1 Introduction

In our previous paper, we have studied the excess molar volume and ultrasonic speed of binary mixtures of polyethers with 2-methoxylethanol at 298.15 K and atmospheric pressure. In continuation of these investigations on the thermodynamic properties of some mixtures of polyethers with organic solvents, we report in this paper new experimental speeds of sound \( u \) for mixtures of ethyl acetate with ethylene glycol dimethyl ether, diethylene glycol dimethyl ether, or triethylene glycol dimethyl ether at the temperature 298.15 K and atmospheric pressure.

The excess molar volumes \( \delta V \) were converted to densities which were combined with the measured ultrasonic speeds to estimate the isentropic compressibility \( \kappa_S \) for all the mixtures. The molar volumes \( V \) were multiplied by the isentropic compressibilities to obtain estimates of \( \kappa^e_{Sm} \). Also, we have calculated the deviations \( u^d \) of the ultrasonic speeds from those in the ideal mixtures \( u^i \), together with the excess molar quantities \( K^e_{Sm} \) and the mixing function \( \delta u \). Theoretical values of speeds of sound have been estimated using Prigogine-Flory-Patterson (PFP) theory and the results obtained from PFP theory are compared with experimental results.

2 Experimental Details

2.1 Materials

Ethylene glycol dimethyl ether (Acros, USA, mass fraction > 0.99), diethylene glycol dimethyl ether (Acros, USA, mass fraction > 0.99) were dried over FeSO_4 (A.R., BDH) and then fractionally distilled under reduced nitrogen gas pressure. Triethylene glycol dimethyl ether (Acros, USA, mass fraction > 0.99) was used without further purification. Ethyl acetate (SRL, Bombay, mass fraction > 0.998) was dried over potassium carbonate, filtered, fractionally distilled and only the middle fraction was used for all the measurements. Prior to measurements, all liquids were kept over 0.4 nm molecular sieves to reduce water content, and were partially degassed at low pressure. The purities of the final samples were checked by comparing the densities at 298.15 K with their corresponding literature values in Table 1. Also given in Table 1 are our measured or literature values of those quantities which were required in the estimation \( \kappa_{Sm} \), \( K^e_{Sm} \), and \( u^d \).
2.2 Apparatus and procedure

The densities $\rho^0$ were measured with a bi-capillary pycnometer with an accuracy of $\pm 5 \times 10^{-3}$. The mole fraction of each mixture was obtained with an accuracy of $1 \times 10^{-4}$ from the measured apparent masses of the components. All masses were corrected for buoyancy.

All molar quantities were based upon the IUPAC table of atomic weights. The speeds of sound in both the pure liquids and the binary mixtures were measured at 298.15K using a NUSONIC (Makeco, Model 6080) velocimeter based on the slong-around technique with a single transducer cell. The ultrasonic speeds at 298.15 K are directly obtained from the average round trip period of the ultrasonic wave in a fixed path length between the piezoelectric transducer and reflector. The maximal error of the speed measured relative to water (1496.687 m s$^{-1}$ at 298.15 K) is estimated to be less than 0.2 m s$^{-1}$. Further details concerning this apparatus, experimental set-up and operational procedures have been given previously. A thermostatically controlled, well stirred water bath whose temperature was controlled to $\pm 0.01$ K was used for all the measurements.

3 Results and Discussion

The ultrasonic speeds at 298.15 K for all the mixtures at various composition are summarized in Table 2, together with the values of $K_{S,m}$. The measured speeds of sound $u$ were fitted to a polynomial of type:

$$u = \sum_{i=1}^{n} a_i x_i^j$$

by the method of least squares with each point weighted equally. The values of coefficients $a_i$ and standard deviations $\sigma$ are summarized in Table 3.

Isentropic compressibilities $K_s$ and molar isentropic compressibilities $K_{S,m}$ were calculated from:

$$K_s = (p_u)^{-1} = V(M_u)^{-1}$$

$$K_{S,m} = -\left(\frac{\partial V}{\partial p}\right)_s = V(K_s = V/ (M_u)^{-1})$$

where $p$ is the density and $M = \Sigma x_i M_i^0$ is the molar mass of the mixture.

The excess molar quantities $K_{S,m}^\ell$ were calculated from:

$$K_{S,m}^\ell = K_{S,m} - \ell K_s$$

where:

$$K_{S,m}^\ell = \Sigma x_i \left[ K_{S,i} - \ell A_{p,i} \left( \Sigma x_j A_{p,j} / \Sigma x_j C_{p,j} \right) - (A_{p,i} / C_{p,i}) \right]$$

where $A_{p,i}$ (the product of the molar volume and the isobaric expansivity $\alpha_{p,i}$), $C_{p,i}$ (the isobaric molar heat capacity), and $K_{S,i}$ (the product of the molar volume $V$ and the isentropic compressibility $K_s$) are properties of the pure liquid component $i$. Molar volumes of the components and densities of the mixtures were calculated from the densities of the pure components and the excess molar volumes reported by Tovar et al.2.

The deviations of the measured ultrasonic speeds from their values in an ideal mixture were calculated from:

$$u' = u - u^\ell$$

where

$$u^\ell = V_m^\ell / (M_{S,m}^\ell)^{1/2}$$

by the method of least squares with each point weighted equally. The values of coefficients $a_i$ and standard deviations $\sigma$ are summarized in Table 3.

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where $A_{p,i}$ (the product of the molar volume and the isobaric expansivity $\alpha_{p,i}$), $C_{p,i}$ (the isobaric molar heat capacity), and $K_{S,i}$ (the product of the molar volume $V$ and the isentropic compressibility $K_s$) are properties of the pure liquid component $i$. Molar volumes of the components and densities of the mixtures were calculated from the densities of the pure components and the excess molar volumes reported by Tovar et al.2.

The deviations of the measured ultrasonic speeds from their values in an ideal mixture were calculated from:

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where

$$u^\ell = V_m^\ell / (M_{S,m}^\ell)^{1/2}$$

The values of coefficients $a_i$ and standard deviations $\sigma$ are summarized in Table 3.
Table 2 — Ultrasonic speed $u$, and the product $K_{S,m}$ of the molar volume and isentropic compressibility at 298.15 K

<table>
<thead>
<tr>
<th>$u'$ (m/s)</th>
<th>$K_{S,m}$ (nm$^3$ mol$^{-1}$ MPa$^{-1}$)</th>
<th>$\gamma$</th>
<th>$u$ (m/s)</th>
<th>$K_{S,m}$ (nm$^3$ mol$^{-1}$ MPa$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0038 1139.4</td>
<td>84.851</td>
<td>0.5307</td>
<td>1153.8</td>
<td>87.226</td>
</tr>
<tr>
<td>0.0137 1139.7</td>
<td>84.890</td>
<td>0.5636</td>
<td>1153.6</td>
<td>87.408</td>
</tr>
<tr>
<td>0.0215 1139.9</td>
<td>84.927</td>
<td>0.5973</td>
<td>1154.6</td>
<td>87.535</td>
</tr>
<tr>
<td>0.0351 1140.3</td>
<td>84.982</td>
<td>0.6343</td>
<td>1155.6</td>
<td>87.689</td>
</tr>
<tr>
<td>0.0563 1140.8</td>
<td>85.087</td>
<td>0.6755</td>
<td>1156.8</td>
<td>87.847</td>
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<tr>
<td>0.0727 1141.2</td>
<td>85.166</td>
<td>0.7183</td>
<td>1158.2</td>
<td>87.986</td>
</tr>
<tr>
<td>0.0956 1141.8</td>
<td>85.269</td>
<td>0.7435</td>
<td>1158.7</td>
<td>88.117</td>
</tr>
<tr>
<td>0.1163 1142.3</td>
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<td>0.7725</td>
<td>1159.6</td>
<td>88.217</td>
</tr>
<tr>
<td>0.1393 1142.8</td>
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<td>0.1674 1143.5</td>
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<td>0.8819</td>
<td>1162.5</td>
<td>88.668</td>
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<td>0.2830 1146.6</td>
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<td>0.9042</td>
<td>1163.0</td>
<td>88.772</td>
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<tr>
<td>0.3307 1147.8</td>
<td>86.344</td>
<td>0.9257</td>
<td>1163.6</td>
<td>88.855</td>
</tr>
<tr>
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<td>0.9378</td>
<td>1164.0</td>
<td>88.892</td>
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<tr>
<td>0.4244 1150.1</td>
<td>86.780</td>
<td>0.9615</td>
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<td>88.976</td>
</tr>
<tr>
<td>0.4612 1151.1</td>
<td>86.935</td>
<td>0.9819</td>
<td>1164.9</td>
<td>89.110</td>
</tr>
<tr>
<td>0.4913 1151.8</td>
<td>87.080</td>
<td>0.1120</td>
<td>1166.0</td>
<td>89.284</td>
</tr>
</tbody>
</table>

$\text{CH}_3(\text{OC}_2\text{H}_5)\text{OCH} + (1-x) \text{CH}_3\text{COO}C_2\text{H}_5$
Also, the mixing function $\delta u$ is defined:
$$\delta u = u - u^n \sum_k a_k \exp(b_k) \quad \ldots (8)$$

The values of $K_{sn}^E$, $u^n$, and $\delta u$ were fitted for each mixture by an equation of the type:
$$F(x) = x(1-x) \sum_{j=0}^n a_j (2x-1)^j \quad \ldots (9)$$
by the method of least squares with each point weighted equally. The values of coefficients $a_j$ and standard deviations $\sigma$ are summarized in Table 3. Experimental results for $u$, $K_{sn}^E$, $u^n$, and $\delta u$ are plotted against $x$ in Figs 1-4.

For all the mixtures measured in the present study, $K_{sn}^E$ is negative over the entire range of composition and shows a minimum in the sequence: EGDME < EGDM < Tri-EGDME. The behaviour is similar to that of $u$ and $u^n$, with opposite sign. There is a decrease in $K_{sn}^E$ with each addition of $-OC_2H_5$ group in the molecule of ethylene glycol dimethyl ether. Also, the behaviour of excess molar volume of these mixtures seems to be consistent with a minimum value of $K_{sn}^E$ and a maximum value for $u^n$. This is normal because $u$ is generally higher when the structure has high rigidity. Again, the $K_{sn}^E$ is negative, that is the mixture is less compressible than the corresponding ideal mixture, and $u^n$ likewise positive for all mixtures, indicating that when the mixtures are created free volume increases (Table 5), and are higher in mixtures containing triethylene glycol dimethyl ether. Again, the effect is that the molecules of the two components can be easily accommodated due to difference in molecular size. Finally there is a little deviation in the $\delta u$ for the mixture containing ethylene glycol dimethyl ether and increases in the positive direction with the increase of the polar head group in polyether. Again from Figs. 2-4, it is interesting to note that both $\delta u$ and $u^n$ can be correlated well with $K_{sn}^E$.

The theoretical values of speeds of sound $u$ for both the liquid components and the liquid mixtures have been estimated using Prigogine–Flory–Patterson (PFP) theory.

The speed of sound $u$ is related to isentropic compressibility by
$$\nu = V(M \cdot K_s) = -V^2/[M \cdot (\partial V/\partial P)_s] \quad \ldots (10)$$

The term $(\partial V/\partial P)_s$, $(\partial V/\partial T)_s$, and $(\partial V/\partial T)_n$ are interrelated through the thermodynamic equation
$$\nu = (\partial V/\partial P)_s + T.C^2 \cdot (\partial V/\partial T)_n \quad \ldots (11)$$

According to Flory's statistical theory, based on van der Waals potential energy model, the reduced equation of state is given by:

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**Fig. 1** — Speeds of sound $u$ for $x\text{CH}_2\text{OC}_2\text{H}_5\text{OC}_2\text{H}_4\text{OH} + (1-x)\text{CH}_2\text{COO}_2\text{H}$ at $298.15 K$. O: $n = 1$; $\triangle$: $n = 2$; $\bullet$: $n = 3$. Solid points represent the theoretical values using Prigogine–Flory–Patterson (PFP) theory.
Fig. 2 — Values of $\gamma$ for $\{x \text{CH}_3(\text{OC}_2\text{H}_5)_n \cdot \text{OCH}_3 + (1-x)\text{CH}_3\text{COOC}_2\text{H}_5\}$ at 298.15 K: $\Delta$, $n = 1$; $\bigcirc$, $n = 2$; $\square$, $n = 3$.

Fig. 3 — Deviations $\Delta u$ of speeds of sound from their ideal values for $\{x \text{CH}_3(\text{OC}_2\text{H}_5)_n \cdot \text{OCH}_3 + (1-x)\text{CH}_3\text{COOC}_2\text{H}_5\}$ at 298.15 K: $\Delta$, $n = 1$; $\bigcirc$, $n = 2$; $\square$, $n = 3$. 
Table 3

(a) Parameters of Eq. (1) and the standard deviations $\sigma$

\[
\begin{array}{cccc}
\text{Parameter} & a_0 & a_1 & a_2 & \sigma \\
\text{m}^2 \text{s}^{-1} & 1139.376 & 24.781 & 1.516 & 0.114 \\
\text{m}^2 \text{s}^{-1} & 1139.105 & 194.339 & -61.256 & 7.374 & 0.176 \\
\text{m}^2 \text{s}^{-1} & 1139.200 & 349.750 & -202.902 & 55.669 & 0.239 \\
\end{array}
\]

(b) Parameters of Eq. (9) and the standard deviations $\sigma$

\[
\begin{array}{cccc}
\text{Parameter} & a_0 & a_1 & a_2 & \sigma \\
\text{m}^2 \text{s}^{-1} & -0.751 & 0.806 & 4.123 & 0.117 \\
\text{m}^2 \text{s}^{-1} & 1.692 & 0.900 & 3.599 & 0.113 \\
\text{m}^2 \text{s}^{-1} & -0.132 & -0.122 & -0.528 & 0.017 \\
\text{m}^2 \text{s}^{-1} & -5.448 & -3.457 & 0.233 \\
\text{m}^2 \text{s}^{-1} & 56.040 & -9.961 & -2.471 & 0.238 \\
\text{m}^2 \text{s}^{-1} & -8.882 & 1.862 & 0.149 & 0.035 \\
\text{m}^2 \text{s}^{-1} & 119.577 & 27.032 & 2.569 & 0.232 \\
\text{m}^2 \text{s}^{-1} & 112.107 & -38.468 & 8.182 & 0.237 \\
\text{m}^2 \text{s}^{-1} & 18.061 & -2.006 & -2.006 & 0.036 \\
\end{array}
\]

Fig. 4 — Mixing function $\delta r$ for $\{\alpha \text{CH}_{3}(\text{OC})_{2}\text{H}_{4}\text{OCCH} + (1-\alpha)\text{CH}_{3}\text{COOC}_{2}\text{H}_{5}\}$ at 298.15 K. $\alpha = 1 \Delta \alpha = 2$, $\alpha = 3$.
\[ \vec{v} / T = \left[ \frac{\vec{v}}{V^{1/3} - 1} \right] - \left( \frac{\vec{v}}{T} \right) \]  \hspace{1cm} (12) \\

where \( \vec{v} = V/V_0 \), \( T = T/T_0 \), \( P = P/P_0 \). 

Here \( P_0 \), \( V_0 \), and \( T_0 \) are the characteristic parameters. 

At \( P = 0 \), Eq. (12) becomes: 

\[ T = \left[ (\vec{v}^{1/3} - 1) \right] / \vec{v}^{1/3} \]  \hspace{1cm} (13) \\

The thermodynamic expansion coefficient serves to define \( P_\alpha \) as:

\[ P_\alpha = (\alpha/K_1) T \vec{v}^{2/3} \]  \hspace{1cm} (14) \\

By differentiating Eq. (12) with respect to \( P \) at constant \( T \), then using Eq. (13) and substituting \( V \) by \( \vec{v} V_0 \), one obtains the equation:

\[ \left( \frac{\partial V}{\partial P} \right)_T = \frac{\vec{v}}{V_0} \left( \frac{\vec{v}^{1/3}}{T} - \vec{v}^{2/3} \right) \]  \hspace{1cm} (15) \\

Similarly, differentiating Eq. (12) with respect to \( T \) at constant \( P \) gives:

\[ \left( \frac{\partial V}{\partial T} \right)_P = \frac{\vec{v}}{V_0} \left( \frac{\vec{v}^{1/3}}{T} - \vec{v}^{2/3} \right) \]  \hspace{1cm} (16) \\

The theory developed for the pure components can be extended to the mixtures by defining the characteristic parameters for the mixtures with the assumption that they are equivalent to a single component liquid. The characteristic volume for the mixture \( V_{1/z}^* \) is related to \( V_0^* \), the volumes of the pure components \( i \) by:

\[ V_{1/z}^* = \sum x_i V_0^* \]  \hspace{1cm} (17) \\

where \( x_i \) is the mole fraction of component \( i \). The characteristic pressure for the mixture \( P_{1/z}^* \) is defined as:

\[ P_{1/z}^* = \sum \phi_i P_i^* - \phi_i \theta_i \chi_{12} \]  \hspace{1cm} (18) \\

where \( \phi_i \) is the segment fraction and \( \theta_i \) the surface fraction are expressed as:

\[ \phi_i = 1 - \phi_i = x_i / x_1 + x_i (r_1 r_2) \]  \hspace{1cm} (19) \\

and

\[ \theta_i = \phi_i / (\phi_i + \phi_1 (x_1 x_2)) \]  \hspace{1cm} (20) \\

where \( r_1 \) and \( r_2 \) are in the ratio of the respective molar core volumes \( V_1^* \) and \( V_2^* \) i.e. \( r_1 r_2 = V_1^* / V_2^* \). Similarly \( x_1 \) and \( x_2 \) are the ratio of the molecular surface areas of contact per segment and \( \chi_{12} \) in Eq. (18) is the interaction parameter which accounts for interaction among the neighboring segments.

The characteristic temperature for the mixture, \( T_{1/z}^* \) is given by:

\[ T_{1/z}^* = P_{1/z}^* / \left( \sum \phi_i P_i^* / T_i^* \right) \]  \hspace{1cm} (21) \\

The theoretical values of \( \mu \) have been estimated using Eqs (10)-(21). The contact interaction parameter \( \chi_{12} \) is obtained according to FF model using excess molar volumes at equimolar composition, through the following relation:

\[ \psi_1 = 1 - \psi_2 = \frac{\phi_1 P_1^*}{\phi_1 P_1^* + \phi_2 P_2^*} \]  \hspace{1cm} (22) \\

where \( \psi_1 \) represents the contact energy fraction, given by:

\[ \psi_1 = 1 - \psi_2 = \frac{\phi_1 P_1^*}{\phi_1 P_1^* + \phi_2 P_2^*} \]  \hspace{1cm} (23) \\

The parameters for the pure liquid components derived using FF model expression are listed in Table 4 and the contact interaction parameter \( \chi_{12} \) together with interaction, free volume, and \( P^2 \) contributions are summarized in Table 5.

Theoretical values of speeds of sound \( u \) for the binary mixtures have been plotted in Fig. 1 along with the experimental values. Fig. 1 show that the agreement between the FF model values and the experimental values is quite good for all the mixtures and it may be concluded that FF theory is quite successful in giving

<table>
<thead>
<tr>
<th>Component</th>
<th>( K_1 ) (TPa)</th>
<th>( \overline{v} )</th>
<th>( V ) (cm(^3) mol(^{-1}))</th>
<th>( V_0 ) (cm(^3) mol(^{-1}))</th>
<th>( T_0 ) (K)</th>
<th>( \rho_0 ) (g cm(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_3)CO-CH(_2)CH(_3)</td>
<td>1116.51</td>
<td>1.3019</td>
<td>104.48</td>
<td>80.25</td>
<td>4611</td>
<td>577.96</td>
</tr>
<tr>
<td>CH(_3)CO-CH(_2)OCH(_3)</td>
<td>819.42</td>
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<td>142.88</td>
<td>113.50</td>
<td>5081</td>
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</tr>
<tr>
<td>CH(_3)CO-OCH(_2)CH(_3)</td>
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<tr>
<td>CH(_3)CO-CH(_3)</td>
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<td>98.50</td>
<td>74.74</td>
<td>4470</td>
<td>597.68</td>
</tr>
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</table>
a good theoretical account of the speeds of sound in the present binary liquid mixtures.

Acknowledgements
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