TOPOLOGICAL INVESTIGATION OF SOME ALKANOL + WATER BINARY MIXTURES: MOLAR EXCESS VOLUME AT 298.15 AND 308.15 K.

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ABSTRACT

The excess molar volume $V^E$ \( \{ x(CH_3 OH \text{ or } CH_3 CH_2 OH \text{ or } CH_3 CH_2 CH_2 OH \text{ or } CH_3 CH(OH)CH_3 \text{ or } CH_3 CH_2 CH(OH)CH_3 \text{ or } \text{ water} \} \) has been calculated from measured values of density over the whole composition range at the temperature 298.15K and 308.15K in order to investigate OH...O specific interactions. The results are explained in term of the strong self association of the alkanols, the specific interaction between the alkanol and water and packing effects up on mixing. The experimental $V^E$ results presented here has been analyzed in term of the graph theory which in turn deals with topology of the constituents of mixtures. It has been observed that $V^E$ values predicted by the graph theory compare well with their corresponding experimental values.

**Keywords:** Alkanols (Methanol, Ethanol, Propan-1-ol, Propan-2-ol, Butan-1-ol, Butan-2-ol), Excess molar volume, Binary mixture, Hydrogen bond.

INTRODUCTION

Industry demand reliable and accessible reference data on the thermodynamic properties (excess molar volumes) of wide variety of liquid mixtures. These properties not only provide reliable data and empirical rules for science and technology, but also enhance the understanding of the behavior of liquid mixtures. We have calculated $V^E$, which in turn deals with topology of the constituents of mixtures. It has been observed that $V^E$ values predicted by the graph theory compare well with their corresponding experimental values.
Eq. (2): adjustable parameters were evaluated by fitting the $V$ data of $V$ where $m$ is number of data points and $p$-is the number of adjustable parameters of equation (1) in table 1 our $V$ values at $X_i=0.5$ for water + butan-1-ol are 0.05 cm$^3$ mol$^{-1}$ higher than value at 298.15 K reported in literature 18. There are no literature values of $V$ for other mixtures with which to compare our results.

$V$ data for the studied $i$-mixtures are negative over the whole composition range and for an equimolar composition vary in the order: butan-2-ol > propan-2-ol > butan-1-ol > propan-1-ol > ethanol > methanol.

Graph theory and results
Molar excess volumes, $V$ are a packing effect due to the replacement of $i$-i and $j$-j contacts in pure state by $i$-$j$ contacts in mixture state. The replacement of $i$-i and $j$-j contacts by $i$-$j$ may then lead to change in topology of $i$-$j$ components of $i$-$j$ mixtures. According to mathematical discipline of graph theory, if the atoms in a structural formula of a molecule are represented by letters and bonds joining them by lines then the resulting graph describes the total information contained in that molecule 17,18. Consequently, if $δ_n$, $σ_m$ etc. represent the degree of $m$ and $n$ etc. vertices of the graph of a molecule, then connectivity parameter of third degree, $ξ$ is defined 23 by

\[ ξ = \frac{2E}{V} \]

Table II: Values of parameters $V^*$ ($n = 0$ – 2) along with standard deviation, $σ (V^*)$ of the molar excess volumes, $V^*$ for the various (i+j) binary mixtures at 298.15 K and 308.15 K

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Temperature</th>
<th>$V(0)$</th>
<th>$V(1)$</th>
<th>$V(2)$</th>
<th>$σ (V^*)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water (i) + Methanol (j)</td>
<td>298.15 K</td>
<td>-1.879</td>
<td>-0.303</td>
<td>-0.286</td>
<td>0.004</td>
</tr>
<tr>
<td>Water (i) + Ethanol (j)</td>
<td>308.15 K</td>
<td>-1.084</td>
<td>-0.086</td>
<td>-0.023</td>
<td>0.003</td>
</tr>
<tr>
<td>Water (i) + Propan-1-ol (j)</td>
<td>298.15 K</td>
<td>-1.417</td>
<td>-0.568</td>
<td>-0.096</td>
<td>0.003</td>
</tr>
<tr>
<td>Water (i) + Propan-2-ol (j)</td>
<td>298.15 K</td>
<td>-1.043</td>
<td>-0.186</td>
<td>-0.418</td>
<td>0.002</td>
</tr>
<tr>
<td>Water (i) + Butan-1-ol (j)</td>
<td>298.15 K</td>
<td>-0.961</td>
<td>-0.45</td>
<td>-0.041</td>
<td>0.002</td>
</tr>
<tr>
<td>Water (i) + Butan-2-ol (j)</td>
<td>298.15 K</td>
<td>-0.469</td>
<td>-0.103</td>
<td>-0.031</td>
<td>0.001</td>
</tr>
<tr>
<td>Water (i) + Butan-1-ol (j)</td>
<td>308.15 K</td>
<td>-0.584</td>
<td>-0.341</td>
<td>-1.445</td>
<td>0.001</td>
</tr>
<tr>
<td>Water (i) + Butan-2-ol (j)</td>
<td>308.15 K</td>
<td>-0.418</td>
<td>-0.010</td>
<td>-0.094</td>
<td>0.001</td>
</tr>
</tbody>
</table>

Where $x_i$ is the mole fraction of component $i$ and $x(n)$ ($n=0$-2) are adjustable parameters were evaluated by fitting the $V$ data of various mixture to Eq.(1) by the least square method and are recorded along with standard deviation $σ (X^E_X = V^*)$ defined by Eq.(2):

\[ σ(X^E_X) = \left[ \sum (X^E_X - X^E_X_{calc.eq.(1)})^2/(m-p) \right]^{0.5} \]

Where $m$ is number of data points and $p$ is the number of adjustable parameters of equation (1) in table 1 our $V^*$ values at $X_i=0.5$ for water + butan-1-ol are 0.05 cm$^3$ mol$^{-1}$ higher than value at 298.15 K reported in literature 18. There are no literature values of $V$ for other mixtures with which to compare our results.

$V$ data for the studied $i$-mixtures are negative over the whole composition range and for an equimolar composition vary in the order: butan-2-ol > propan-2-ol > butan-1-ol > propan-1-ol > ethanol > methanol.
\[
\sum_{i=1}^{\text{max}} \left( \delta_{ij}^v \sigma_{ij}^v \delta_{oij}^v \right)^{-0.5} \tag{3}
\]

Where \( \delta_{ij} \), etc. values explicitly reflect the valency of the atoms forming the bond and is expressed as \( \delta = 2n - h \), where \( n \) is the maximum valency of atom and \( h \) is the number of hydrogen atoms attached to it. Consequently, for carbon in CH₃ (δ=C: 4-3=1) and for carbon in CH₄ (δ=C: 4-2=2). The addition of \( i \) and \( j \) causes structural changes in the topology of \( i \) or \( j \) in \( i+j \) mixture, so it would be of interest to analyze \( V^e \) data of the studied mixtures in terms of graph theoretical approach that takes into consideration the connectivity of parameters of third degree of the constituents of mixture (which describes the topology of molecule). According to this theory \( V^e \) is given by \(^2,^2\)

\[
V^e = a_{ij} \left[ \sum \chi_i \left( \frac{3}{\xi} \right)^{-1} - \sum \chi_j \left( \frac{3}{\xi} \right)^{-1} \right] \tag{4}
\]

Where \( \chi_i \) is the mole fraction of component \( i \) and \( \left( \frac{3}{\xi} \right)_i \) and \( \left( \frac{3}{\xi} \right)_j \) are \( \alpha \) parameters for the various \([i+\ell] \) binary mixtures as functions of \( X_i \), the mole fraction of component \( i \) at 298.15 K and 308.15 K.

### Table III: Comparison of \( V^e \) values calculated with their corresponding experimental values along with various \( \left( \frac{3}{\xi} \right)_i \) \( \left( \frac{3}{\xi} \right)_j \) \( (i = i \text{ or } j) \) \( \alpha \) parameters for the various \([i+\ell] \) binary mixtures as functions of \( X_i \) 

<table>
<thead>
<tr>
<th>Property</th>
<th>Mole Fraction ((X_i))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.1</td>
</tr>
<tr>
<td>( V^e _{\text{Exp}} )</td>
<td>-0.174</td>
</tr>
<tr>
<td>( V^e _{\text{Graph}} )</td>
<td>-0.143</td>
</tr>
<tr>
<td>( \left( \frac{3}{\xi} \right)_i ) ( (i = i \text{ or } j) )</td>
<td>( a_{ij} = 9.767 )</td>
</tr>
</tbody>
</table>

\( a_{ij} \) are in \( \text{cm}^3\text{mol}^{-1} \)

As the degree of association of \( i \) and \( j \) is not known with certainty, \( \left( \frac{3}{\xi} \right)_i \) \( (i = i \text{ or } j) \), etc. parameters were regarded as adjustable parameters. These parameters were determined by fitting \( V^e \) data to Eq. (4) and only those \( \xi \) and \( \left( \frac{3}{\xi} \right)_i \) \( (i = i \text{ or } j) \) were retained that best reproduced the experimental \( V^e \) values. These parameters calculated via Eq.(4) along with \( V^e \) are recorded in table III and \( V^e \) values are also compared with their corresponding experimental values. Examination of table III reveals that \( V^e \) values compare reasonably well with their corresponding values thus \( \left( \frac{3}{\xi} \right)_i \) \( (i = i \text{ or } j) \) values can be relied on to extract information about the state of components in pure as well as mixture state.

A number of structures were assumed for components in pure and mixture state and \( \left( \frac{3}{\xi} \right)_i \) values were calculated from their structural considerations via Eq. (3). Only those structure or combination of structures that yielded \( \left( \frac{3}{\xi} \right)_i \) [calculated via Eq.(3)]
which compare well with $3 \xi'$ values (determined from eqn. (4)) were taken to be good representative structures of that component. for W(i) + methanol or ethanol or propan-1-ol or butan-1-ol (j) binary mixtures, it was assumed that W, methanol, ethanol, propan-1-ol, butan-1-ol exist as molecular entities I-II, III-IV, V-VI, VII-VII and IX-X (Scheme-I) respectively. $3 \xi'$ values for these molecular entities were then calculated to be 0.426, 1.379, 0.447, 1.587, 0.663, 1.326, 0.721, 2.063, 1.032 and 2.194 respectively. $3 \xi'$ values of 0.952, 0.902, 0.901 and 0.701 (Table III) of methanol, ethanol, propan-1-ol and butan-1-ol suggest that methanol, ethanol and propan-1-ol exist as a mixture of monomer and dimer ($3 \xi' = 1.032, 0.908, 0.877$); butan-1-ol exist as monomer ($3 \xi' = 1.010$) Further, $3 \xi'$ values of 0.601, 0.750, 0.650 and 0.541 for W(i) in these mixtures suggest that W(i) exist as molecular entities XI-XIV. ($3 \xi'$)m values were evaluated (via Eq. 3) to understand the state in which various alkanols exist in W(i). It was assumed that studied [i+j] mixture may contain molecular entities XI-XIV (Scheme-I) respectively and characterized by interaction between hydrogen/oxygen atom of W(i) and oxygen / Hydrogen atom of alkanol group of alkanols. In calculating ($3 \xi'$)m values for these molecular entities, it was assumed further that only O-H edge of alkanol is involved in hydrogen bond interaction with oxygen atom of W (i). The ($3 \xi'$)m values for molecular entities XI-XIV were then calculated to be 1.159; ($3 \xi'$)m values of 0.952, 0.902, 0.901 and 0.701 (Table-III) suggest the presence of molecular entities XI-XIV in the studied mixtures.

**CONCLUSIONS**

Molar excess volumes of Methanol, Ethanol, Propan-1-ol, Propan-2-ol, Butan-1-ol, Butan-2-ol (A) with Water (B) measured with V-shaped dilatometer at 298.15 K. data were interpreted in terms of specific interactions of electron donor-acceptor type between oxygen/hydrogen atom of water and hydrogen/oxygen atom of alkanols.
Scheme I: Connectivity parameters of various molecular entities I-XIV

REFERENCES