248.1</td>
<td>0.0783</td>
<td>3356.9</td>
<td>0.0514</td>
<td>3255.9</td>
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<tr>
<td>1,3-PPD</td>
<td>3254.1</td>
<td>0.1011</td>
<td>3270.9</td>
<td>0.1017</td>
<td>3255.4</td>
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<tr>
<td>1,5-PTD</td>
<td>3261.4</td>
<td>0.2019</td>
<td>3380.0</td>
<td>0.2008</td>
<td>3255.4</td>
</tr>
<tr>
<td>1,4-BTD</td>
<td>3272.2</td>
<td>0.3177</td>
<td>3359.7</td>
<td>0.2942</td>
<td>3271.3</td>
</tr>
<tr>
<td>1,5-PTD</td>
<td>3293.5</td>
<td>0.4604</td>
<td>3372.0</td>
<td>0.3886</td>
<td>3306.0</td>
</tr>
<tr>
<td>1,4-BTD</td>
<td>3211.1</td>
<td>0.5605</td>
<td>3387.0</td>
<td>0.4790</td>
<td>3324.8</td>
</tr>
<tr>
<td>1,5-PTD</td>
<td>3228.4</td>
<td>0.6543</td>
<td>3335.5</td>
<td>0.5820</td>
<td>3333.9</td>
</tr>
<tr>
<td>1,4-BTD</td>
<td>3236.0</td>
<td>0.7513</td>
<td>3339.9</td>
<td>0.6827</td>
<td>3338.8</td>
</tr>
<tr>
<td>1,5-PTD</td>
<td>3312.3</td>
<td>0.762</td>
<td>3354.8</td>
<td>0.7812</td>
<td>3337.1</td>
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<td>1,4-BTD</td>
<td>3313.3</td>
<td>0.8980</td>
<td>3355.5</td>
<td>0.9095</td>
<td>3338.2</td>
</tr>
<tr>
<td>1,5-PTD</td>
<td>3353.8</td>
<td>0.9491</td>
<td>3392.3</td>
<td>1.0000</td>
<td>3350.1</td>
</tr>
<tr>
<td>1,4-BTD</td>
<td>3391.0</td>
<td>1.0000</td>
<td>3391.0</td>
<td>1.0000</td>
<td>3338.1</td>
</tr>
</tbody>
</table>

### Table 7b

Wave number $v$ values at maximum absorbance of –CO groups for

<table>
<thead>
<tr>
<th>x</th>
<th>$v$ cm$^{-1}$</th>
<th>x</th>
<th>$v$ cm$^{-1}$</th>
<th>x</th>
<th>$v$ cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,2-ED</td>
<td>1696.0</td>
<td>0.1011</td>
<td>1677.8</td>
<td>0.0514</td>
<td>1690.3</td>
</tr>
<tr>
<td>1,3-PPD</td>
<td>1693.7</td>
<td>0.2019</td>
<td>1675.0</td>
<td>0.1017</td>
<td>1692.0</td>
</tr>
<tr>
<td>1,5-PTD</td>
<td>1690.6</td>
<td>0.3177</td>
<td>1674.1</td>
<td>0.2008</td>
<td>1690.2</td>
</tr>
<tr>
<td>1,4-BTD</td>
<td>1686.3</td>
<td>0.4604</td>
<td>1674.0</td>
<td>0.2942</td>
<td>1690.8</td>
</tr>
<tr>
<td>1,5-PTD</td>
<td>1681.8</td>
<td>0.5605</td>
<td>1666.9</td>
<td>0.3886</td>
<td>1690.0</td>
</tr>
<tr>
<td>1,4-BTD</td>
<td>1686.3</td>
<td>0.6543</td>
<td>1664.4</td>
<td>0.4790</td>
<td>1688.1</td>
</tr>
<tr>
<td>1,5-PTD</td>
<td>1673.0</td>
<td>0.7513</td>
<td>1664.4</td>
<td>0.5820</td>
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</tr>
<tr>
<td>1,4-BTD</td>
<td>1670.4</td>
<td>0.7962</td>
<td>1668.2</td>
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<td>1683.9</td>
</tr>
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<td>1,5-PTD</td>
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TABLE 8

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<td>$\delta_{-OH}^{10^{-6}}$</td>
<td>$\delta_{-NH}^{10^{-6}}$</td>
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<td>$\delta_{-NH}^{10^{-6}}$</td>
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TABLE 9

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<th>1,5-PTD</th>
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</thead>
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<td>$\delta_{-NH}^{13C}$</td>
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<tr>
<td>1,2-ED</td>
<td></td>
<td>5.381</td>
<td></td>
<td></td>
<td></td>
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<td>5.481</td>
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</tbody>
</table>

increase in $\delta$ values (downfield shift) for hydroxyl protons with the addition of diol in PY, infer the formation of C=O—H—O hydrogen bonding in the (ω,ω-alkanediols + PY) mixtures. The $\delta^{13C}$ values for hydroxyl protons are measured experimentally whereas $\delta_{-OH}^{13C}$ values for the same protons have been estimated by extrapolation of $\delta$ values for the –OH protons to infinite dilution (figure 7).

Both values are listed in table 10 Excess values, $\delta^E$, estimated from equation (10) are depicted in figure 8. These vary in order 1,5-PTD < 1,3-PTD < 1,2-ED.

3.3.2. Chemical shift of –NH group

The variation of 1H n.m.r. chemical shifts $\delta$ of –NH proton against mole fraction are presented in figure 9 that show the up field shift with the addition of diol in PY. This shielding of the –NH proton over the whole composition range indicates the dissociation of self-associated PY dimer. The $\delta_{-NH}^{10^{-6}}$ values for –NH proton are measured experimentally whereas $\delta_{-NH}^{10^{-6}}$ values for the –NH proton have been estimated by extrapolation of $\delta$ values of –NH proton to infinite dilution (figure 9). Table 10 lists the estimated values. The $\delta^E$ values calculated using equation (10) are
FIGURE 8. Plot of $^{1}H$ n.m.r. excess chemical shifts $\delta_E$ of hydroxyl protons against mole fraction for $x \alpha, \omega$-alkanediols: $\bigcirc$, 1,2-ED; $\bigcirc$, 1,3-PPD; $\Box$, 1,5-PTD; and $-$–$-$ fitting with equation (5) + (1 - $x$) PY.

graphically depicted in figure 10. The change in chemical shift, $\delta_E$, varies as 1,2-ED < 1,3-PPD < 1,5-PTD.

3.3.3. Chemical shift of $\gamma$C=O group

The experimentally measured $^{13}C$ n.m.r. chemical shifts values for mixtures of $\alpha, \omega$-alkanediols and PY are graphically presented in figure 11. With addition of diol, $^{13}C$ n.m.r. chemical shifts of $\gamma$CO group shifts downfield over the whole composition range, which again infer the formation of C=O - H - O hydrogen bonding between hydroxyl groups of $\alpha, \omega$-alkanediols and $\gamma$CO group of PY. The $\delta^0$ values for the $\gamma$CO group are experimentally measured whereas $\delta^f$ values for the $\gamma$CO group have been estimated by extrapolation of $\delta$ values of $\gamma$CO group to infinite dilution (figure 11). The values are also listed in table 10. The $\delta^0$ of the carbonyl group have also been estimated from equation (10) and $\delta^f$ values of the $^{13}C$ n.m.r. of the carbonyl group are graphically depicted in figure 12. The values increase as 1,2-ED < 1,5-PTD < 1,3-PTD.

All the $\delta^E$ values were also fitted to equation (5). The values of coefficient $A_1$ and the standard deviation are also tabulated in table 4. Comparison of n.m.r. measurements with excess molar volume data shows an interesting correlation (table 11). The maximum/minimum values of $^{1}H$ and the $^{13}C$ n.m.r. excess chemical shift $\delta^E$ and excess molar volume $\delta^M$ are positioned at about same mole fraction for all the mixtures. We conclude that in ($\alpha, \omega$-alkanediols + PY) mixtures, interactions are mainly taking place between carbonyl group of PY and hydroxyl groups of $\alpha, \omega$-alkanediols.

FIGURE 10. Plot of $^{1}H$ n.m.r. excess chemical shifts $\delta_E$ of -NH proton against mole fraction for $x \alpha, \omega$-alkanediols: $\bigcirc$, 1,2-ED; $\bigcirc$, 1,3-PPD; $\Box$, 1,5-PTD; and $-$–$-$, fitting with equation (5) + (1 - $x$) PY.

FIGURE 9. Plot of $^{1}H$ n.m.r. chemical shifts $\delta$ of -NH proton against mole fraction for $x \alpha, \omega$-alkanediols: $\bigcirc$, 1,2-ED; $\bigcirc$, 1,3-PPD; and $\Box$, 1,5-PTD + (1 - $x$) PY.
FIGURE 11. Plot of $^1$H n.m.r. chemical shifts $\delta$ of carbonyl group against mole fraction for $x_1$,2-alkanediols: $\phi$, 1,2-BTD; $\bigcirc$, 1,3-BTD; and $\square$, 1,5-PTD; $\bigstar$ (1-x) PY.

FIGURE 12. Plot of $^{13}$C n.m.r. excess chemical shifts $\Delta\delta$ of carbonyl group against mole fraction for $x_1$,2-alkanediols: $\phi$, 1,2-BTD; $\bigcirc$, 1,3-BTD; $\square$, 1,5-PTD; and -----, fitting with equation (5) + (1 - x) PY.

TABLE 11
The values of mole fractions corresponding to the maxima/minima of excess molar volume $\Delta^\rho$ and excess chemical shifts $\Delta\delta$.

<table>
<thead>
<tr>
<th>PY</th>
<th>$\Delta^\rho$</th>
<th>$\Delta\delta$</th>
<th>$\Delta\delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(cm$^3$ mol$^{-1}$)</td>
<td>-OH $^1$H</td>
<td>-NH $^1$H</td>
</tr>
<tr>
<td></td>
<td>n.m.r.</td>
<td>n.m.r.</td>
<td>n.m.r.</td>
</tr>
<tr>
<td>1,2-ED</td>
<td>0.4615</td>
<td>0.4604</td>
<td>0.4827</td>
</tr>
<tr>
<td>1,3-PPD</td>
<td>0.5115$^a$</td>
<td>0.5115$^a$</td>
<td>0.5115</td>
</tr>
<tr>
<td>1,5-PTD</td>
<td>0.5634</td>
<td>0.5712</td>
<td>0.5442</td>
</tr>
</tbody>
</table>

* Indicate the mole fractions at transition point since the three systems show S-shape behaviour for $\Delta^\rho$.

4. Conclusions

Strong interactions between PY and $x_1$,2-alkanediol mixtures have been analyzed by thermodynamic and transport properties. On the basis of spectroscopic measurement, we conclude that these interactions are through the $\pi$C=O group of PY and $\pi$-OH groups of $x_1$,2-alkanediol. The results obtained from spectroscopic measurements correlate well with the thermodynamic and transport studies.

Acknowledgements

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References


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Structural and interactional studies of homologous series of \( \alpha,\omega \)-alkanediols in \( N,N \)-dimethylformamide

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Abstract

The thermodynamic parameters viz. excess molar volume \( \bar{V}_m \) and ultrasonic velocity \( u \), transport parameter viscosity \( \eta \) and spectroscopic parameters viz. IR, \( ^1H \) and \( ^13C \) NMR have been measured for the mixtures of \( \alpha,\omega \)-alkanediols (1,2-ethanediol, 1,3-propanediol and 1,5-pentanediol) and \( N,N \)-dimethylformamide over the whole composition range at \( T = 308.15K \). The partial molar quantities \( \bar{V}_m \), isentropic compressibility \( K_s \), deviation in ultrasonic velocity \( \delta u \), viscosity deviation \( \delta \eta \), deviation in Gibbs free energies of activation for viscous flow \( \delta G^* \) and excess NMR chemical shift \( \delta \delta \) have been estimated and analysed. The results reveal distinctly that the interaction between unlike molecules takes place through hydroxyl groups of \( \alpha,\omega \)-alkanediols and the \( \gamma \)-CO group of \( N,N \)-dimethylformamide. An excellent correlation between thermodynamic and spectroscopic measurements has been observed.

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Keywords: Thermodynamic parameters; Viscosity; Spectroscopic measurements (IR, NMR); \( \alpha,\omega \)-Alkanediols; \( N,N \)-dimethylformamide

1. Introduction

Accurate knowledge of various thermophysical properties viz. excess molar volume, \( \bar{V}_m \), ultrasonic speed, \( u \), viscosity, \( \eta \), of mixtures of organic liquids is essential for the right design of several types of relevant industrial equipment [1–6]. Alkanediols are the simplest model structural units for polyhydroxy compounds. Alkanediols are chemically very similar to alcohols and the hydration properties have been observed for these compounds by several authors [2,3,7–11]. The presence of the additional hydroxyl group in the diol molecule makes the position of the two-hydroxyl groups very important for the hydrophobic hydration. \( \alpha,\omega \)-Alkanediols play a significant role in industry due their wide range of practical applications. For example, 1,2-ethanediol is an ingredient in photographic developing solutions, hydraulic brake fluids and inks used in stamp pads, ballpoint pens, and print shops. The 1,3-propanediol is used to absorb extra water and maintain moisture in certain medicines, cosmetics, and food products. It is also used to create artificial smoke or fog used in fire-fighting training and in theatrical productions. The 1,4-butanediol is a versatile intermediate for the chemical industry. The most important fields of application are the manufacture of polyurethane and polybutylene terephthalate. The 1,5-pentanediol shows activity against virus, bacteria, and fungi. It is also effective against dermatitis and is also used as preservative for shampoo and hand creams.

Most of the studies have dealt with the structural and interactional analysis of alkanediols in aqueous media [2,3,7,12–16]. It has been confirmed that \( \alpha,\omega \)-alkanediols facilitate heteroatomic hydrogen bonding whereas terminal hydrophobic –CH3 groups induce the compression effects in surrounding water molecules. The present report deals with the behavior of \( \alpha,\omega \)-alkanediols in non-aqueous medium. Thermodynamic (\( \bar{V}_m \), \( u \)) and transport (\( \eta \)) and spectroscopic (IR, \( ^1H \), and \( ^13C \) NMR) parameters of \( \alpha,\omega \)-alkanediols (1,2-ethanediol (ED), 1,3-propanediol (PPD), and
1,5-pentanediols (PTD) have been measured in N,N-dimethylformamide (DMF) over the whole range of composition. The N,N-dimethylformamide is a versatile reagent used in synthesis of pharmaceuticals, in agricultural chemistry and as an organic solvent [1,17,18]. The N,N-dimethylformamide, however, is not self-associated by H-bonding, although a certain degree of association due to dipole-dipole interaction is expected. The aim of the work is to obtain information about the structural effects on the basis of the influence of the successive addition of the \(-\text{CH}_2\) group in the series of \(\alpha,\omega\)-alkanediols in N,N-dimethylformamide.

2. Experimental

2.1. Materials

The N,N-dimethylformamide (DMF; mass fraction purity >0.999 GLC), 1,2-ethanediol (1,2-ED; mass fraction purity >0.995 GC), 1,3-propanediol (1,3-PPD; mass fraction purity >0.99 GC), and 1,5-pentanediol (1,5-PTD; mass fraction purity >0.96 GC) were obtained from Fluka. Prior to use, all the chemicals were stored over molecular sieves to remove traces of water. The purity of all the chemicals was checked by comparing their densities (measured using Anton Paar digital precision densimeter) with the literature values [1,10,16,20] (table 1). The uncertainty in density measurements was ±1 \(\times 10^{-4}\) kg m\(^{-3}\).

2.2. Methods

The measurement of excess molar volume was carried out in a continuous dilution dilatometer. The dilatometer was immersed in a water bath controlled to better than ±0.01 K. Temperature control was achieved using a circulating water bath, regulated to ±0.01 K, using a proportional temperature controller. The temperature was calibrated to (308.15 ± 0.01) K with a precision platinum resistance thermometer. Details of the experimental setup and the measuring procedure have been described elsewhere [21]. The results for \(V^E\) are estimated to be accurate to ±0.002 cm\(^3\) mol\(^{-1}\).

An ultrasonic time intervalometer (UTI-101) from Innovative instruments based on the pulse-echo-overlap technique (PET) coupled with an oscilloscope was used for the ultrasonic velocity measurements. The frequency of sound was 2.0 MHz. The cell for the speed of sound measurements was calibrated with water [22] as a reference. The uncertainty in the measurement of ultrasonic velocity was within ±2 \(\times 10^{-2}\) m s\(^{-1}\).

Viscosity measurements were made using a modified form of a Ubbelohde viscometer placed in a water thermostat, the temperature of which was controlled to 308.15 ± 0.01 K. The flow time of a specified volume of liquid through the capillary was measured with a stopwatch with a resolution of 1 \(\times 10^{-4}\) s. Viscosity values are uncertain to within ±0.001 mPa s. \(^1\)H and \(^13\)C NMR chemical shifts were observed with a JEOL AL FT NMR spectrometer operating at 300 MHz. In order to determine the chemical shift, \(\delta\), for liquid mixtures of DMF and \(\alpha,\omega\)-alkanediols at entire composition range, CDC\(_3\) was used as an external solvent for all the NMR measurements. A Perkin-Elmer (RX1) FT-IR spectrometer in the frequency range (4400-350) cm\(^{-1}\) was utilized to record IR spectra.

3. Results and discussion

3.1. Thermodynamic parameters

The experimentally measured excess molar volumes, \(V^E/(\text{cm}^3 \cdot \text{mol}^{-1})\), values for mixtures of DMF and \(\alpha,\omega\)-alkanediols at \(T = 308.15\) K are listed in table 2 and are presented graphically in figure 1. The \(V^E\) values are negative for all the mixtures over the whole composition range and decrease in the order 1,5-PTD < 1,4-BTD < 1,3-PPD < 1,2-ED. Results for the 1,4-BTD system are taken from our previous paper [19]. Negative \(V^E\) values indicate strong interactions between DMF and \(\alpha,\omega\)-alkanediols. In these mixtures, interaction is mainly because of strong hydrogen bonding between \(\text{C}=\text{O}\) group of DMF and \(-\text{OH}\) groups of diols. Variation in \(V^E\) with successive addition of \(-\text{CH}_2\) group in these systems is related to an

<table>
<thead>
<tr>
<th>TABLE 1</th>
<th>Densities ((\rho)), ultrasonic velocities ((u^*)), viscosities ((\eta)), isobaric thermal expansivities ((\alpha)) and molar heat capacities ((C_p)) for the component liquids at (T = 308.15) K</th>
</tr>
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<td>1,5-PTD</td>
<td>974.30</td>
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</tbody>
</table>

\(^a\) Reference [1].
\(^b\) Reference [15].
\(^c\) Reference [10].
\(^d\) Reference [20].
\(^e\) Reference [12].
\(^f\) Derived from density [1,2,10,16,20].
\(^g\) At 298.15 K.
TABLE 2
Excess molar volumes \( V^E \) for \( x \hspace{0.5mm} \alpha,\alpha' \)-alkanediols + (1 - \( x \)) DMF at \( T = 308.15 \) K.

<table>
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<tr>
<th>( x )</th>
<th>1,2-ED</th>
<th>1,3-PPD</th>
<th>1,5-PTD</th>
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<tr>
<td>( V^E / (\text{cm}^3 \cdot \text{mol}^{-1}) )</td>
<td>( V^E / (\text{cm}^3 \cdot \text{mol}^{-1}) )</td>
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<tr>
<td>0.9960</td>
<td>0.2421</td>
<td>0.2218</td>
<td></td>
</tr>
</tbody>
</table>

FIGURE 1. Plot of excess volumes \( V^E \) against mole fraction for \( x \hspace{0.5mm} \alpha,\alpha' \)-alkanediols: O, 1,2-ED; C, 1,3-PPD; ..., 1,4-BTD; □, 1,5-PTD + (1 - \( x \)) DMF.

increase in hydrophobicity resulting from the extension of the hydroxyl groups.

Volume loss of these \( \alpha,\alpha' \)-alkanediols in aqueous media [7] is larger than that in DMF and in aqueous medium \( V^E \) values decrease as 1,2-ED < 1,3-PPD < 1,4-BTD. This reverse trend in aqueous medium is related to the occupation of free volume, or cavity in the open ice-like structure of water by diol molecules.

The ultrasonic velocities \( u/(\text{m} \cdot \text{s}^{-1}) \) for the \((\text{DMF} + \alpha,\alpha'\text{-alkanediols})\) are summarized in table 3. Combining ultrasonic velocity \( u \) with excess volume \( V^E \) data, one can calculate the isentropic compressibility \( \kappa_S \) as

TABLE 3
Ultrasonic velocities \( u \) for \((x \hspace{0.5mm} \alpha,\alpha'\text{-alkanediols} + (1 - x) \text{ DMF})\) at \( T = 308.15 \) K.

<table>
<thead>
<tr>
<th>( x )</th>
<th>1,2-ED</th>
<th>1,3-PPD</th>
<th>1,5-PTD</th>
</tr>
</thead>
<tbody>
<tr>
<td>( u/(\text{m} \cdot \text{s}^{-1}) )</td>
<td>( u/(\text{m} \cdot \text{s}^{-1}) )</td>
<td>( u/(\text{m} \cdot \text{s}^{-1}) )</td>
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<tr>
<td>0.0209</td>
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<tr>
<td>0.9680</td>
<td>1624.51</td>
<td>0.9716</td>
<td>1602.18</td>
</tr>
</tbody>
</table>

\[ \kappa_S = -V^{-1} \frac{\partial V}{\partial P} \bigg|_s = \left( \mu u^2 \right)^{-1} \frac{\sum x_i V_i + \rho \bar{E}}{\rho \sum x_i M_i} = \frac{V}{M u^2}, \quad (1) \]

where \( M \) is the molar mass of the mixture. Since the \( u \) and \( V^e \) measurements have not been made on the same samples, the \( V^e \) data were interpolated to the mole fractions of the ultrasonic velocity using least square method.

The corresponding molar quantity is given by

\[ K_S = -\frac{\partial V}{\partial P} \bigg|_s = \nu K_S = \nu^2 \rho u^2, \quad (2) \]

which assumes that dissipative effects are negligible and that the hydrodynamic equation of motion can be linearised. The excess molar isentropic compressibilities, \( \kappa_S^e \), deviation in ultrasonic velocity, \( \nu^D \), were determined using the equations:

\[ K_S^e = K_S - K_S^d, \quad (3) \]

\[ K_S^d = K_S - K_S^d = -\frac{\nu^D}{\rho u^2}, \quad (4) \]

\[ \nu^D = \nu - \nu^e, \quad (5) \]

where

\[ \nu^e = \frac{\partial u}{\partial P} \bigg|_s \]

\[ \kappa_S^e = \frac{\partial^2 \kappa_S}{\partial x_i \partial x_j} \frac{\partial x_i}{\partial x_j} \]

\[ \kappa_S^d = \frac{\partial^2 \kappa_S}{\partial x_i \partial x_j} \frac{\partial x_i}{\partial x_j} \]

\[ \nu^D = \frac{\partial \nu^D}{\partial x_i} \frac{\partial x_i}{\partial x_j} \]

\[ \kappa_S^e = \frac{\partial^2 \kappa_S}{\partial x_i \partial x_j} \frac{\partial x_i}{\partial x_j} \]

\[ \kappa_S^d = \frac{\partial^2 \kappa_S}{\partial x_i \partial x_j} \frac{\partial x_i}{\partial x_j} \]

The excess molar isentropic compressibilities \( \kappa_S^e \) and deviation in ultrasonic velocity \( \nu^D \) against mole fraction for 1,2,6-alkanediols: O, 1,2-ED; O, 1,3-PPD; ..., 1,4-BTD: □, 1,5-PTD + (1 - x) DMF.

The partial molar volumes \( \varphi^P \) shown in figure 3 are negative for mixtures of (diols + DMF) and vary as 1,2-ED < 1,3-PPD < 1,4-BTD < 1,5-PTD. The negative value of partial molar volumes may be taken as a sign of strong...

**FIGURE 2.** Plot of excess isentropic compressibilities \( K_S^e \) and deviation in ultrasonic velocity \( \nu^D \) against mole fraction for 1,2,6-alkanediols: O, 1,2-ED; O, 1,3-PPD; ..., 1,4-BTD; □, 1,5-PTD + (1 - x) DMF.
TABLE 4
Least-squares coefficients of equation (7) and standard deviations of \(x_{\alpha,\omega}\)-alkanediols + (1 \(- x\)) DMF at \(T = 308.15\) K

<table>
<thead>
<tr>
<th>DMF</th>
<th>(a_1)</th>
<th>(a_2)</th>
<th>(a_3)</th>
<th>(a_4)</th>
<th>(a_5)</th>
<th>(\sigma)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,2-ED</td>
<td>-1.061</td>
<td>-0.028</td>
<td>-0.205</td>
<td>-0.090</td>
<td>0.396</td>
<td>0.004</td>
</tr>
<tr>
<td></td>
<td>2.77</td>
<td>0.02</td>
<td>-1.57</td>
<td>33.87</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,3-PPD</td>
<td>-14.285</td>
<td>-7.950</td>
<td>-4.060</td>
<td>-4.384</td>
<td>-3.246</td>
<td>0.195</td>
</tr>
<tr>
<td></td>
<td>1.17</td>
<td>-1.00</td>
<td>-1.89</td>
<td>3.65</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,4-BTD</td>
<td>-1427</td>
<td>-395</td>
<td>1315</td>
<td>-1752</td>
<td>-2762</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-355</td>
</tr>
<tr>
<td>1,5-PTD</td>
<td>0.214</td>
<td>-0.033</td>
<td>0.083</td>
<td>0.116</td>
<td>-0.034</td>
<td>0.003</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.053</td>
</tr>
</tbody>
</table>

interaction between diols and DMF. Figure 3 reveals that for short-chain diols, the existence of strong hydrogen bonding through C=O \(-\) H=O between the more polar DMF and the two hydroxyl groups on the diols causes a decrease in volume. With longer-chain \(\alpha,\omega\)-alkanediols, attractive interactions between unlike species decrease.

However, in aqueous medium this trend is reversed [7,10]. The estimated values of partial molar quantities at infinite dilution are listed in Table 5.

Figure 4 shows the variation of partial molar excess compressibilities \(K_m^E\). The estimated values of partial molar excess compressibilities at infinite dilution are also given in
TABLE 5  
Excess partial molar volumes $V_f^{0\infty}$ and excess partial molar isentropic compressibilities $K_f^{0\infty}$ of $\{x$ α,ω-alkanediols + (1 - x) DMF\} at infinite dilution at $T = 308.15$ K.

<table>
<thead>
<tr>
<th></th>
<th>$V_f^{0\infty}$/(cm$^3$/mol)</th>
<th>$K_f^{0\infty}$/(PPa$^{-1}$·m$^3$/mol)</th>
<th>$\Delta\pi$/(MPa·s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,2-ED</td>
<td>-0.950</td>
<td>-1.109</td>
<td>0.0250</td>
</tr>
<tr>
<td>1,3-PPD</td>
<td>-0.894</td>
<td>-0.945</td>
<td>0.0250</td>
</tr>
<tr>
<td>1,5-PTD</td>
<td>-0.504</td>
<td>-1.100</td>
<td>0.0250</td>
</tr>
</tbody>
</table>

FIGURE 4. Plot of partial molar excess compressibilities against mole fraction for $x$ α,ω-alkanediols: O, 1,2-ED; O, 1,3-PPD; □, 1,4-BTD; □, 1,5-PTD + (1 - x) DMF.

Table 5. Negative $K_f^{0\infty}$ values for all the mixtures (figure 4) imply that hydroxyl groups in diols facilitate hydrogen bonding with the carbonyl group of DMF, that these compression effects are maximum for 1,2-ED, and that the magnitude decreases with the addition of methylene groups.

3.2. Transport parameters

Experimental viscosity $\eta$ (mPa·s) data for mixtures of (DMF + α,ω-alkanediols) is given in table 6. Viscosity deviations $\Delta\pi$ of measured values were calculated using the following equation

$$\Delta\pi = \eta - \exp(\sum x_i \ln \eta_i^0),$$  \hspace{1cm} (10)

where $\eta$ and $\eta_i^0$ are the viscosities of mixture and of pure component $i$. The variation of viscosity deviations $\Delta\pi$ for the binary mixtures of DMF with BTD over the whole composition range at $T = 308.15$ K are presented in figure 5. The $\Delta\pi$ follow the order 1,2-ED < 1,3-PPD < 1,4-BTD < 1,5-PTD. These results show that dispersion forces are responsible for dissociation of self-associated diol molecules and the magnitude of these dispersion forces are more for 1,5-PTD than 1,2-ED. The dispersion forces are probably due to the longer alkyl chain length rendering the molecule more flexible.

Deviations in Gibbs free energies of activation for viscous flow $g(x)$ values may also be considered a reliable measure to detect the presence of interactions between molecules [23,24] and are calculated using the equation

TABLE 6  
Viscosities $\eta$ for $\{x$ α,ω-alkanediols + (1 - x) DMF\} at $T = 308.15$ K.

<table>
<thead>
<tr>
<th></th>
<th>$\eta$(mPa·s)</th>
<th>$\eta$(mPa·s)</th>
<th>$\eta$(mPa·s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,2-ED</td>
<td>0.738</td>
<td>0.729</td>
<td>0.760</td>
</tr>
<tr>
<td>1,3-PPD</td>
<td>0.816</td>
<td>0.848</td>
<td>0.834</td>
</tr>
<tr>
<td>1,5-PTD</td>
<td>0.972</td>
<td>0.994</td>
<td>0.904</td>
</tr>
<tr>
<td></td>
<td>1.131</td>
<td>1.2048</td>
<td>1.267</td>
</tr>
<tr>
<td></td>
<td>1.453</td>
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<td>1.814</td>
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<tr>
<td></td>
<td>2.392</td>
<td>3.516</td>
<td>3.880</td>
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<tr>
<td></td>
<td>3.131</td>
<td>4.994</td>
<td>5.516</td>
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<td>4.137</td>
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</tr>
<tr>
<td></td>
<td>5.498</td>
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<td>7.454</td>
<td>10.901</td>
<td>17.743</td>
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</tr>
<tr>
<td></td>
<td>9.960</td>
<td>10.483</td>
<td>1.446</td>
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</tbody>
</table>

3.3. Spectroscopic parameters

By comparing thermophysical properties with spectroscopic measurements i.e. IR and NMR, selection of suitable associations and contributions to non-ideal behaviour of a mixture can be evaluated [19,25–29]. The IR measurements for mixtures of (DMF + α,ω-alkanediols) over the entire composition range have been carried out. The shift in wave number $\nu$ appears for the hydroxyl groups of diols and the $\nu$CO group of DMF. The results indicate that the interactions take place through both the $-\text{OH}$ and the $\nu$CO groups. Table 7 depicts the wave number $\nu$ at maximum absorbance of the $-\text{OH}$ and the $\nu$CO stretching frequencies for mixtures of diols in DMF over the whole composition range.

We observed for the present systems that there is no appreciable change in chemical shift $\delta$ values for $\text{CH}_2$ proton of DMF and diols. The change in $^1H$ NMR chemical shift, $\delta$, for hydroxyl protons of diols and aldehydic proton

### Table 7a

<table>
<thead>
<tr>
<th>Wave numbers $\nu$ at maximum absorbance of $-\text{OH}$ groups for ${x , \alpha,\omega$-alkanediols $\pm (1 - x)$ DMF</th>
<th>1,2-ED</th>
<th>1,3-PPD</th>
<th>1,5-PTD</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x$</td>
<td>$\nu$/cm$^{-1}$</td>
<td>$x$</td>
<td>$\nu$/cm$^{-1}$</td>
</tr>
<tr>
<td>0.0257</td>
<td>3470.1</td>
<td>0.0229</td>
<td>3462.7</td>
</tr>
<tr>
<td>0.0458</td>
<td>3465.8</td>
<td>0.0468</td>
<td>3448.3</td>
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<td>0.5882</td>
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<td>3369.8</td>
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<tr>
<td>0.6889</td>
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<tr>
<td>0.7303</td>
<td>3355.7</td>
<td>0.7983</td>
<td>3345.6</td>
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<td>3349.4</td>
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<td>3324.0</td>
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</table>

### Table 7b

<table>
<thead>
<tr>
<th>Wave numbers $\nu$ at maximum absorbance of $\nu$CO groups for ${x , \alpha,\omega$-alkanediols $\pm (1 - x)$ DMF</th>
<th>1,2-ED</th>
<th>1,3-PPD</th>
<th>1,5-PTD</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x$</td>
<td>$\nu$/cm$^{-1}$</td>
<td>$x$</td>
<td>$\nu$/cm$^{-1}$</td>
</tr>
<tr>
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<td>1673.8</td>
<td>0.0229</td>
<td>1673.8</td>
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<td>1673.9</td>
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<td>0.3032</td>
<td>1670.1</td>
</tr>
<tr>
<td>0.3222</td>
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</tr>
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</tr>
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<td>1663.9</td>
</tr>
<tr>
<td>0.9344</td>
<td>1654.4</td>
<td>0.9477</td>
<td>1665.5</td>
</tr>
<tr>
<td>0.9680</td>
<td>1659.9</td>
<td>0.9716</td>
<td>1665.6</td>
</tr>
</tbody>
</table>
TABLE 8
1H NMR chemical shifts $\delta$ (10$^{-6}$) for $x \omega,\omega$-alkanediols + (1 - $x$) DMF

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Table 9</th>
<th>Table 10a</th>
</tr>
</thead>
<tbody>
<tr>
<td>Component</td>
<td>$\delta^N$ (10$^{-6}$)</td>
<td>$\delta^N$ (10$^{-6}$)</td>
</tr>
<tr>
<td></td>
<td>1H NMR</td>
<td>1H NMR</td>
</tr>
<tr>
<td>DMF</td>
<td>8.505</td>
<td>162.845</td>
</tr>
<tr>
<td>1,2-ED</td>
<td>5.381</td>
<td>5.414</td>
</tr>
<tr>
<td>1,3-PPD</td>
<td>5.527</td>
<td>5.481</td>
</tr>
<tr>
<td>1,4-BTD</td>
<td>5.381</td>
<td>5.414</td>
</tr>
<tr>
<td>1,5-PTD</td>
<td>5.381</td>
<td>5.414</td>
</tr>
</tbody>
</table>

of DMF is listed in table 8. Excess NMR chemical shift, $\delta^E$, were determined using the equations:

$$\delta^E = \delta - (x_1\delta_1^N + x_2\delta_2^N),$$

(12)

where $\delta$ and $\delta^N$ are the NMR chemical shifts of mixture and the pure components at infinite dilution, respectively. $\delta_1^N$ values for pure components and at infinite dilution are tabulated in table 10. The $\delta^E$ values were also fitted to the equation (7) to obtain the values of coefficients $a_i$ and the standard deviations (table 4). 1H NMR excess chemical shifts, $\delta^E$, for hydroxyl protons as a function of mole fraction of diol for all the mixtures are presented in figure 7. Hydroxyl protons shift downfield with the addition of diol in DMF, indicating the formation of

FIGURE 7. Plot of 1H NMR excess chemical shifts $\delta^E$ of hydroxyl protons against mole fraction for $x \omega,\omega$-alkanediols: $\circ$, 1,2-ED; $\circ$, 1,3-PPD; $...$, 1,4-BTD; $\square$, 1,5-PTD - (1 - $x$) DMF.
C=O • H—O hydrogen bonds. The change in chemical shift increases as 1,2-ED < 1,3-PPD < 1,4-BTD < 1,5-PTD. However, addition of diol in DMF shields the aldehyde proton over the entire composition range. Although in (diol + DMF) mixtures, hydrogen bonding between the H-O groups of diol and the C=O group of DMF is expected, the upfield shifting of aldehydic protons may be due to conjugation of the one pair of electron at nitrogen [19]. The C=O • H—O hydrogen bonding creates a partial positive centre: the carbon atom of the aldehydic group in DMF that can further accept the electrons from the adjacent electron rich nitrogen atom. The change in chemical shift, $\delta^E$, decreases as 1,2-ED < 1,3-PPD < 1,5-PTD < 1,4-BTD as shown in figure 8.

To seek more information about structural and interac­ tional behaviour, $^{13}$C NMR chemical shift $\delta$ has been stud­ ied. The results of $^{13}$C NMR are tabulated in table 9 and are graphically depicted in figure 9. With the addition of diol, the $^{13}$C signal shifts downfield over the whole com­ position range and the $^{13}$C NMR chemical shift $\delta$ increases as 1,5-PTD < 1,4-BTD < 1,3-PTD < 1,2-ED. These results correlate with the results obtained from the above thermo­ dynamic and transport studies.

Comparison of NMR measurements with excess molar volume data shows an interesting correlation (table 11). The maximum/minimum values of $^{1}$H and $^{13}$C NMR excess chemical shift $\delta^E$ and excess molar volume $\nu^E$ are positioned at about the same mole fraction for all the mixtures. We conclude that the carbonyl group of DMF and the hydroxyl groups of $\alpha,\omega$-alkanediols are the two active sites of interactions in (DMF + $\alpha,\omega$-alkanediols) mixtures.

4. Conclusion

Strong interactions between DMF and $\alpha,\omega$-alkanediols mixtures have been analysed by their thermodynamic and transport properties. The interactions between different components decrease with the addition of successive meth­ ylene groups. On the basis of spectroscopic measurement, we conclude that these interactions are through the C=O group of DMF and the —OH groups of the diols. The results obtained from spectroscopic measurements correlate with the thermodynamic and transport studies.

Acknowledgement

The authors thank the UGC (India) for financial assistance.

References

A comparative study of thermophysical and spectroscopic properties in mixtures of isomeric butanediol and $N,N$-dimethylformamide

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Abstract

The thermodynamic parameters viz. excess molar volume $V_E$ and ultrasonic speed $u$, transport parameter viscosity $\eta$, and spectroscopic parameters viz. IR, $^1$H, $^{13}$C NMR have been measured for the mixtures of isomeric butanediol (1,2-, 1,3-, 1,4- and 2,3-butanediol) and $N,N$-dimethylformamide over the whole composition range at 308.15 K. The partial molar quantities $Q_f$, isentropic compressibility $K_s$, deviation in ultrasonic velocity $u_D$, viscosity deviation $\Delta \eta$, deviation in Gibbs energies of activation for viscous flow $g(x)$, and excess NMR chemical shift $\delta E$ have also been estimated and analyzed. Results show that the interaction between unlike molecules takes place through hydroxyl groups of isomeric butanediol and \textit{\textsuperscript{\textbf{C}}=O} group of $N,N$-dimethylformamide. Excellent correlation between thermodynamic and spectroscopic measurements is observed.

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Keywords: Thermodynamic characterization; Spectroscopic measurements; Isomeric butanediol; $N,N$-Dimethylformamide

1. Introduction

This report is in continuation of the series of investigations on internal structures of binary liquid mixtures. Recently, extensive database on the thermodynamic and spectroscopic interactions in mixtures of isomeric butanediol with pyrrolidin-2-one was presented [1]. In the present work, we have analyzed the mutual intermolecular interactions in the liquid mixtures of isomeric butanediol (BTD) and $N,N$-dimethylformamide (DMF).

Polyhydroxy compounds are used in a wide variety of end-use applications, from cosmetics and household detergents to paints and automotive brake fluids. Alkanedials are the simplest and model structural units for polyhydroxy compounds. These compounds play a significant role in industry due to their wide range of practical applications, such as antifreezes, coolants, aircraft deicing fluids, heat transfer fluids, hydraulic fluids, solvents, food, flavor and fragrances, pharmaceuticals, chemical intermediates, plasticizers, thermoset plastic formulations, petroleum, textile, and other industries.

DMF being very versatile in nature is used in synthesis of pharmaceuticals, in agricultural chemistry and as an organic solvent [2-4]. DMF, however, is not self-associated by H-bonding, although a certain degree of association due to dipole-dipole interactions is expected. A fundamental understanding of DMF with polar, non-polar, associated, and non-associated solvents is therefore important. Iloukhani and Ghorbani [5] reported the excess and partial molar volumes of (1,2-alkanediols + $N,N$-dimethylformamide) mixtures. The results were explained in terms of dissociation of the self-associated 1,2-alkanedial and the formation of aggregates between unlike molecules through $\text{C}=\text{O} \cdot \cdot \cdot \text{H-O}$ hydrogen bonding. Marchetti et al. [6,7] have also investigated various thermophysical properties of ethanediol with DMF and showed that the observations were very useful to verify the possibility of a (solvent + cosolvent) complex formation.

The detailed analysis is presented for liquid mixtures of BTD and DMF at 308.15 K in terms of volumetric ($V_E$, $u$), transport ($\eta$), and spectroscopic (IR, $^1$H and $^{13}$C NMR)
results. Several related parameters were estimated and discussed in comparison with (BTD + pyrrolidin-2-one (PY)) mixtures reported earlier [1].

2. Experimental

2.1. Materials

N,N-Dimethylformamide (DMF; >99 GC) and 1,2-butanediol (1,2-BTD; >98 GC) obtained from Fluka and 1,3-butanediol (1,3-BTD; >99 GC), 1,4-butanediol (1,4-BTD; >99 GC), and 2,3-butanediol (2,3-BTD; >98 GC) were supplied by Merck. Prior to use, all the chemicals were stored over molecular sieves to remove any traces of water. The purity of all the chemicals was checked by comparing their densities (measured using Anton Paar digital precision densimeter) with the literature values [2,8,9] (table 1). The uncertainty in density measurements was ±1 · 10⁻⁵ g · cm⁻³.

2.2. Methods

The measurement of excess molar volume was carried out in a continuous dilution dilatometer. The dilatometer was immersed in a water bath controlled to better than ±0.01 K. Temperature control was achieved using a circulating water bath, regulated to ±0.01 K, using a proportional temperature controller. The temperature was calibrated to 308.15 ±0.01 K with a precision platinum resistance thermometer. Details of the experimental set-up and the measuring procedure have been described elsewhere [10]. The results for \( \Delta V^E \) are estimated to be accurate to ±0.002 cm³ · mol⁻¹.

An ultrasonic time intervalometer (UTI-101) from Innovative instruments based on the pulse-echo-overlap technique (PET) coupled with an oscilloscope was used for the ultrasonic velocity measurements. The frequency of sound was 2.0 MHz. The cell for the speed of sound measurements was calibrated with water [11] as a reference. The uncertainty in the measurement of ultrasonic velocity was within ±2 · 10⁻² m · s⁻¹.

Viscosity measurements were made using modified form of Ubbelohde viscometer placed in a water thermostat, the temperature of which was controlled to ±0.01 K. The flow time of definite volume of liquid through the capillary was measured with an accurate stopwatch with a resolution of 1 · 10⁻² s. Viscosity values are uncertain to within the range 0.001 mPa · s. ¹H and ¹³C NMR chemical shifts were observed with the help of a JEOL AL 300 MHz FT NMR spectrometer operating at 300 MHz. In order to determine the chemical shift \( \delta \) for liquid mixtures of DMF and BTD at entire composition range, CDCl₃ was used as an external solvent for all the NMR measurements. Perkin Elmer (RX1) FT-IR spectrometer in the frequency range (4400 to 350) cm⁻¹ is utilized to record the FT-IR spectra.

3. Results and discussion

3.1. Thermodynamic parameters

The experimentally measured excess molar volumes \( \Delta V^E \) (cm³ · mol⁻¹) values for mixtures of DMF and BTD at 308.15 K are listed in table 2 and graphically presented in figure 1. The \( \Delta V^E \) values are negative for 1,4-BTD, positive for 1,3-BTD and 2,3-BTD, and both negative and positive for 1,2-BTD. Results show that in the case of 1,4-BTD strong hydrogen bonding between \( ^=O \) groups of DMF and -OH groups of 1,4-BTD (which are present on extreme ends of the molecule and are more available to form hydrogen bonding than the other isomers) dominates the breaking of self-associated diols (which contribute positively to \( F^E \)) resulting in overall negative \( \Delta V^E \). As the hydroxyl groups shift from ends (i.e., 1,4-position), the interaction between \( ^=O \) group and -OH groups is expected to decrease in the order 1,4-BTD > 1,2-BTD > 1,3-BTD > 2,3-BTD. The breaking of self-associated diols, particularly in the case of 1,3-BTD and 2,3-BTD dominates, making \( \Delta V^E \) positive.

A comparative analysis of \( \Delta V^E \) values of BTD in DMF than those of same diols in PY [1] reveals that volumetric behavior of 2,3-BTD and 1,3-BTD is nearly same, however,
TABLE 2
Excess molar volume $V^E$ values for (xBTD + (1-x)DMF) at 308.15 K

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volume loss is significant for 1,4-BTD and 1,2-BTD in DMF. These results indicate that DMF interacts strongly with the exposed hydroxyl groups of BTD than PY in which the disruption of PY dimers through breaking of hydrogen bonds and comparatively weak interactions between molecules result in an increase in volume.

The ultrasonic velocities $u$ (m s⁻¹) for the DMF + BTD have been summarized in table 3. Combining ultrasonic velocity $u$ with excess volume $V^E$ data, one can calculate the isentropic compressibility $\kappa_S$ as

TABLE 3

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FIGURE 1. Excess volumes $V^E$ for $x_{BTD} + (1-x)_{DMF}$: O, 1,2-BTD; □, 1,3-BTD; A, 1,4-BTD; and □, 2,3-BTD.

TABLE 3

Ultrasonic speed $u$ values for $x_{BTD} + (1-x)_{DMF}$ at 308.15 K

<table>
<thead>
<tr>
<th>x</th>
<th>$u$</th>
<th>m s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0519</td>
<td>1428.61</td>
<td></td>
</tr>
<tr>
<td>0.1000</td>
<td>1429.64</td>
<td></td>
</tr>
<tr>
<td>0.2013</td>
<td>1431.18</td>
<td></td>
</tr>
<tr>
<td>0.2983</td>
<td>1432.60</td>
<td></td>
</tr>
<tr>
<td>0.4099</td>
<td>1433.63</td>
<td></td>
</tr>
<tr>
<td>0.4883</td>
<td>1434.54</td>
<td></td>
</tr>
<tr>
<td>0.5694</td>
<td>1434.41</td>
<td></td>
</tr>
<tr>
<td>0.6926</td>
<td>1432.21</td>
<td></td>
</tr>
<tr>
<td>0.7139</td>
<td>1431.83</td>
<td></td>
</tr>
<tr>
<td>0.8896</td>
<td>1428.10</td>
<td></td>
</tr>
<tr>
<td>0.9489</td>
<td>1424.39</td>
<td></td>
</tr>
</tbody>
</table>

volume loss is significant for 1,4-BTD and 1,2-BTD in DMF. These results indicate that DMF interacts strongly with the exposed hydroxyl groups of BTD than PY in which the disruption of PY dimers through breaking of hydrogen bonds and comparatively weak interactions between molecules result in an increase in volume.

The ultrasonic velocities $u$ (m s⁻¹) for the DMF + BTD have been summarized in table 3. Combining ultrasonic velocity $u$ with excess volume $V^E$ data, one can calculate the isentropic compressibility $\kappa_S$ as

FIGURE 1. Excess volumes $V^E$ for $x_{BTD} + (1-x)_{DMF}$: O, 1,2-BTD; □, 1,3-BTD; A, 1,4-BTD; and □, 2,3-BTD.

TABLE 3

Ultrasonic speed $u$ values for $x_{BTD} + (1-x)_{DMF}$ at 308.15 K

<table>
<thead>
<tr>
<th>x</th>
<th>$u$</th>
<th>m s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0519</td>
<td>1428.61</td>
<td></td>
</tr>
<tr>
<td>0.1000</td>
<td>1429.64</td>
<td></td>
</tr>
<tr>
<td>0.2013</td>
<td>1431.18</td>
<td></td>
</tr>
<tr>
<td>0.2983</td>
<td>1432.60</td>
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</tr>
<tr>
<td>0.4099</td>
<td>1433.63</td>
<td></td>
</tr>
<tr>
<td>0.4883</td>
<td>1434.54</td>
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</tr>
<tr>
<td>0.5694</td>
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<td></td>
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<tr>
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</tr>
<tr>
<td>0.8896</td>
<td>1428.10</td>
<td></td>
</tr>
<tr>
<td>0.9489</td>
<td>1424.39</td>
<td></td>
</tr>
</tbody>
</table>

(continued on next page)
TABLE 3 (continued)

\[ \begin{array}{lcc}
\hline
x & u & \text{m s}^{-1} \\
\hline
0.0369 & 2.3-BTD & 1428.13 \\
0.1003 & & 1427.10 \\
0.1898 & & 1426.21 \\
0.4065 & & 1427.23 \\
0.494 & & 1428.90 \\
0.6314 & & 1434.17 \\
0.7498 & & 1441.18 \\
0.8947 & & 1449.18 \\
0.9174 & & 1450.50 \\
\hline
\end{array} \]

KS can be expressed as follows:

\[ K_S^E = \sum_i x_i \left[ \frac{C_{pi}}{C_{pi}} \right] - T \left[ \frac{\sum_i x_i (A_{pi})^2}{(\sum_i x_i C_{pi})} \right], \]

(4)

\[ u^D = u - u_i, \]

(5)

where

\[ u = \frac{V_i}{(K^s_i \sum M_i)^{1/2}}. \]

(6)

The excess values of $K_S^E, K^S_2$, and $u^D$ have been fitted by the conventional curve fitting strategy for the excess properties of binary mixtures by using the Redlich-Kister type equation in the form

\[ y^E = x(1-x) \sum_A (2x-1)^i, \]

(7)

where $y^E$ represent the excess properties. The values for the coefficient $A_i$ and the standard deviation of the fit for each system are given in table 4.

The partial molar excess quantities viz. volume, $V^E_i$, and isentropic compressibility $K^E_i$, were calculated from the following equations:

\[ V_i^E = \frac{\partial V}{\partial P} \left. \right|_{T}, \]

\[ K_i^E = K_S^E - K^E_i, \]

FIGURE 2. Excess isentropic compressibilities $K^E_i$ and deviation in ultrasonic velocity $u^D$ for x-BTD: $\circ$, 1,2-BTD; $\bigcirc$, 1,3-BTD; $\triangle$, 1,4-BTD; and $\square$, 2,3-BTD + (1 - x)DMF.
TABLE 4
Least-square coefficients of equation (7) and standard deviation \( \sigma \) of \( \chi_{x\text{BTD}} + (1 - x)\text{DMF} \) at 308.15 K

<table>
<thead>
<tr>
<th>DMF</th>
<th>( A_0 )</th>
<th>( A_1 )</th>
<th>( A_2 )</th>
<th>( A_3 )</th>
<th>( A_4 )</th>
<th>( \sigma )</th>
<th>( \chi^2(x = 0.5) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,2-BTD</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( s_x^E/(\text{cm}^3 \cdot \text{mol}^{-1}) )</td>
<td>-0.087</td>
<td>0.064</td>
<td>0.189</td>
<td>-0.347</td>
<td>0.188</td>
<td>0.002</td>
<td>-0.021</td>
</tr>
<tr>
<td>( k_x^F/(\text{PPa}^{-1} \cdot \text{m}^3 \cdot \text{mol}^{-1}) )</td>
<td>-2.71</td>
<td>-0.37</td>
<td>1.17</td>
<td>0.41</td>
<td>-2.08</td>
<td>0.03</td>
<td>-0.67</td>
</tr>
<tr>
<td>( \theta_x/(\text{m} \cdot \text{s}^{-1}) )</td>
<td>43.50</td>
<td>8.53</td>
<td>-17.72</td>
<td>-13.70</td>
<td>39.31</td>
<td>0.49</td>
<td>10.71</td>
</tr>
<tr>
<td>( \gamma_x/(\text{PPa} \cdot \text{s}) )</td>
<td>-51.09</td>
<td>-33.20</td>
<td>-11.48</td>
<td>-30.37</td>
<td>-37.33</td>
<td>0.22</td>
<td>-12.61</td>
</tr>
<tr>
<td>( \Delta_x/(\text{mol} \cdot \text{mol}^{-1}) )</td>
<td>-3530</td>
<td>357</td>
<td>5678</td>
<td>-656</td>
<td>-9734</td>
<td>33</td>
<td>-1319</td>
</tr>
<tr>
<td>( \delta_x^E/\text{ppm} (\text{H-OH}) )</td>
<td>-0.391</td>
<td>0.298</td>
<td>-0.330</td>
<td>-0.540</td>
<td>0.023</td>
<td>0.006</td>
<td>-0.098</td>
</tr>
<tr>
<td>( \delta_x^E/\text{ppm} (\text{H-CHO}) )</td>
<td>-0.202</td>
<td>0.042</td>
<td>0.053</td>
<td>-0.117</td>
<td>-0.275</td>
<td>0.003</td>
<td>-0.051</td>
</tr>
<tr>
<td>( \delta_x^E/\text{ppm} (\text{C-CHO}) )</td>
<td>0.229</td>
<td>-0.154</td>
<td>-0.130</td>
<td>-0.225</td>
<td>0.802</td>
<td>0.007</td>
<td>0.057</td>
</tr>
</tbody>
</table>

| 1,3-BTD | | | | | | | |
| \( s_x^E/(\text{cm}^3 \cdot \text{mol}^{-1}) \) | 0.235 | -0.004 | -0.240 | 0.010 | 0.194 | 0.001 | 0.058 |
| \( k_x^F/(\text{PPa}^{-1} \cdot \text{m}^3 \cdot \text{mol}^{-1}) \) | 2.14 | -2.10 | 1.14 | -1.66 | -1.38 | 0.03 | 0.53 |
| \( \theta_x/(\text{m} \cdot \text{s}^{-1}) \) | -41.81 | 35.37 | -22.65 | 30.52 | 22.27 | 0.35 | -10.34 |
| \( \gamma_x/(\text{PPa} \cdot \text{s}) \) | -96.51 | 62.54 | -9.07 | -57.71 | -87.60 | 0.82 | -24.16 |
| \( \Delta_x/(\text{mol} \cdot \text{mol}^{-1}) \) | -1593 | 2494 | 5453 | -2124 | 9714 | 38 | -1267 |
| \( \delta_x^E/\text{ppm} (\text{H-OH}) \) | -0.224 | 0.088 | 0.371 | -0.021 | -0.294 | 0.005 | -0.056 |
| \( \delta_x^E/\text{ppm} (\text{H-CHO}) \) | -0.027 | 0.255 | 0.184 | 0.059 | -0.281 | 0.002 | -0.007 |
| \( \delta_x^E/\text{ppm} (\text{C-CHO}) \) | 0.584 | 0.155 | 0.102 | -0.111 | -0.332 | 0.002 | 0.143 |

| 1,4-BTD | | | | | | | |
| \( s_x^E/(\text{cm}^3 \cdot \text{mol}^{-1}) \) | -0.646 | -0.001 | 0.040 | -0.357 | -0.294 | 0.002 | -0.162 |
| \( k_x^F/(\text{PPa}^{-1} \cdot \text{m}^3 \cdot \text{mol}^{-1}) \) | -1.89 | 0.27 | 1.23 | -1.60 | -0.10 | 0.03 | -0.48 |
| \( \theta_x/(\text{m} \cdot \text{s}^{-1}) \) | 25.47 | -0.84 | -22.30 | 22.27 | -2.16 | 0.52 | 6.31 |
| \( \gamma_x/(\text{PPa} \cdot \text{s}) \) | -78.68 | -42.75 | -1.08 | -19.56 | -34.59 | 0.13 | -19.52 |
| \( \Delta_x/(\text{mol} \cdot \text{mol}^{-1}) \) | -2130 | 3135 | 1782 | -41 | -5337 | 40 | -313 |
| \( \delta_x^E/\text{ppm} (\text{H-OH}) \) | -0.004 | 0.200 | -0.203 | 0.198 | -0.081 | 0.002 | -0.001 |
| \( \delta_x^E/\text{ppm} (\text{H-CHO}) \) | -0.156 | 0.002 | -0.052 | -0.090 | -0.072 | 0.002 | 0.039 |
| \( \delta_x^E/\text{ppm} (\text{C-CHO}) \) | 0.746 | -0.182 | -0.555 | 0.044 | 0.784 | 0.09 | 0.177 |

| 2,3-BTD | | | | | | | |
| \( s_x^E/(\text{cm}^3 \cdot \text{mol}^{-1}) \) | 0.638 | 0.249 | 0.097 | 0.233 | 0.203 | 0.003 | 0.159 |
| \( k_x^F/(\text{PPa}^{-1} \cdot \text{m}^3 \cdot \text{mol}^{-1}) \) | 3.25 | -0.09 | -0.29 | 2.33 | -1.50 | 0.04 | 0.79 |
| \( \theta_x/(\text{m} \cdot \text{s}^{-1}) \) | -43.91 | -61 | 4.53 | 36.57 | 30.82 | 0.63 | -10.83 |
| \( \gamma_x/(\text{PPa} \cdot \text{s}) \) | -92.05 | -62.68 | -28.32 | -60.00 | -62.83 | 0.19 | -22.97 |
| \( \Delta_x/(\text{mol} \cdot \text{mol}^{-1}) \) | -6979 | 3687 | 5051 | -4626 | -6893 | 71 | -1546 |
| \( \delta_x^E/\text{ppm} (\text{H-OH}) \) | -0.240 | -0.024 | -0.139 | 0.284 | 0.147 | 0.002 | -0.060 |
| \( \delta_x^E/\text{ppm} (\text{H-CHO}) \) | -0.203 | -0.089 | 0.104 | -0.044 | -0.330 | 0.004 | -0.050 |
| \( \delta_x^E/\text{ppm} (\text{C-CHO}) \) | 0.530 | 0.199 | -0.591 | -0.074 | 0.944 | 0.007 | 0.108 |

FIGURE 3. Partial molar excess volumes for \( x \) BTD: \( 0, 1,2\)-BTD; \( CD, 1,3\)-BTD; \( \Delta, 1,4\)-BTD; and \( \Box, 2,3\)-BTD + (1 - \( x \))DMF.
The partial molar volumes $\nu_f^m$ shown in figure 3 varies as $1,4\text{-}BTD < 1,2\text{-}BTD < 1,3\text{-}BTD < 2,3\text{-}BTD$. This trend is similar to as obtained for BTD + PY mixtures [1]. The estimated values of partial molar quantities at infinite dilution are listed in table 5. The negative value of partial molar volumes for 1,4-BTD may be taken as sign of strong interaction with DMF than other isomers. Figure 4 shows the variation of partial molar excess compressibilities $K_f^{*}$ for the given systems. The estimated values of partial molar excess compressibilities at infinite dilution are also given in table 5. Negative $K_f^{*}$ values for 1,2-BTD and 1,4-BTD (figure 4) infer that structure-making effects are dominating in these systems, whereas structure-breaking ability is more prominent for 2,3-BTD and 1,3-BTD mixtures, which show positive $K_f^{*}$ values.

\[
\nu_f^m = \nu_f^E + (1 - x) \left( \frac{\partial \nu_f^E}{\partial x} \right)
\]

\[
K_f^{*} = K_f^{*E} + (1 - x) \left( \frac{\partial K_f^{*E}}{\partial x} \right)
\]
3.2. Transport parameters

Experimental viscosity (mPa s) data for mixtures of DMF + BTD is given in table 6. Viscosity deviation $\Delta \eta$ of measured values were calculated using the following equation:

$$\Delta \eta = \eta - \exp \left( \sum x_i \ln \eta_i' \right).$$

Deviation in Gibbs energies of activation for viscous flow $g(x)$ values may also be considered a reliable measure to detect the presence of interactions between molecules \[12,13\] are calculated using the equation

$$g(x) = R \left[ \ln \eta - \left( \sum \eta_i' \frac{V}{V'} \right) \right],$$

where $\eta$ and $\eta'$ are the viscosities of mixture and of pure component $i$. The variation of viscosity $\eta$ and its deviation $\Delta \eta$ values for the binary mixtures of DMF with BTD over the whole composition range at 308.15 K are presented in figure 5. The $\Delta \eta$ values follow the order 1,3-BTD $< 2,3$-BTD $< 1,4$-BTD $< 1,2$-BTD. These results show that dispersion forces are responsible for dissociation of self-associated diol molecules and the magnitude of these dispersion forces are more for 2,3-BTD and 1,3-BTD than 1,4-BTD and 1,2-BTD.

Deviation in Gibbs energies of activation for viscous flow $g(x)$ values may also be considered a reliable measure to detect the presence of interactions between molecules \[12,13\] are calculated using the equation

$$g(x) = R \left[ \ln \eta - \left( \sum \eta_i' \frac{V}{V'} \right) \right],$$

where $\eta$ and $\eta'$ are the viscosities of mixture and of pure component $i$. The variation of viscosity $\eta$ and its deviation $\Delta \eta$ values for the binary mixtures of DMF with BTD over the whole composition range at 308.15 K are presented in figure 5. The $\Delta \eta$ values follow the order 1,3-BTD $< 2,3$-BTD $< 1,4$-BTD $< 1,2$-BTD. These results show that dispersion forces are responsible for dissociation of self-associated diol molecules and the magnitude of these dispersion forces are more for 2,3-BTD and 1,3-BTD than 1,4-BTD and 1,2-BTD.

Deviations of $\Delta \eta$ and $g(x)$ values were fitted to equation (7) and parameters are listed in table 4.

### 3.3. Spectroscopic parameters

By comparing thermophysical properties with spectroscopic measurements, i.e., IR and NMR, selection of suitable associations and contributions to non-ideal behavior of a mixture can be evaluated \[1,14-18\]. IR measurements for mixtures of DMF + BTD over the entire composition range have been carried out. The shift in wave number $\nu$...
TABLE 7a
Wave number v values at maximum absorbance of -OH groups for 
$\{x$BTD $+ (1-x)DMF\}$

<table>
<thead>
<tr>
<th>x</th>
<th>1,2-BTD</th>
<th>1,3-BTD</th>
<th>1,4-BTD</th>
<th>2,3-BTD</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0519</td>
<td>3438.9</td>
<td>3448.8</td>
<td>3456.6</td>
<td>3468.4</td>
</tr>
<tr>
<td>0.1008</td>
<td>3424.1</td>
<td>3418.2</td>
<td>3417.5</td>
<td>3439.6</td>
</tr>
<tr>
<td>0.2013</td>
<td>3415.5</td>
<td>3414.2</td>
<td>3442.0</td>
<td>3422.3</td>
</tr>
<tr>
<td>0.2983</td>
<td>3409.0</td>
<td>3401.0</td>
<td>3398.1</td>
<td>3408.1</td>
</tr>
<tr>
<td>0.4999</td>
<td>3402.8</td>
<td>3401.0</td>
<td>3402.3</td>
<td>3408.1</td>
</tr>
<tr>
<td>0.4883</td>
<td>3399.4</td>
<td>3398.1</td>
<td>3399.8</td>
<td>3390.5</td>
</tr>
<tr>
<td>0.5694</td>
<td>3377.8</td>
<td>3377.6</td>
<td>3381.9</td>
<td>3377.0</td>
</tr>
<tr>
<td>0.6926</td>
<td>3372.0</td>
<td>3377.6</td>
<td>3381.9</td>
<td>3377.0</td>
</tr>
<tr>
<td>0.7139</td>
<td>3372.0</td>
<td>3372.0</td>
<td>3372.0</td>
<td>3372.0</td>
</tr>
<tr>
<td>0.8896</td>
<td>3351.3</td>
<td>3351.3</td>
<td>3351.3</td>
<td>3351.3</td>
</tr>
<tr>
<td>0.9489</td>
<td>3352.0</td>
<td>3352.0</td>
<td>3352.0</td>
<td>3352.0</td>
</tr>
</tbody>
</table>

TABLE 7b
Wave number v values at maximum absorbance of $\geq CO$ groups for 
$\{x$BTD $+ (1-x)DMF\}$

<table>
<thead>
<tr>
<th>x</th>
<th>1,2-BTD</th>
<th>1,3-BTD</th>
<th>1,4-BTD</th>
<th>2,3-BTD</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0519</td>
<td>1673.9</td>
<td>1665.8</td>
<td>1673.8</td>
<td>1671.8</td>
</tr>
<tr>
<td>0.1008</td>
<td>1672.8</td>
<td>1673.9</td>
<td>1672.5</td>
<td>1672.0</td>
</tr>
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</tr>
<tr>
<td>0.4999</td>
<td>1668.4</td>
<td>1668.4</td>
<td>1666.9</td>
<td>1666.9</td>
</tr>
<tr>
<td>0.4883</td>
<td>1669.4</td>
<td>1672.6</td>
<td>1670.0</td>
<td>1668.0</td>
</tr>
<tr>
<td>0.5694</td>
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<td>1667.7</td>
<td>1667.7</td>
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<td>0.6926</td>
<td>1664.5</td>
<td>1666.7</td>
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</tr>
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<td>1655.2</td>
<td>1667.3</td>
<td>1667.3</td>
<td>1666.7</td>
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<tr>
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<td>1664.5</td>
<td>1667.6</td>
<td>1667.5</td>
<td>1667.3</td>
</tr>
<tr>
<td>0.9489</td>
<td>1668.8</td>
<td>1667.0</td>
<td>1666.7</td>
<td>1666.7</td>
</tr>
</tbody>
</table>

In many examples, NMR can provide meaningful physical information about structural and molecular interactions [1,16–19]. It has been observed for the present systems that there is no appreciable change in chemical shift $\delta$ values for $-CH_2$ proton of DMF and BTD. The change in $^1$H NMR chemical shift $\delta$ for hydroxyl protons of BTD and aldehydic proton of DMF is listed in table 8. Excess NMR chemical shift $\delta^E$ were determined using the equations:

appears for hydroxyl groups of BTD and $\geq CO$ group of DMF in comparison to BTD + PY mixtures [1], where the change in $\nu$ values of CO group of PY was very small and non-specific. The results indicate that the interactions are taking place through both -OH and $\geq CO$ groups. Tables 7a and 7b depict the wave number $\nu$ values at maximum absorbance of -OH and $\geq CO$ stretching frequencies for mixtures of BTD in DMF over the whole composition range.
TABLE 8
$^1$H NMR chemical shift $\delta$ (ppm) values for $\{x$BTD $+ (1-x)$DMF$\}$

<table>
<thead>
<tr>
<th>$x$</th>
<th>$\delta$ ppm</th>
<th>$-\text{HCO}$</th>
<th>$-\text{OH}$</th>
</tr>
</thead>
<tbody>
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<td>4.964</td>
<td></td>
</tr>
<tr>
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<td>8.474</td>
<td>4.957</td>
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</tr>
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<td></td>
</tr>
<tr>
<td>0.2983</td>
<td>8.359</td>
<td>4.950</td>
<td></td>
</tr>
<tr>
<td>0.4099</td>
<td>8.303</td>
<td>4.989</td>
<td></td>
</tr>
<tr>
<td>0.4883</td>
<td>8.267</td>
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TABLE 9
$^{13}$C NMR chemical shift $\delta$ (ppm) values for $\{x$BTD $+ (1-x)$DMF$\}$

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<th>$x$</th>
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<td>0.1985</td>
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<td>0.9487</td>
<td>163.653</td>
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$\delta^e = \delta - (x_1\delta_1^p + x_2\delta_2^p)$, \hspace{1cm} (12)

where $\delta$ and $\delta^p$ are the NMR chemical shifts of mixture and the pure components at infinite dilution, respectively. The $\delta^p$ values were also fitted to equation (7) to obtain the values of coefficient $A_i$ and the standard deviation (table 4). $^1$H NMR chemical shift $\delta$ and excess chemical shift $\delta^e$ for hydroxyl protons as a function of mole fraction of diol for all the mixtures are presented in figure 7. Hydroxyl protons shift downfield with the addition of diol in DMF indicating the formation of $\text{C=O} - \cdot \text{H-O}$ hydrogen bonding. The change in chemical shift increases as 2,3-BTD < 1,2-BTD < 1,3-BTD < 1,4-BTD. However, the addition of diol in DMF shields aldehydic proton over whole composition range. Although in diol + DMF mixtures hydrogen bonding between H-O groups of diol and $\text{C=O}$ group of DMF is expected, the upfield shifting of aldehydic proton may be due to conjugation of lone pair of electron at nitrogen. The $\text{C=O} - \cdot \text{H-O}$ hydrogen bonding create a partial positive center at carbon atom of aldehydic group in DMF that can further accept the electrons from adjacent electron rich nitrogen atom. The change in chemical shift decreases as 2,3-BTD > 1,2-BTD > 1,3-BTD > 1,4-BTD as shown in figure 8.

To seek more information about structural and interactional behavior, $^{13}$C NMR chemical shift $\delta$ has been studied. The results of $^{13}$C NMR are tabulated in table 9 and are graphically depicted in figure 9. With addition of diol, $\text{CO}$ signal shifts downfield over the whole composition range. 

$\delta^e = \delta - (x_1\delta_1^p + x_2\delta_2^p)$, \hspace{1cm} (12)
FIGURE 7. \( ^1 \)H NMR chemical shifts $\delta$ and \( ^1 \)H NMR excess chemical shifts $\delta^E$ of hydroxyl protons for $x$ BTD: $\Phi$, 1,2-BTD; $\bigcirc$, 1,3-BTD; $\Delta$, 1,4-BTD; and $\square$, 2,3-BTD + (1 - $x$)DMF.

FIGURE 8. \( ^1 \)H NMR chemical shifts $\delta$ and \( ^1 \)H NMR excess chemical shifts $\delta^E$ of aldehydic proton for $x$ BTD: $\Phi$, 1,2-BTD; $\bigcirc$, 1,3-BTD; $\Delta$, 1,4-BTD; and $\square$, 2,3-BTD + (1 - $x$)DMF.
The values of mole fractions corresponding to the maxima/minima of excess molar volume $V^E$ and excess chemical shifts $\delta^E$ are positioned at about same mole fraction for all the mixtures. It can be concluded that carbonyl group of DMF and hydroxyl groups of BTD are the two active sites of interactions in DMF + BTD mixtures whereas in BTD + PY systems [1], hydroxyl groups of BTD was the only active site of interactions.

Acknowledgment

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References


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Effect of placement of hydroxyl groups in isomeric butanediol on the behaviour of thermophysical and spectroscopic properties of pyrrolidin-2-one

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Abstract

The thermophysical parameters, viz. excess molar volume $V^\text{ex}$, ultrasonic speed $u$, viscosity $\eta$ and spectroscopic parameters, viz. IR and $^1$H NMR have been measured for the mixtures of pyrrolidin-2-one and isomeric butanediol (1,2-, 1,3-, 1,4- and 2,3-BTD) over the whole composition range at 308.15 K. Results indicate that intermolecular interactions for different mixtures increase in the order: 2,3-BTD < 1,2-BTD < 1,3-BTD < 1,4-BTD. The partial and apparent molar quantities $\Omega^P$, isentropic compressibility $K_s^I$, excess viscosity $\eta^E$ and excess Gibbs free energies of activation for viscous flow $A^*G^E$ have also been estimated and analyzed. The spectroscopic measurements (IR and $^1$H NMR) confirm that the interaction between unlike molecules takes place through hydroxyl groups of isomeric butanediol. A good agreement is obtained between excess quantities and spectroscopic data.

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Keywords: Thermophysical characterization; Spectroscopic measurements; Pyrrolidin-2-one; Isomeric butanediol

1. Introduction

Polyhydroxy compounds have number of applications in biochemical research because of their connection to biological system. These compounds are used as fogging agent in theatrical productions and are widely used in pharmaceuticals, cosmetics, petroleum, textile and other industries. More attention has been paid to study the physicochemical and thermodynamic properties of aqueous solution of polyhydroxy compounds. Thermophysical characterization of a system by experimental determination of properties such as excess molar volume, ultrasonic speed, viscosity and their composition variation are important tools to gain insight into solute-solvent interactions and packing effects of solute molecule in the stabilization/destabilization of a system [1–8]. Czechowski et al. [9] and Nakanishi et al. [10] obtained excess molar volume of aqueous solution of different diols at different temperatures. Houkhan and Bahram [11] carried out excess and partial molar volume measurements of aqueous solutions of 1,2-alkanediols at different temperatures. The results have been explained in terms of dissociation of the self-associated diol molecules and the formation of the aggregates between unlike molecules. The density and viscosity data of aqueous solutions of isomeric butanediol and poly(ethylene glycol)s have been reported by Teja and co-workers [12,13]. Palepu and co-workers [14,15] studied various properties of aqueous solutions of isomeric butanediol in order to analyze the interactions of butanediols with water in terms of placement of hydroxyl groups in isomeric butanediol molecules. Recently, George and Sastry [16] reported densities, viscosities, speed of sound...
and relative permittivities for (water + alkanediols) at different temperatures.

The study of isomeric butanediol (BTD) in non-aqueous media is also important from a fundamental point of view since it allows us to examine in detail the influence of spacing of the –OH groups on the thermodynamic properties of these compounds. In the present work, pyrrolidin-2-one (PY) is selected as a non-aqueous medium. The γ-butyrolactam (n = 3), i.e. PY is one of the cyclic amide which possess the basic (CO) and acidic (NH) group, in addition to high dipole moment. Cyclic amides are interesting compounds in which the nitrogen and carbon of a peptide bond are linked by a ring composed of methylene groups. These amide functional groups [17–20] are structural part of peptide, polypeptide and proteins and constitute an important tool in the interpretation of numerous problems of molecular biology.

The excess molar volumes \(\nu^E\), ultrasonic speed \(u\), viscosity \(\eta\) and \(^1\)H NMR and IR spectra have been measured for liquid binary mixtures of pyrrolidin-2-one and isomeric butanediol at 308.15 K temperature. The partial and apparent molar quantities \(\Omega^E\), isentropic compressibility \(A_{is}^E\), excess viscosity \(\eta^E\), excess Gibbs free energies of activation for viscous flow \(\Delta G^E\) and deviation in \(^1\)H NMR chemical shift \(\delta^H\) have been analyzed for the same mixtures. The aim of the work is to measure new data and to provide results for the characterization of the effect of placement of hydroxyl groups in BTD on the thermodynamic properties of PY. The results have been compared with aqueous based systems of diols and analyzed.

2. Experimental

2.1. Materials

Pyrrolidin-2-one (>99 GC) and 1,2-butanediol (>98 GC) were obtained from Fluka and 1,3-butanediol (>99 GC), 1,4-butanediol (>99 GC) and 2,3-butanediol (>98 GC) were supplied by Merck. Pyrrolidin-2-one was dried with CaO and fractionally distilled as described elsewhere [21]. Diols were used as received. Prior to use, all the chemicals were stored over molecular sieves to remove any traces of water. The water impurity in the chemicals was as low as <0.005%. The purity of all the chemicals was checked by comparing their densities (measured using Anton Paar digital precision densimeter) with the literature values (table 1). The uncertainty in density measurements was ± 2 • 10^{-5} g • cm^{-3}.

2.2. Methods

The measurement of excess molar volume was carried out in a continuous dilution dilatometer. The dilatometer was immersed in a water bath controlled to better than ±0.01 K. Temperature control was achieved using a circulating water bath, regulated to ±0.01 K, using a proportional temperature controller. The temperature was calibrated to 308.15 ± 0.01 K with a precision platinum resistance thermometer. Details of the experimental set-up and the measuring procedure have been described elsewhere [22]. The results for \(\nu^E\) are estimated to be accurate to ±0.002 cm^{3} • mol^{-1}.

An ultrasonic time intervalometer (UTI-101) from Innovative instruments based on the pulse-echo-overlap technique (PET) coupled with an oscilloscope was used for the ultrasonic speed measurements. The frequency of sound was 2.0 MHz. The cell for the ultrasonic speed measurements was calibrated with water [23] as a reference. The uncertainty in the measurement of ultrasonic speed was within ± 2 • 10^{-3} m • s^{-1}.

Combining ultrasonic speed \(u\) with excess molar volume \(\nu^E\), one can calculate the isentropic compressibility \(\kappa_A\) as

\[
\kappa_A = -\nu^E \left(\frac{\partial \nu^E}{\partial p}\right)_s = \left(\frac{\partial u}{\partial p}\right)_s^{-1} \frac{\nu^E}{u^2} = \frac{\nu}{\rho u^2}.
\]

where \(M\) is the molar mass of the mixture. Since the \(u\) and \(\nu^E\) measurements have not been made on the same

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<th>Component</th>
<th>(\rho_{exptl}) kg • m^{-3}</th>
<th>(\rho_{cal}) kg • m^{-3}</th>
<th>(\nu_0^E) m^{3} • mol^{-1}</th>
<th>(u_0^E) m • s^{-1}</th>
<th>(\eta_0^E) mPa • s</th>
<th>(\eta^E/10^{-4}) K^{-1}</th>
<th>(C^E) J • K^{-1} • mol^{-1}</th>
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</table>

\[a\] Reference [14].
\[b\] Reference [16].
\[c\] Derived from densities [14].
A\text{G}^* = RT \ln \eta V - \left( \sum_i x_i \ln \eta_i V_i \right), \quad (8)

where \( \eta \) is the isobaric molar heat capacity, \( \eta \) is the isentropic compressibility, \( x_i \) is the mole fraction and \( A_{ij} \) is the product of molar volume \( V^*_i \) and thermal expansivity \( \alpha^*_i \) for the pure component \( i \). \( \eta \) and \( \eta^*_i \) are the viscosities of mixture and of pure component \( i \), \( R \) is the gas constant and \( T \) is the absolute temperature. The \( V \) and \( V^*_i \) are the molar volume of the mixture and that of the pure components, respectively. Table 1 lists the \( C^*_i \) and \( \alpha^*_i \) values of the pure components.

The excess molar volume as a function of composition for all the studied mixtures is graphically depicted in figure 1. Figure 2 shows the variation of \( \eta^* \) and \( u^0 \) as a function of \( x \) at 308.15 K. The excess properties \( \Delta G^* \) have been fitted to a Redlich-Kister type equation in the form

\[ \eta^* = x(1 - x) \sum A_i (2x - 1)^i. \quad (9) \]

The values for the coefficient \( A_i \) and the standard deviation of the fit for each system are given in table 2.

The partial molar excess quantities, viz. volume, \( \Delta V^* \) and isentropic compressibility \( \Delta \eta^* \), were calculated from the following equations:

\[ \Delta V^* = V^* - \left( \sum_i x_i V^*_i \right), \quad (10) \]

\[ \Delta \eta^* = \eta - \left( \sum_i x_i \eta^*_i \right), \quad (7) \]

\[ \Delta G^* = RT \ln \eta V - \left( \sum x_i \ln \eta_i V_i \right), \quad (8) \]

\[ \Delta V^* = RT \ln \eta V - \left( \sum x_i \ln \eta_i V_i \right), \quad (8) \]

\[ \Delta \eta^* = \eta - \left( \sum_i x_i \eta^*_i \right), \quad (7) \]

\[ \Delta G^* = RT \ln \eta V - \left( \sum x_i \ln \eta_i V_i \right), \quad (8) \]

\[ \Delta V^* = V^* - \left( \sum_i x_i V^*_i \right), \quad (10) \]

\[ \Delta \eta^* = \eta - \left( \sum_i x_i \eta^*_i \right), \quad (7) \]

\[ \Delta G^* = RT \ln \eta V - \left( \sum x_i \ln \eta_i V_i \right), \quad (8) \]
The apparent molar volumes $V_{\phi,2}$ and apparent molar compressibilities $K_{\phi,2}$ of BTD in PY have been calculated by using the following relations:

$$V_{\phi,2} = V_2 + \frac{\nu_1}{\nu_0}$$  \hspace{1cm} (12)

and

$$K_{\phi,2} = K_{2,2} + \frac{K_1}{S_2}$$  \hspace{1cm} (13)

Figure 3 shows the variation of $V_{\phi,2}$ and $K_{\phi,2}$ as a function of composition from which the partial molar volumes $V^m_2$ and partial molar compressibilities $K^m_2$ of BTD in PY at infinite dilution have been obtained graphically by extrapolation to infinite dilution. The change in volume and compressibility at infinite dilution have been computed from the following expressions:

$$\Delta V = V^m_2 - V_2$$  \hspace{1cm} (14)

and

$$\Delta K = K^m_2 - K_{2,2}$$  \hspace{1cm} (15)

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<th>$A_0$</th>
<th>$A_1$</th>
<th>$A_2$</th>
<th>$A_3$</th>
<th>$A_4$</th>
<th>$\sigma$</th>
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3.1. Analysis of excess quantities

The $\xi^e$ values presented in table 3 are positive for all the mixtures except for (PY + 1,4-BTD) for which it shows S-shaped behaviour and vary in order: 1,4-BTD > 1,2-BTD > 1,3-BTD > 2,3-BTD. The position of hydroxyl groups caused a noticeable effect on the $\xi^e$ values. The volumetric behaviour of isomeric butanediol in pyrrolidin-2-one differs considerably from that of the same butanediols in water [14]. For the latter $\xi^e$ values for each diol show a large negative value with a pronounced minimum occurring at $x_{BTD}$ from (0.3 to 0.4) mole fraction. The negative $\xi^e$ values of aqueous solution of BTD follow the order: 2,3-BTD > 1,3-BTD > 1,2-BTD > 1,4-BTD and has been explained on the basis of hydrophobic hydration and hydrogen bonding ability of diols.

The ultrasonic speed listed in table 4 help to gain information in understanding the behaviour of (PY + BTD) mixtures. Figure 2 shows the variation of $K_f^e$ for the given systems. The values increase in the order: 1,3-BTD > 2,3-BTD > 1,4-BTD > 1,2-BTD. The trend in $K_f^e$ is different than those of $\xi^e$, since different shapes of structural isomer affect $K_f^e$ and $\xi^e$ differently. The larger negative values of $K_f^e$ for aqueous binary mixtures of BTD [14] than the binary mixtures of PY and BTD indicate that more compressible species are being formed for the former. Trend of $K_f^e$ and $\xi^e$ are reverse to each other.

The partial molar volume $V_m^e$ and partial molar excess isentropic compressibility $K_{es}^e$ are indicative of the type of effect dominating the overall behaviour of $\xi^e$ and $K_f^e$, respectively, in PY. The estimated values of partial molar quantities at infinite dilution are listed in table 5. In the dilute PY region, partial molar quantities show a marked increase from a negative value for 1,4-BTD to a positive value of 2,3-BTD. The negative partial molar quantities are indicative of interaction by hydrogen bonding between $\text{C=O}$ group of pyrrolidin-2-one and -OH groups of 1,4-butanediol which are present on extreme ends of the molecule and are more available to form hydrogen bonding than the other isomers. The breaking of self-associated PY and 2,3-BTD > 1,3-BTD > 1,2-BTD > 1,4-BTD seems to be more significant and makes a positive contribution accordingly.

Smaller values of apparent molar quantities for 1,4-BTD than the other isomers may be taken either as a sign of strong solvation by H-bonding or as a sign of fitting of 1,4-BTD in the cavity of self-associated PY than other isomers, due to both -OH groups of 1,4-BTD at both ends. $\Delta V^*$ values listed in table 6 are positive for BTD in PY whereas these values are negative in comparison to aqueous based systems [14]. Although $\Delta K^*$ values are negative but the magnitude is quite small as compare to aqueous solution of butanediols. These observations show that diol molecules cannot fit as much in self-associated PY molecule cavity, as that in pure water which has an open, partially ice-like, structure and diol molecules can fit into the spaces in liquid water.

The viscosity $\eta$ (table 7) and its excess $\eta^e$ values for the binary mixture of pyrrolidin-2-one with isomeric butanediol at 308.15 K are presented in figure 6. The excess viscosity $\eta^e$ shows the relative strength of the interactions between PY and BTD. It increases in the order: 2,3-BTD > 1,3-BTD > 1,2-BTD > 1,4-BTD. This order is reflected in the relative position of hydroxyl groups on each isomer and their ability to form hydrogen bonds with PY. A comparative analysis of excess viscosity $\eta^e$ with aqueous mixtures of BTD [15], which is positive with a well defined maximum in all diol systems points towards is indicative of strong interaction between diols and water than between diol and PY. A correlation between the sign of excess viscosity $\eta^e$ and excess molar volume $\phi^e$ has been observed for a number of solvent systems [24,25] that is if $\phi^e$ is positive, $\eta^e$ is negative and vice versa. In the present study, this holds true except for (PY + 1,4-BTD) for which $\eta^e$ shows S-shaped behaviour.
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The ΔG°E values may also be considered a reliable measure to detect the presence of interactions between molecules [6,26,27]. The variation of ΔG°E for PY and BTD is shown graphically in figure 7 and is negative for all the mixtures except for (PY + 1,4-BTD) for which it shows S-shaped behaviour and its negative value for different PY and BTD mixtures increases in the order: 1,4-BTD < 1,2-BTD < 1,3-BTD < 2,3-BTD.

### 3.2. Spectroscopic analysis

In order to correlate the volume, compressibility and viscosity results, spectroscopic analysis of the same mixtures were undertaken. Combined use of IR and NMR measurements can yield valuable information about the way in which the solute behaves in mixtures...
FIGURE 6. Viscosity $\eta$ and excess viscosity $\eta^e$ for (x pyrrolidin-2-one + (1 - x) isomeric butanediol): O, 1,2-BTD; $\square$, 1,3-BTD; $\triangle$, 1,4-BTD; $\Box$, 2,3-BTD.

Through these hydroxyl groups. The change in wave number $v$ values for carbonyl group (CO) of PY is very small and does not show the regular pattern, i.e., non-specific in nature. Shift in wave number $v$ at maximum absorbance of -OH stretching frequency for mixtures of BTD in PY over the whole composition range have been presented in table 8.

The $^1$H NMR chemical shift $\delta$ for mixtures of pyrrolidin-2-one and isomeric butanediol was measured and tabulated in table 9 to seek more information about placement of hydroxyl groups. Figure 8 depicts the mag-

### TABLE 4

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<td>cm$^3$ mol$^{-1}$</td>
<td>cm$^3$ mol$^{-1}$</td>
</tr>
<tr>
<td>1,2-BTD</td>
<td>0.19</td>
<td>0.07</td>
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<td>-2.87</td>
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<td>-0.68</td>
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<td>1,4-BTD</td>
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<tr>
<td>2,3-BTD</td>
<td>1.03</td>
<td>0.88</td>
<td>0.97</td>
<td>1.24</td>
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</table>

### TABLE 6

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<th>PY</th>
<th>$V_f^{m}$</th>
<th>$V_f^{e}$</th>
<th>$\Delta \rho$</th>
<th>$K_s'^{m}$</th>
<th>$K_s'^{e}$</th>
<th>$\Delta K$</th>
</tr>
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<td>cm$^3$ mol$^{-1}$</td>
<td>cm$^3$ mol$^{-1}$</td>
<td>cm$^3$ mol$^{-1}$</td>
<td>cm$^3$ mol$^{-1}$</td>
<td>cm$^3$ mol$^{-1}$</td>
<td>cm$^3$ mol$^{-1}$</td>
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<td>1,2-BTD</td>
<td>91.20</td>
<td>91.26</td>
<td>0.06</td>
<td>45.63</td>
<td>42.70</td>
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<td>90.91</td>
<td>91.24</td>
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<td>41.02</td>
<td>40.29</td>
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<tr>
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<td>89.99</td>
<td>0.22</td>
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</tr>
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<td>91.85</td>
<td>0.87</td>
<td>43.29</td>
<td>42.04</td>
<td>-1.25</td>
</tr>
</tbody>
</table>

From IR study, it has been observed that out of -NH group of PY and -OH groups of BTD, shift in wave number $v$ appears only in hydroxyl groups of BTD, indicating that interactions are taking place through these hydroxyl groups. The change in wave number $v$ values for carbonyl group (CO) of PY is very small and does not show the regular pattern, i.e., non-specific in nature. Shift in wave number $v$ at maximum absorbance of -OH stretching frequency for mixtures of BTD in PY over the whole composition range have been presented in table 8.
FIGURE 7. Excess Gibbs free energies of activation for viscous flow \( \Delta G^\circ \) for \( x \text{ pyrrolidin-2-one} + (1 - x) \) isomeric butanediol: O, 1,2-BTD; □, 1,3-BTD; ▲, 1,4-BTD; △, 2,3-BTD.

The magnitude of change in \(^1\text{H} \) NMR chemical shift \( \delta \) of hydroxyl protons of BTD in PY. It increases in the order as excess viscosity \( \eta^E \) and excess molar volume \( V^E \) measurements. More conclusive experimental evidence from \(^1\text{H} \) NMR chemical shifts \( \delta \) can be obtained by estimating their deviation from additive properties, i.e. \( \delta^A \). The excess chemical shift \( \delta^E \) have also been fitted to a Redlich-Kister type equation (7), the values for its coefficients \( A_i \), and the standard deviation of the fit for each system are also listed in table 2. The values are presented graphically in figure 9. A comparison of the maximum value of excess chemical shift \( \delta^E \) and excess molar volume \( V^E \) in table 2 shows good agreement. It has also been noticed in \(^1\text{H} \) NMR study that there is no appreciable change in chemical shift \( \delta \) values for \(-\text{NH} \) proton of PY and \(-\text{CH} \) protons of PY and BTD, which confirms that hydroxyl groups of isomeric butanediol are the active sites of interactions in (PY + BTD) mixtures.

TABLE 7
Viscosity \( \eta \) values for \( x \text{ PY} + (1 - x) \) isomeric butanediol at 308.15 K

<table>
<thead>
<tr>
<th>x</th>
<th>1,2-BTD</th>
<th>1,3-BTD</th>
<th>1,4-BTD</th>
<th>2,3-BTD</th>
</tr>
</thead>
<tbody>
<tr>
<td>mPa* s</td>
<td>mPa* s</td>
<td>mPa* s</td>
<td>mPa* s</td>
<td>mPa* s</td>
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<tr>
<td>0.0270</td>
<td>28.334</td>
<td>0.0261</td>
<td>51.567</td>
<td>0.0265</td>
</tr>
<tr>
<td>0.0512</td>
<td>27.116</td>
<td>0.0526</td>
<td>46.608</td>
<td>0.0524</td>
</tr>
<tr>
<td>0.0797</td>
<td>25.572</td>
<td>0.0755</td>
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<td>0.0977</td>
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<td>0.0990</td>
</tr>
<tr>
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<td>22.315</td>
<td>0.1543</td>
<td>36.151</td>
<td>0.1515</td>
</tr>
<tr>
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<td>20.822</td>
<td>0.2041</td>
<td>31.476</td>
<td>0.1970</td>
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<tr>
<td>0.3017</td>
<td>17.814</td>
<td>0.3003</td>
<td>26.188</td>
<td>0.2914</td>
</tr>
<tr>
<td>0.4061</td>
<td>15.685</td>
<td>0.3932</td>
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<td>0.3911</td>
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</tr>
<tr>
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<td>0.6030</td>
<td>15.455</td>
<td>0.5997</td>
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<td>0.7038</td>
<td>11.520</td>
<td>0.6985</td>
<td>13.170</td>
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</tr>
<tr>
<td>0.7980</td>
<td>10.784</td>
<td>0.7935</td>
<td>11.851</td>
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</tr>
<tr>
<td>0.8484</td>
<td>10.259</td>
<td>0.8390</td>
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<tr>
<td>0.9028</td>
<td>9.435</td>
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<td>9.984</td>
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<tr>
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<tr>
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TABLE 8
Wave number \( v \) values at maximum absorbance of -OH groups for \( x \text{ PY} + (1 - x) \) isomeric butanediol

<table>
<thead>
<tr>
<th>x</th>
<th>1,2-BTD</th>
<th>1,3-BTD</th>
<th>1,4-BTD</th>
<th>2,3-BTD</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{cm}^{-1} )</td>
<td>( \text{cm}^{-1} )</td>
<td>( \text{cm}^{-1} )</td>
<td>( \text{cm}^{-1} )</td>
<td>( \text{cm}^{-1} )</td>
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<td>3394.8</td>
<td>0.0581</td>
</tr>
<tr>
<td>0.1126</td>
<td>3369.4</td>
<td>0.1171</td>
<td>3352.3</td>
<td>0.1259</td>
</tr>
<tr>
<td>0.2079</td>
<td>3364.9</td>
<td>0.2668</td>
<td>3348.1</td>
<td>0.2169</td>
</tr>
<tr>
<td>0.3019</td>
<td>3367.7</td>
<td>0.3412</td>
<td>3337.9</td>
<td>0.3207</td>
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<tr>
<td>0.3981</td>
<td>3358.5</td>
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<td>3328.2</td>
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<tr>
<td>0.4884</td>
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TABLE 9

<table>
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<th>d/ppm</th>
<th>x</th>
<th>1,3-BTD</th>
<th>d/ppm</th>
<th>x</th>
<th>1,4-BTD</th>
<th>d/ppm</th>
<th>x</th>
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<td>0.0566</td>
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<td>0.2169</td>
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</table>

FIGURE 8. 'H NMR chemical shifts δ (ppm) for (x PY + (1 - x) isomeric butanediol): O, 1,2-BTD; O, 1,3-BTD; A, 1,4-BTD; □, 2,3-BTD.

FIGURE 9. 'H NMR excess chemical shifts δE (ppm) for (x pyrrolidin-2-one + (1 - x) isomeric butanediol): O, 1,2-BTD; O, 1,3-BTD; A, 1,4-BTD; □, 2,3-BTD.

TABLE 10

<table>
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<th>PY</th>
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</tr>
<tr>
<td>1,3-BTD</td>
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</tr>
<tr>
<td>1,4-BTD</td>
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</tr>
<tr>
<td>2,3-BTD</td>
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<td>0.6688</td>
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Acknowledgement

The authors thank the UGC (India) for financial assistance.

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JCT 04-199