



Viscosity B-coefficient and partial molar volume between 25^oc and 45^oc 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^oC. All these parameters exhibit the following order: $H_3PO_4 < HPO_4^{2-} < H_2PO_4^-$. Φ_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^oC for all the two salt and phosphoric acid. Hydration number (n_H) at 25^oC, obtained through viscosity show satisfactory agreement and follow the order $HPO_4^{2-} > H_2PO_4^- > H_3PO_4$. Similarly, the magnitude of $B/\Phi_V^0 \times 10^3$ 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 $H_2PO_4^{6-}$. 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 solvation 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 ± 0.01 mg.

Measurement

Densities of electrolytic solutions at various temperatures were obtained from the mathematical equation, proposed by Neff and Schaefer, 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 $25-45^{\circ}$ 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 $(303.15 \pm 0.02)K$. The deviation of the measured value from the standard 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 $\pm 0.02^{\circ}C$ reproducibility of the viscosity η_1 was ± 0.002 m pas.

Treatment of data

The apparent molar volume, Φ_v , is calculated from the density data by using following expression;

$$\varphi = \frac{1000(d_0 - d)}{cd_0} + \frac{M_2}{d_0} \quad (1)$$

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

The apparent molar volume has been found to vary linearly with square root of the concentration and the data can be expressed by the Masson's equation [9],

$$\Phi_v = \Phi_v^0 + S_v \sqrt{c} \quad (2)$$

Where

Φ_v^0 is the partial molar volume.

S_v is the experimental slope.

The value of Φ_v^0 at different temperatures for the acid and two ions are set out in table 1. Φ_v^0 for the anions were derived by subtracting Φ_v^0 (Na^+) [10], from the Φ_v^0 of salt. For phosphoric acid the equation (2) was modified as $\Phi_v = \Phi_v^0 + S_{vc}$.

Relative viscosity, η_r , is obtained by expression,

$$\eta_r = t_1 d_1 / t_0 d_0 \quad (3)$$

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 η_r by equation (4)

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

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, Φ_v^0 , follow the order $\text{H}_3\text{PO}_4 > \text{H}_2\text{PO}_4^- > \text{HPO}_4^{2-}$. Our values of Φ_v^0 are in good agreement with the literature values at 25°C (Φ_v^0 H_2PO_4^- 29.10-, Φ_v^0 HPO_4^{2-} 7.7) [10]. Φ_v^0 represent the solute-solvent interaction. Literature survey [10] revealed that only few anions exhibit values beyond 100. There are $[\text{Fe}(\text{CN})_6]^{3-}$, $[\text{Pt}(\text{Cl})_6]^{4-}$ and Pb_4B^- which have Φ_v^0 values as 120.0, 150.0 and 277.6 respectively. Charge size and hydration behavior of an ion determine Φ_v^0 . This aspect has been discussed later. The change in Φ_v^0 with temperature is positive for H_3PO_4 and H_2PO_4^- . Φ_v^0 on the other hand decreased with the increase in temperature for HPO_4^{2-} . The increase in Φ_v^0 with increasing temperature is attributed to the increase in solution. The apparent molar expansibilities are given by

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

Φ_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 Φ_E^0 should decrease with increasing temperature. Φ_E^0 shows constancy for H_3PO_4^- and decrease for H_2PO_4^- 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 $\text{H}_3\text{PO}_4 < \text{H}_2\text{PO}_4^- < \text{HPO}_4^{2-}$. 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

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

The internal volume V_{ion}^- was calculated by the expression

$$V_{\text{ion}}^{-} = \left[\frac{4}{3} \pi N_A r^3 \right] \quad (7)$$

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

$$R_{\text{ion}} = d_{\text{ion-water}} - r_{\text{water}}$$

and $r_{\text{water}} = 0.142 \pm 0.005$ nm. $d_{\text{ion-water}}$ being available for phosphate ion, the calculated radius of HPO_4^{2-} , H_2PO_4^- and H_3PO_4 were 0.164 nm, 0.238 nm, 0.222 nm respectively. The value of V_{ion}^{-} derived for the two ions, respectively are 12.23, 56.44, $\text{cm}^3 \text{mol}^{-1}$. The value of η_{H} thus derived by the use of equation 6 is 3.2, 6.2, and 10.8. η_{H} follows the order



The hydration number obtained by our measurement is in line with the accepted structure of phosphate ion. A molecular dynamics computer – simulation study has yielded a very low value for the P-o(water) distance, 0.306 nm, in small phosphate –water cluster, containing 6-8 water molecules per PO_4^{3-} anions. The P-O (water) distance in H_2PO_4^- and H_3PO_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°C, remains almost constant. B coefficient for simple anion like Cl^- , Br^- , I^- , ClO_3^- and NO_3^- are negative while these are positive for OH^- and SO_4^{2-} . The two phosphate ions are structure-makers but dB/dT in all these cases are negative between 25 to 35°C and a little positive between 35 to 45°C. As the temperature increases, the ice structure of water breaks down, and the condition for the attachment of water molecules to the ion is more favorable. [15,16]

Table 1 Partial molar volume of H_3PO_4 , H_2PO_4^- and HPO_4^{2-} at different temperature

Temp (0°C)	Φ_v^0 $\text{Cm}^3 \cdot \text{mol}^{-1}$		
	H_3PO_4	H_2PO_4^-	HPO_4^{2-}
25	56.29	29.12	7.42
30	59.12	29.42	6.12
35	61.96	29.88	4.43
40	64.81	30.12	2.27
45	67.67	30.36	0.02

Table 2 Viscosity B-coefficient of H_3PO_4 , H_2PO_4^- and HPO_4^{2-} at different temperature

Temp (0°C)	B-coefficient $\text{Cm}^3 \cdot \text{mol}^{-1}$		
	H_3PO_4	H_2PO_4^-	HPO_4^{2-}
25	0.218	0.362	0.545
30	0.219	0.340	0.537
35	0.220	0.339	0.551
40	0.216	0.355	0.568
45	0.232	0.386	0.611

Another quantity used to measure hydration is $B/\Phi_v^0 \times 10^3$ [14]. A value between 0 and 2.5 points to unsolvated species and any higher value to solvated one. This value at 25°C for HPO_4^{2-} , H_2PO_4^- and H_3PO_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 $\Phi\nu^0$. This system interacts much more strongly with water molecules.

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