# **Central Asian Journal of Medicine**

Volume 2021 | Issue 4

Article 9

12-29-2021

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#### **Recommended Citation**

Bazarbayev, Muratali I.; Narziqulova, Qumrijon I.; Mullojonov, Islom; and Ermetov, Erkinbay Ya. (2021) "STUDY OF APPARENT MOLAR VOLUMES OF ELECTROLYTE SOLUTIONS AND ITS APPLICATION IN MEDICINE," *Central Asian Journal of Medicine*: Vol. 2021 : Iss. 4 , Article 9. Available at: https://uzjournals.edu.uz/tma/vol2021/iss4/9

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### STUDY OF APPARENT MOLAR VOLUMES OF ELECTROLYTE SOLUTIONS AND ITS APPLICATION IN MEDICINE

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#### ABSTRACT

All biological processes in plant or animal organisms, including in the human body, are carried out in solutions. Therefore, the progress of sciences such as biology, medicine, etc., is closely related to the development of the doctrine of solutions. When dissolved, various chemical interactions occur between the components and due to Van der Waals force, etc. One of the methods for determining the ion molecular interaction is the study of the partial molar volume of electrolytes.

**Key words:** molar volume, partial molar volume, solution volume, chemical reactions, potassium phosphate, phosphate anions, electrolyte, activity coefficient.

#### **INTRODUCTION**

The doctrine of solutions is the most important branch of physical chemistry. Due to the requirements of practice, much attention has always been paid to the study of solutions, since most chemical reactions used in chemical, pharmaceutical, food, metallurgical and other industries take place in solutions [1, 2, 3].

All biological processes in plant or animal organisms, including in the human body, are carried out in solutions. Therefore, the progress of sciences such as biology, medicine, etc., is closely related to the development of the doctrine of solutions. When dissolved, various chemical interactions occur between the components and due to the Van der Waals force, etc. One of the methods for determining the ion molecular interaction is the study of the partial molar volume of electrolytes [4, 5, 6].

### MATERIAL AND RESEARCH METHODS

**Partial molar volume of ions.** When studying ion-solvent interactions, a very useful parameter can be the partial molar volume of the electrolyte, which is defined as a change in the volume of the solution when one mole of salt is added to it (temperature and pressure are assumed to be constant).

$$\overline{V}_2 = \left(\frac{dV}{dn_2}\right)_{T,P_1} \tag{1}$$

If more than one mole of electrolyte is added to the solvent, for example, to water, by any number, then they are not talking about the partial molar volume of the salt, but about the apparent molar volume:

$$V = n_2 \varphi_V + n_1 \overline{V_1}^0 \qquad \qquad \overline{V_1}^0 = \frac{M_1}{\rho_0}$$
(2)

where V is the volume of a solution containing  $n_1$  moles of water and  $n_2$  moles of salt,

 $\overline{V_1}^0$  - is the molar volume of pure water at given T and P.

From equation (2) we define  $\varphi_V$ :

$$\varphi_{V}n_{2} = V - n_{1}\overline{V_{1}}^{0}$$

$$\varphi_{V} = \frac{1}{n_{2}} \left( V - \frac{n_{1}M_{1}}{\rho_{0}} \right)$$
(3)

V is the volume of the solution in  $1000 \text{ cm}^3$ 

 $n_2$  is the number of moles of salt expressed in terms of  $C_2$  concentrations. The total mass of the entire electrolyte is determined by the expression

$$n_1 M_1 + n_2 M_2 = 1000\rho$$
  

$$n_1 M_1 = 1000\rho - n_2 M_2$$
 T.K.  $n_2 = c_2$  (4)

$$n_1 M_1 = 1000 \rho - C_2 M_2 \tag{5}$$

Substituting the value of V and expression (5) in equation (3) we obtain

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$$\varphi_{V} = \frac{1}{C_{2}} \left( 1000 - \frac{1000\rho - C_{2}M_{2}}{\rho_{0}} \right)$$
$$\varphi_{V} = \left( \frac{1000\rho_{0} - 1000\rho - C_{2}M_{2}}{C_{2}\rho_{0}} \right)$$

or

$$\varphi = \frac{1000(\rho_0 - \rho)}{M\rho_0} + \frac{M_2}{\rho_0}$$
(6)

 $C_2$  concentrations were expressed in terms of molarity M. Molarity is determined by the ratio of concentration to the molecular weight of salt, M=10 c% Solution/mol. weight.

When the densities  $\rho_0$  and  $\rho$  molecular weights of the salt M<sub>2</sub> are known, respectively, then the apparent molar volume of the electrolyte is from the ratio (6). In the case of dilute electrolyte solutions, it linearly depends on  $(\sqrt{M})$ :

$$\varphi_V = \varphi_V^0 + S_V \sqrt{M} \tag{7}$$

The apparent molar volume is a change in the volume of the solvent under the action of salt ions. In extremely dilute solutions, each individual ion is located inside a cavity that is free of water molecules [7, 8, 9, 10]. This cavity represents an effective volume of ion. As long as the radius of the cavity is much larger than the radius of the ion itself, the cavity can be considered spherical. Around this cavity, the water molecules are compressed, i.e. there is a decrease in the volume of the solvent because of electrostriction (the magnitude of this decrease depends on the radius and charge of the ion). Hence,  $\varphi_v^0$  with infinite dilution, it becomes equal to this effective volume of the spherical cavity V<sup>0</sup> minus the total compression undergone by the solvent V<sup>e</sup>:

$$\varphi_V^0 = V^0 - V^e \tag{8}$$

It is assumed that the parameter  $S_v$  in equation (7), which determines the slope of the straight line, is associated with the action of interionic forces and depends on the valence, ionic dimensions and interionic distance in the crystal lattice of the salt. The proof that  $S_v$  depends only on the type of valence was the work of many authors. They examined the valence electrolytes, which are shown in Table 1.

				ſ	[able №1
Type of electrolyte valence	1:1	2:1	2:2	3:1	2:1
Parameter m <sup>3</sup> . $10^6$ mol·l <sup>1/2</sup>	1,9	9,7	14,9	27,5	59,1

Using the example of a larger number of sulfates and nitrates, it was shown that  $S_v$  does not remain constant in a series of salts of the same valence and is an

individual coefficient for each electrolyte if measurements of the apparent molar volume are carried out with concentrations > 0.5 m. By the way, two rectilinear sections are most often observed on the dependence  $\varphi_v(\sqrt{M})$  one for the area of large dilutions, the other is the longest section, with the corresponding parameters  $\varphi_v^0$  and  $S_v$ . In the literature, as a rule, this second section is discussed. In the study of ion-molecular interactions, the parameter of equation  $\varphi_v^0$  (7) is used, which is the limit value of the apparent molar volume, which in most cases coincides with the partial molar volume  $V_2$  of the electrolyte. Temperature dependence  $\varphi_v^0$  can provide very useful information with ion-solvent interaction. The application of the parameter  $\varphi_v^0$  to the study of the ion-solvent interaction is based on the fact that the partial molar volume of the salt is equal to the sum of the ionic partial volumes:

$$V_{MX}^{0} = \overline{V}_{M^{+}}^{0} + \overline{V}_{X^{-}}^{0}$$
<sup>(9)</sup>

In the literature, data  $\overline{V}_{M^+}^0$  and  $\overline{V}_{X^-}^0$  are also given for cations and anions, depending on temperature, having different valences and structures. In the study of hydration interaction using the partial molar volume of the electrolyte, the question of the correct assessment of the electrostrictive contribution  $\overline{V}_{el.str}^e$  in  $\varphi_V^0$ .

$$\overline{V}_{el.str}^{e} = -\frac{e^{2}Z^{2}}{2\overline{r}\varepsilon} \cdot \left(\frac{d\ln\varepsilon}{dP}\right)_{T}$$
(10)

All of the above theories in describing the bulk properties of electrolytes are based on the assumption that ion hydration is a purely electrostatic interaction, although most experimental work suggests the need for (hydrogen bonding, donoracceptor interactions).

As an example, consider the determination of the apparent molar volume  $\varphi_V$  of the salt of various potassium phosphates.

#### **RESEARCH RESULTS**

The apparent molar volume of the salt  $\varphi_V$  is determined by the formula (6). Figure 1 shows the dependences  $\varphi_V$  from  $\sqrt{M}$  on aqueous solutions of KH<sub>2</sub>PO<sub>4</sub>, K<sub>2</sub>HPO<sub>4</sub> and K<sub>3</sub>PO<sub>4</sub> for two temperatures of 293 - 353<sup>0</sup> K.

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**Fig.1.** Dependence of the apparent molar volume on the square root of the molarity: a)  $K_3PO_4$  b)  $KH_2PO_4$  c)  $K_2HPO_4$ 

At 293<sup>0</sup> K, two rectilinear sections can be noted for KH<sub>2</sub>PO<sub>4</sub>, K<sub>2</sub>HPO<sub>4</sub>, one refers  $\varphi_V(\sqrt{M})$  to low concentrations of electrolyte, the other to moderate and high concentrations. With an increase in temperature, both rectilinear sections merge into one. For tri-substituted potassium phosphate (K<sub>3</sub>PO<sub>4</sub>), a rectilinear dependence is observed without breaks at 293<sup>0</sup>K and at 353<sup>0</sup>K. As already mentioned, a clear physical meaning has a limit value of the apparent molar volume  $\varphi_V^0$ , which is equal to the partial molar volume of salt see table 2. This parameter for both double-substituted potassium phosphate (K<sub>2</sub>NPO<sub>4</sub>) and single-substituted potassium phosphate (KN<sub>2</sub>PO<sub>4</sub>) increases monotonically with increasing temperature, but for K<sub>3</sub>PO<sub>4</sub> the dependence  $\varphi_V^0$  (T) has a maximum in the temperature range of 293<sup>0</sup>-353<sup>0</sup>K. As we will see from further consideration, the maximum dependence  $\varphi_v^0$  (T) for K<sub>3</sub>PO<sub>4</sub> is due to the contribution to the salt, which is given by three potassium ions. It is known that  $\varphi_v^0$  (T) K<sup>+</sup> has a maximum also in the range of 293<sup>0</sup>-353<sup>0</sup> K, table.3.

Using the ratio (9), it is possible to find the dependence on the temperature of  $\varphi_v^0$  phosphate anions.

The temperature dependence of the partial volume of the cation  $K^+$ , necessary for calculation, is taken from the literature data.

If the partial molar volume of anions  $HPO_4^{2-}$  and  $PO_4^{3-}$  almost does not change with increasing temperature, then the H<sub>2</sub>O<sub>4</sub> anion increases from 26.8×10-<sup>6</sup> m<sup>3</sup>/mol at 293<sup>0</sup>K to 30.2×10-<sup>6</sup> m<sup>3</sup>/mol at 353<sup>0</sup>K (Table 3).

Table No 2 Dependence of parameters  $\varphi_V^0 \cdot 10^6 \text{ m}^3/\text{mol}$  from the temperature for salts KH<sub>2</sub>PO<sub>4</sub>, K<sub>2</sub>HPO<sub>4</sub>, K<sub>3</sub>PO<sub>4</sub>.

Salt	KH <sub>2</sub> PO <sub>4</sub>		K <sub>2</sub> HPO <sub>4</sub>		K <sub>3</sub> PO <sub>4</sub>	
T <sup>0</sup> K	$arphi_V^0$	$S_v$	$arphi_V^0$	$S_v$	$arphi_V^0$	$S_v$
293	35,3±0,4	$10,6\pm0,4$	27,6±0,2	13,5±0,1	19,0±1	$12,2\pm0,7$
303	35,7±0,5	$10,2\pm0,5$	$28,3\pm0,3$	12,8±0,2	20,0±1	11,7±0,9
313	36,5±0,4	$10,9{\pm}0,3$	29,0±0,5	12,5±0,3	22,5±2	$10,5\pm1,2$
323	37,9±0,4	9,4±0,3	29,5±0,2	12,7±0,1	24±1	10,0±0,9
333	38,3±0,4	9,1±0,3	31,1±0,5	12,0±0,2	25±1	$9,5{\pm}0,9$
343	39,2±0,4	$8,7\pm0,5$	31,0±0,5	12,4±0,4	$24\pm1$	$10,3\pm0,9$
353	$40,3\pm0,3$	$7,9\pm0,2$	31,8±0,3	11,38±0,2	23±1	$9,4{\pm}0,9$

It is known that the scattering spectra of aqueous solutions of H<sub>3</sub>PO<sub>4</sub>, H<sub>2</sub>PO<sub>4</sub>, K<sub>2</sub>NPO<sub>4</sub> are interpreted in the sentence that anions  $PO_4^{3-}$ ,  $HPO_4^{2-}$ ,  $H_2PO_4^{-1}$  form hydrogen bonds with water molecules.

However, the thermodynamic properties of aqueous solutions of potassium phosphates have a number of significant differences, for example:

- a) average activity coefficient, decreases in a row  $K_3PO_4 > K_2HPO_4 > KH_2PO_4$ .
- b) salts K<sub>3</sub>PO<sub>4</sub> and K<sub>2</sub>HPO<sub>4</sub> form crystallohydrates with water molecules, but KH<sub>2</sub>PO<sub>4</sub> is anhydrous salt.

c) solubility in water  $KH_2PO_4$  significantly less than  $K_2HPO_4 \varkappa K_3PO_4$ .

Analyzing the data about  $\varphi_v^0$  anions given in Table 2, we see that the dependence  $\varphi_v^0$  (T) for  $\exists \pi H_2 PO_4^{-1}$  is also different from that for anions  $PO_4^{3-}$  and

 $HPO_4^{2-}$ . This difference is naturally explained by the different nature of the interaction of these particles with water molecules.

# CONCLUSIONS

Every physician should carefully examine the patient before prescribing the drug and examine him in accordance with the standards of diagnosis and treatment. After receiving tests and determining the stage of the disease, prescribe treatment. When prescribing a drug, it is important to recommend the appropriate dose depending on the stage of the disease. When taking the medicine, it interacts with the body's water to form a solution, the concentration of which will determine the therapeutic effect. It is necessary to prescribe a dose corresponding to the stage of the disease and the degree of damage to organs and tissues. With insufficient concentration, there will be a low therapeutic effect, which will prolong the recovery time, with excessive concentration; the drug will cause side effects. Therefore, it is necessary to prescribe a dose corresponding to the degree of damage, for this, it is necessary to determine the parameters of the partial molar volume of the drug solution, depending on its concentration

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