Viscosity B-coefficient and partial molar volume between 25\(^{0}\)c and 45\(^{0}\)c for mono and diphosphate ions in aqueous solution

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ABSTRACT

Partial molar volume and viscosity B-Coefficient of phosphoric acid, sodium salt of mono and diphosphates were determined in water in the temperature range 25-45\(^{0}\)C. All these parameters exhibit the following order: \(H_3PO_4\)<\(HPO_4\)<\(HPO_4^{2-}\). \(\Phi V_0\) increased with temperature for \(H_3PO_4\) and \(H_2PO_4^{-}\) and decreased for \(HPO_4^{2-}\). Viscosity B-Coefficient exhibit constancy between 25-35\(^{0}\)C for all the two salt and phosphoric acid. Hydration number \((n_H)\) at 25\(^{0}\)C, obtained through viscosity show satisfactory agreement and follow the order \(HPO_4^{2-}\)>\(H_2PO_4^{-}\)>\(H_3PO_4\). Similarly, the magnitude of \(B/\Phi V_0\times10^3\) is also analyzed.

Keywords: Partial molar volume, Viscosity, B-Coefficient, Apparent molar volume.

INTRODUCTION

Ionic size, shape and charge affects in the interaction of anions with water. The specificity of ion-solvent interaction behavior, especially in an aqueous medium has been emphasized and its role in various biophysical processes has been recognized [1]. The significances of volume of ion in solution has been explored by Akkit [2] who in particular has shown the dependence of ionic volumes on charge, through electrostriction effect and the role of cavities in the water liquid lattice.[3, 4] A very good example of anions worth studying in light of the factor, mentioned above are the phosphate ions. Mono, di and triphosphates differ in charges and ionic size. X-ray diffraction study of aqueous phosphoric acids showed that 4 and 8 water molecule as the nearest neighbors (hydrogen bonded to the phosphate group) and 6-18 water molecule per \(PO_4^{3-}\) anion are present in phosphate–water cluster. The importance of phosphoric acid and sodium phosphate in well established in the aqueous buffer solutions [5]. Inorganic phosphate in blood plasma in mainly in two forms \(HPO_4^{2-}\) and \(H_2PO_4^{-}\). Also the adenosine triphosphate is an intra cellular storehouse of energy [6]. Hydration behavior of anions at various temperatures would be
useful for biochemist. This behavior can be determined quantitatively through hydration number. Partial molar volume and viscosity studies have been done to understand the salvation behavior of the phosphate ions.

**MATERIALS AND METHODS**

**Chemicals**
The reagents, phosphoric acid, monosodium dihydrogen phosphate and disodium hydrogen phosphate were from E. Mark (A.R) grade. Double distilled deionised and degassed water with specific conductance of $2-3 \times 10^6$ Mhos was used. All weighing were done in a single pan mettle balance (Switzerland, model AE 72940) to an accuracy of ±0.01mg.

**Measurement**
Densities of electrolytic solutions at various temperatures were obtained from the mathematical equation, proposed by nevently and sohael, expressing the density of binary aqueous solution as a function of concentration \[7, 8\]. These authors have considered the reliable density data and have correlated it in the range 25-45°C at an interval of five degrees.

The measurements of relative viscosity were made with a Schott-Gerate AVS 350 unit. The viscometer was calibrated, and two constants, \(C\) and \(B\) of the viscometer in the equation \(n/d = Ct - Bt\) were obtained by measuring the flow time \(t\) with pure water, benzene and cyclohexane at (303.15±0.02)K. The deviation of the measured value from the slandered value was less than 0.3%. The temperature of the solution were maintained constant by circulating water coming from a thermostat (Julabo F25, made in Germany), which has an accuracy ±0.02°C reproducibility of the viscosity \(\eta\) was ±0.002m pas.

**Treatment of data**
The apparent molar volume, \(\Phi_v\), is calculated from the density data by using following expression:

\[
\Phi = \frac{1000(d_0 - d)}{cd_0} + \frac{M_2}{d_0}
\]  

Where \(c\) is the molarity of the electrolytic solution, \(d\) the density of solution and \(d_0\) that of the solvent. \(M_2\)is themolecular weight of the electrolyte. Typically eight spaced concentration in the range (0.05M-0.5M) were selected to calculate \(\Phi_v\).

The apparent molar volume has been found to very linearly with square root of the concentration and the data can be expressed by the Massons equation \[9\],

\[
\Phi_v = \Phi_v^0 + S_v \sqrt{c}
\]  

Where
\(\Phi_v^0\) is the partial molar volume.
\(S_v\) is the experimental slope.
The value of $\Phi_v^0$ at different temperatures for the acid and two ions are set out in table 1. $\Phi_v^0$ for the anions were derived by subtracting $\Phi_v^0 (Na^+)$ [10], from the $\Phi_v^0$ of salt. For phosphoric acid the equation (2) was modified as $\Phi_v^0 = \Phi_v^0 + S_vC$.

Relative viscosity, $\eta_r$, is obtained by expression,

$$\eta_r = \frac{t_1/d_1}{t_0/d_0}$$ (3)

where $t_1$ and $d_1$ are the flow and density of the solution, while $t_0$ and $d_0$ are their corresponding value for water. The viscosity B-coefficient was derived from $\eta_r$ by equation (4)

$$\eta_r = 1 + BC$$ (4)

B-coefficient for anions was obtained by subtraction $B_{Na^+}$ [11] from the B electrolyte. These values are presented in table 2.

RESULTS AND DISCUSSION

The partial molar volume, $\Phi_v^0$, follow the order $H_3PO_4 > H_2PO_4^- > HPO_4^{2-}$. Our values of $\Phi_v^0$ are good agreement with the literature values at 25°C ($\Phi_v^0 H_3PO_4 = 29.10$; $\Phi_v^0 HPO_4^{2-} = 27.7$) [10] $\Phi_v^0$ represent the solute–solvent interaction. Literature survey [10] revealed that only few anions exhibit values beyond 100. There are $[Fe(CN)_6]^{3-}$, $[Pt(Cl)_6]^{4-}$ and $Pb_4B$ which have $\Phi_v^0$ values as 120.0, 150.0 and 277.6 respectively. Charge size and hydration behavior of an ion determine $\Phi_v^0$. This aspect has been discussed later. The change in $\Phi_v^0$ with temperature is positive for $H_3PO_4$ and $H_2PO_4^-$. $\Phi_v^0$ on the other hand decreased with the increase in temperature for $HPO_4^{2-}$. The increase in $\Phi_v^0$ with increasing temperature is attributed to the increase in solution. The apparent molar expansibilities are given by

$$\Phi_E^0 = \Phi_v^0 / T.$$ (5)

$\Phi_E^0$ are positive for $H_3PO_4$ and $H_2PO_4^-$ and negative for $HPO_4^{2-}$. Millero [10] and Hepler [11] separately have shown that common electrolyte $\Phi_E^0$ should decrease with increasing temperature. $\Phi_E^0$ shows constancy for $H_3PO_4$ and decrease for $H2PO4^-$ for $HPO_4^{2-}$, it is less negative at higher temperature.

The viscosity B-coefficient are positive for $H_3PO_4$ and all the two anions and follow the order $H_3PO_4 < H_2PO_4^- < HPO_4^{2-}$. The B-ion values are thus increasing with the decreasing in ionic radius. It is well known that ions, which make the water structure, have positive value for B. it has been emphasized [13] that not B but dB/dt is a better criteria for determining the solute – solvent interaction as ‘ the structure maker ’ ions have negative values and structure breaker’ ions have positive value for it.

Viscosity–partial molar volume

$$\eta H = \frac{0.4B - V_{-Ion}}{V_B}$$ (6)

The internal volume $V_{-Ion}$ was calculated by the expression
\[ V_{\text{ion}} = \left[ \frac{4}{3} \pi N \text{Ar}^3 \right] \]  

(7)

The radii of different ions were calculated by the procedure given by marcus

\[ R_{\text{ion}} = d_{\text{ion-water}} - r_{\text{water}} \]

and \( r_{\text{water}} = 0.142 \pm 0.005 \text{ nm} \). \( d_{\text{ion-water}} \) being available for phosphate ion, the calculated radius of \( \text{HPO}_4^{2-} \), \( \text{H}_2\text{PO}_4^- \) and \( \text{H}_3\text{PO}_4^- \) were 0.164nm, 0.238nm, 0.222nm respectively. The value of \( V_{\text{ion}} \) derived for the two ion, respectively are 12.23, 56.44, cm\(^3\) mol\(^{-1}\). The value of \( \eta_H \) thus derived by the use of equation 6 is 3.2, 6.2, and 10.8. \( \eta_H \) follow the the order

\[ \text{H}_3\text{PO}_4^- < \text{H}_2\text{PO}_4^- < \text{HPO}_4^{2-} \]

The hydration number obtained by our measurement is in line with the accepted structure of phosphate ion. A molecular dynamics computer – simulation study have yielded a very low value for the P-o(water) distance, 0.306nm, in small phosphate-water cluster, containing 6-8 water molecule per \( \text{PO}_4^{3-} \) anions. The P-O (water) distance in \( \text{H}_2\text{PO}_4^- \) and \( \text{H}_3\text{PO}_4^- \) are 0.377 and 0.366 nm respectively.

The variation of viscosity coefficient \( B \) with temperature is not noteworthy, in the range of 25 to 35\(^0\)C, remains almost constant. \( B \) coefficient for simple anion like \( \text{Cl}^-, \text{Br}^-, \text{I}^-, \text{ClO}_3^- \) and \( \text{NO}_3^- \) are negative while these are positive for \( \text{OH}^- \) and \( \text{SO}_4^- \). The two phosphate ions are structure-makers but \( \text{D}b/\text{dt} \) in all these cases are negative between 25 to 35\(^0\)C and a little positive between 35 to 45\(^0\)C. As the temperature increases, the ice structure of water breaks down, and the condition for the attachment of water molecule to the ion is more favorable.[15,16]

<table>
<thead>
<tr>
<th>Temp ((^0)C)</th>
<th>( \Phi_v ) Cm(^3) mol(^{-1})</th>
<th>( \text{H}_3\text{PO}_4^- )</th>
<th>( \text{H}_2\text{PO}_4^- )</th>
<th>( \text{HPO}_4^{2-} )</th>
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<tbody>
<tr>
<td>25</td>
<td>56.29</td>
<td>29.12</td>
<td>7.42</td>
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<td>30</td>
<td>59.12</td>
<td>29.42</td>
<td>6.12</td>
<td></td>
</tr>
<tr>
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<td>61.96</td>
<td>29.88</td>
<td>4.43</td>
<td></td>
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<tr>
<td>40</td>
<td>64.81</td>
<td>30.12</td>
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<tr>
<td>45</td>
<td>67.67</td>
<td>30.36</td>
<td>0.02</td>
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</tr>
</tbody>
</table>

Table 1 Partial molar volume of \( \text{H}_3\text{PO}_4^- \), \( \text{H}_2\text{PO}_4^- \) and \( \text{HPO}_4^{2-} \) at different temperature

<table>
<thead>
<tr>
<th>Temp ((^0)C)</th>
<th>( B ) coefficient Cm(^3) mol(^{-1})</th>
<th>( \text{H}_3\text{PO}_4^- )</th>
<th>( \text{H}_2\text{PO}_4^- )</th>
<th>( \text{HPO}_4^{2-} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
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<td>0.362</td>
<td>0.545</td>
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</tr>
<tr>
<td>30</td>
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<tr>
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<td>0.339</td>
<td>0.551</td>
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<td></td>
</tr>
<tr>
<td>45</td>
<td>0.232</td>
<td>0.386</td>
<td>0.611</td>
<td></td>
</tr>
</tbody>
</table>

Table 2 Viscosity B-coefficient of \( \text{H}_3\text{PO}_4^- \), \( \text{H}_2\text{PO}_4^- \) and \( \text{HPO}_4^{2-} \) at different temperature

Another quantity used to measure hydration is \( B/ \Phi_v^0 \times 10^3 \) [14]. A value between 0 and 2.5 points to unsolved species and any higher value to solvated once. This value at 25\(^0\)C for \( \text{HPO}_4^{2-} \), \( \text{H}_2\text{PO}_4^- \) and \( \text{H}_3\text{PO}_4^- \) are 73, 45, 12.42, and 3.87. All ions are thus solvated. The much higher value
for $\text{H}_2\text{PO}_4^{2-}$ is due to very low value of $\Phi v^0$. This system interacts much more strongly with water molecules.

Acknowledgements
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REFERENCES