Ultrasonic studies on dilute solutions of water in \( n \)-alcohols and 2-alkoxyethanols

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Ultrasonic velocities in dilute solutions of water in \( n \)-alcohols (methanol, ethanol, \( n \)-propanol and \( n \)-butanol), and 2-alkoxyethanols (2-methoxyethanol, 2-ethoxyethanol and 2-butoxyethanol) have been determined at 298.15 K using single crystal variable path interferometer working at 3 MHz. The excess ultrasonic velocities have been evaluated using the formula, which is thermodynamically valid. A distinctive non-linear variation of ultrasonic velocity with concentration of water in both \( n \)-alcohols and 2-alkoxyethanols has been observed over a small range of concentration. A similar behaviour is also observed in the concentration dependence of excess ultrasonic velocity in these solutions. This behaviour has been explained by considering the existence of water molecules as monomers up to a certain optimum concentration, \( (x_o)^{opt} \), of water and the non-linear behaviour observed beyond \( (x_o)^{opt} \) has been explained in the light of water-water and water-alcohol interactions leading to the formation of islands of water-alcohol extended structures.

Keywords: Ultrasonic study, Water, \( n \)-alcohols, 2-alkoxyethanols

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1 Introduction

Literature survey indicates that most of the studies on ultrasonic behaviour of aqueous non-electrolytes\(^1\)-\(^{11}\) have been confined to the water rich region in view of extrema observed at low mole fractions of the non-electrolytes which have been attributed to the modification of the hydrogen bonded structure of water by the non-electrolytes. In the organic rich region, the number of measurements are fewer and do not extend to infinite dilution of water. Most of the data simply show a linear variation in the mole fraction range 0.9-1.0 of the organic solute.

The density and partial molar volume have been measured of solutions of water in organic liquids at infinite dilution\(^2\) and the studies have been found to be highly useful in understanding the structure and molecular interactions between the water and organic solute molecules. The solution structure of water non-electrolytes at infinite dilution of water from ultrasonic velocity measurements has been investigated. The ultrasonic behaviour of dilute solution of water in \( t \)-butanol, \( sec \)-butanol, isobutanol, \( p \)-dioxane, dimethyl sulphoxide and ethylene glycol have been carried out by Ramakrishna \textit{et al.}\(^{13}\). Ramana \textit{et al.}\(^{14,15}\) studied the ultrasonic behaviour of dilute solutions of water in \( n \)-propanol, isopropanol, glycerol, formamide, N-methyl formamide, dimethylformamide, tetrahydrofuran, propylene glycol, diethylene glycol and polyethylene glycol. These studies have been found to be very useful in understanding the molecular interactions between water and organic molecules at infinite dilution of water. The present paper deals with further studies carried out by the researchers on ultrasonic behaviour of dilute solution of water in \( n \)-alcohols and 2-ethoxyethanols.

2 Experimental Details

AR grade methanol, ethanol, \( n \)-butanol, 2-methoxyethanol, 2-ethoxyethanol and 2-butoxyethanol used in the present study were purified as per standard procedures\(^6\). The densities of the pure liquids determined using a bicapillary type pycnometer with an accuracy of 2 parts in 10\(^5\) are 786.44, 785.06, 805.70, 960.03, 925.01 and 896.31 kg m\(^{-3}\) for methanol, ethanol, \( n \)-butanol, 2-methoxyethanol, 2-ethoxyethanol and 2-butoxyethanol at 298.15 K respectively. These values are in good agreement with literature values\(^17\)-\(^{22}\).
The ultrasonic velocities in pure liquids and in solutions were determined at 298.15 K using a single-crystal variable path interferometer working at 3 MHz, the details of which are presented in our earlier paper. In the dilute solution of water in alcohols (non-electrolytes) the accuracy obtained in ultrasonic velocity measurement is ± 0.01% in view of larger temperature coefficient of ultrasonic velocity in non-electrolytes. The solutions of desired concentration of water in alcohols were prepared by weight using triple-distilled degassed water.

3 Results and Discussion

The excess ultrasonic velocities in the solutions of water in \( n \)-alcohols and 2-alkoxyethanols were determined using the following relations, which are thermodynamically consistent.

\[
\alpha_{id} = \phi_1 \alpha_1 + \phi_2 \alpha_2 \quad \cdots (7)
\]

\[
C_{pid} = X_1 C_{p1} + X_2 C_{p2} \quad \cdots (8)
\]

\( \phi, X, \beta, K, \rho, \alpha, V \) and \( C_p \) represent the volume fraction, mole fraction, adiabatic compressibility, isothermal compressibility, density, thermal expansion coefficient, molar volume and molar specific heat at constant pressure respectively. The suffix 1 refers to the organic solvent, suffix 2 refers to pure water and suffix id represents the ideal value of the parameter in the solution. The pure liquid parameters required for calculating \( u^E \) are given in Table 1.

Ultrasonic velocities and excess ultrasonic velocities in dilute solutions of water in methanol, ethanol and \( n \)-butanol as a function of concentration of water are shown in Figs 1 and 2 respectively. The ultrasonic velocity data for the solutions of water in \( n \)-propanol taken from literature are also shown in Figs 1 and 2.

The variation of ultrasonic velocity and excess ultrasonic velocity with mole fraction \( X_2 \) of water in 2-methoxyethanol, 2-ethoxyethanol and 2-butoxyethanol are shown respectively in Figs 3 and 4.

An examination of the data presented in Figs 1 and 3, indicates that the ultrasonic velocity varies non-linearly with concentration of water in all the systems, except at very low concentrations. The optimum concentrations up to which a linearity is observed in \( u \) versus \( X_2 \) are presented in Table 2. Beyond these optimum concentrations, \( (X_2)_{opt} \), \( u \) versus \( X_2 \) is non-linear up to certain extent for all the systems. Normally, one would expect a linear variation if there were no water-water and water-

<table>
<thead>
<tr>
<th>Liquid</th>
<th>( u ) (m s(^{-1}))</th>
<th>( \rho ) (kg m(^{-3}))</th>
<th>( C_p ) (J mol(^{-1}) K(^{-1}))</th>
<th>( \alpha \times 10^4 ) (K(^{-1}))</th>
<th>( \beta \times 10^{11} ) (N(^{-1}) m(^2))</th>
<th>( K \times 10^{11} ) (N(^{-1}) m(^2))</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>1496.7</td>
<td>997.07</td>
<td>75.3</td>
<td>2.59</td>
<td>44.77</td>
<td>45.25</td>
<td>7</td>
</tr>
<tr>
<td>Methanol</td>
<td>1097.6</td>
<td>786.44</td>
<td>81.2</td>
<td>12.01</td>
<td>104.04</td>
<td>125.14</td>
<td>10</td>
</tr>
<tr>
<td>Ethanol</td>
<td>1144.3</td>
<td>785.06</td>
<td>112.6</td>
<td>10.92</td>
<td>97.28</td>
<td>116.34</td>
<td>10</td>
</tr>
<tr>
<td>n-Butanol</td>
<td>1239.9</td>
<td>805.70</td>
<td>177.0</td>
<td>9.32</td>
<td>80.73</td>
<td>94.25</td>
<td>7</td>
</tr>
<tr>
<td>2-Methoxy-ethanol</td>
<td>1344.8</td>
<td>960.03</td>
<td>176.4</td>
<td>8.23</td>
<td>57.52</td>
<td>66.60</td>
<td>25</td>
</tr>
<tr>
<td>2-Ethoxy-ethanol</td>
<td>1309.3</td>
<td>925.01</td>
<td>210.3</td>
<td>8.40</td>
<td>63.03</td>
<td>72.78</td>
<td>25</td>
</tr>
<tr>
<td>2-Butoxy-ethanol</td>
<td>1304.8</td>
<td>896.31</td>
<td>270.6</td>
<td>10.41</td>
<td>65.50</td>
<td>81.24</td>
<td>25</td>
</tr>
</tbody>
</table>
alcohol interactions. The observations therefore indicate some sort of association between the water molecules themselves and also with the \( n \)-alcohol molecules and 2-alkoxyethanol molecules. This behaviour is very well reflected in the excess ultrasonic velocity behaviour as can be seen from Figs 2 and 4. The \( (X_2)_{\text{opt}} \) in \( u^E \) versus \( X_2 \) up to which the variation is linear for all the systems are also given in Table 2.
In the water rich region, methanol, ethanol, n-propanol and n-butanol are known to enhance the hydrogen bonded structure of water. These molecules by interstitial substitution in the water structure, stabilize the hydrogen bonded clusters against thermal collapse and as a result, the solution structure is more structured than pure water.

A sharp maximum in ultrasonic velocity and a sharp minimum in adiabatic compressibility have been observed at low 2-butoxyethanol (BE) concentrations in mixtures of water + 2-butoxyethanol at all temperatures. These extrema have been attributed to the formation of clathrate-like structures of water and 2-butoxyethanol. The specific heat studies also indicate the occurrence of clathrate structures at ~0.02 X_{BE}. Beyond this concentration micro phase aggregates are predicted to occur and at very high concentrations of BE the clathrate and micro phase structures cease to exist.

Douheret et al. studied ultrasonic velocities and isentropic compressibilities of 2-methoxyethanol + water, 2-ethoxyethanol + water and 2-butoxyethanol + water across their entire composition range. These studies reveal significant variations in the patterns of molecular aggregation. While 2-butoxyethanol may not satisfy all the requirements of a truly micellar system, it is obvious that there exist some very dramatic structural changes around X_{BE} ~ 0.02. The composition dependence of the ultrasonic properties of 2-ethoxyethanol + water and 2-methoxyethanol + water show no dramatic changes but appear as smoothed analogues of those of 2-butoxyethanol + water system suggesting that there is a modest degree of hydrophobic aggregation by the smaller amphiphiles resulting in labile clusters. The partial molar heat capacities C_{p2} for alkoxyethanols in aqueous solutions have been observed to be large at 298.15 K and this behaviour has been attributed to the interaction between the hydrophobic alkyl groups and water molecules resulting into a solution, which is more structured than pure water.

In the very high dilution region of water in n-alcohols and in 2-alkoxyethanols, it is how the water molecules exist as clusters or monomers that decide the ultrasonic behaviour as observed, shown in Figs 1 to 4. According to Eucken, water may be considered to be composed of four distinct molecules namely monomers, (H_{2}O), dimers, (H_{2}O)_{2}, quadrumers, (H_{2}O)_{4} and octomers, (H_{2}O)_{8}. The linearity in u versus X_{2} and u^{E} versus X_{2} up to (X_{2})_{opt} may be considered to be due to the existence of water molecules as monomers, dispersed uniformly in n-alcohols and as well in 2-alkoxyethanols.

Beyond (X_{2})_{opt} u versus X_{2} is non-linear and this non-linear behaviour is also seen in u^{E} versus X_{2} curves for all the systems. This non-linear variation indicates that in dilute solutions of water in n-alcohols and in 2-alkoxyethanols water molecules exist as polymeric molecules. This behaviour favours the interpretation of water as distorted ice like structure with bonds constantly breaking and forming and the associations extending throughout the whole solution. As per this view, when water is present in very small amounts in n-alcohols or 2-alkoxyethanols, one may consider the existence of water molecules dispersed homogeneously throughout the bulk of the respective solutions with the possibility of formation of water-water or water-alcohol associations. The limiting partial molar volume of water, V_{w}^{\infty}, for solutions of lower alcohols are smaller than that of pure water and this behaviour has been attributed to the strong hydrogen bond formation between water and alcohol molecules.

Considering the possible dissociation reaction schemes that may exist when water is dissolved in the non-electrolyte, the observed nonlinear and non-ideal behaviour of u versus X_{2} and u^{E} versus X_{2} may be attributed to the existence of hypothetical particles in the solution with the possibility of bond formation.

<table>
<thead>
<tr>
<th>System</th>
<th>(X_{2})_{opt}</th>
<th>u versus X_{2}</th>
<th>u^{E} versus X_{2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol + Water</td>
<td>0.0024</td>
<td>0.0025</td>
<td></td>
</tr>
<tr>
<td>Ethanol + Water</td>
<td>0.0033</td>
<td>0.0036</td>
<td></td>
</tr>
<tr>
<td>n-Propanol + Water</td>
<td>0.0035</td>
<td>0.0035</td>
<td></td>
</tr>
<tr>
<td>n-Butanol + Water</td>
<td>0.0031</td>
<td>0.0036</td>
<td></td>
</tr>
<tr>
<td>2-Methoxyethanol + Water</td>
<td>0.0040</td>
<td>0.0041</td>
<td></td>
</tr>
<tr>
<td>2-Ethoxyethanol + Water</td>
<td>0.0036</td>
<td>0.0075</td>
<td></td>
</tr>
<tr>
<td>2-Butoxyethanol + Water</td>
<td>0.0060</td>
<td>0.0060</td>
<td></td>
</tr>
</tbody>
</table>
with either water molecules or \( n \)-alcohols or 2-alkoxyethanols as the case may be.

The extent of flatness of the \( u \) versus \( X_2 \) curve decreases as one goes from \( n \)-butanol to methanol and is in the order \( n \)-butanol > \( n \)-propanol > ethanol > methanol (Fig. 1). A similar behaviour is also observed in \( u^2 \) versus \( X_2 \) curves as shown in Fig. 2. The excess ultrasonic velocity is positive and increases non-linearly with increase in the concentration of water for dilute solutions of water in \( n \)-alcohols.

As can be seen from Fig. 3, the extent of the inflection region in \( u \) versus \( X_2 \) curve decreases as one goes from 2-methoxyethanol to 2-butoxyethanol and is in the order 2-methoxyethanol > 2-ethoxyethanol > 2-butoxyethanol. This signifies that as molecular weight increases the percentage of water existing as monomers increases in dilute solutions of 2-alkoxyethanols. This behaviour is also reflected in \( u^2 \) versus \( X_2 \) curves as shown in Fig. 4. The excess ultrasonic velocity is positive and increases non-linearly with increase in the concentration of water for dilute solutions of water in 2-alkoxyethanols.

In the concentration region between the two arrows marked in Figs 1 to 4, the extent of change of ultrasonic velocity or excess ultrasonic velocity with concentration is either low or remains unchanged indicating that there is no much change in the intermolecular space as a result of addition of water to the \( n \)-alcohols or 2-ethoxyethanols. One may consider the formation of islands of clusters of water molecules or water – \( n \)-alcohol associations dispersed uniformly throughout the solution in this range of concentration between the two arrows marked in Figs 1 and 3. In the case of water + 2-alkoxyethanol systems in the range of concentration of water between the two arrows shown in Figs 2 and 4, one may consider the existence of an interaction between the hydrophobic alkyl groups and water molecules leading to the formation of isolated extended structures apart from the formation of islands of clusters of water molecules.

At higher concentrations beyond the second arrow shown in Figs 1 and 4, \( u \) versus \( X_2 \) and \( u^2 \) versus \( X_2 \) show a linear or gradual increase with \( X_2 \). This behaviour may be considered to be due to the collapse of water – \( n \)-alcohol associations in water – \( n \)-alcohol systems and collapse of the extended structures of water–alkoxyethanol molecules in water+2-alkoxyethanol systems and destabilization of isolated clusters of water molecules leading to the formation of free water molecules as monomers, dimers, quadrumers and octomers distributed throughout the respective systems.

4 Conclusions

In highly dilute solutions of water in \( n \)-alcohols and 2-alkoxyethanols ultrasonic velocity and excess ultrasonic velocity vary non-linearly with molefraction of water. Close to the region of infinite dilution of water in \( n \)-alcohols and in 2-ethoxyethanols, both ultrasonic velocity and excess ultrasonic velocity vary linearly with mole fraction of water indicating that water molecules exist as monomers distributed uniformly throughout the solution. The non-linear behaviour of the variation of ultrasonic velocity and excess ultrasonic velocity with concentration of water is considered to be due to the existence of islands of clusters of water molecules in association with \( n \)-alcohol or 2-ethoxyethanol molecules as the case may be. Further, addition of water leads to collapse of these extended clusters leading to the formation of free water molecules as monomers, dimers, quadrumers and octomers distributed throughout the solution uniformly as a result of which both ultrasonic velocity and excess ultrasonic velocity vary smoothly with increase in the concentration of water.

References

2. Feng Jau, Ser Fiz I Kim, 16 (1961) 64.