

A study on partial molar volumes of oxalic acid and its salts in water at various temperatures

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Partial molar volumes of oxalic acid and its salts viz. ammonium oxalate, sodium oxalate and potassium oxalate in water have been determined from solution density measurements at various temperatures and solute concentrations. The data have been evaluated by using Masson equation and the obtained parameters have been interpreted in terms of solute-solute and solute-solvent interactions. Structure making/breaking capacities of oxalic acid and its salts have been inferred from the sign of $[\partial^2\phi_v^0/\partial T^2]_p$, i.e. second derivative of partial molar volume with respect to temperature at constant pressure. The oxalic acid and its salts act as structure breakers in water.

Partial molar volumes provide valuable information about different types of interactions occurring in solutions¹. As partial molar volume of a solute reflects the cumulative effects of solute-solute and solute-solvent interactions, it would be of interest to study partial molar volumes of oxalic acid and its salts. Such data are expected to highlight the role of cation and anion of an electrolyte in influencing its partial molar volume at infinite dilution in water. These considerations prompted us to undertake the present study.

Results and discussion

The densities measured for the solutions of oxalic acid and its salts viz. ammonium oxalate, sodium oxalate and potassium oxalate in water at 298.15, 303.15, 308.15, 313.15 and 318.15 K, have been used to calculate the apparent molar volumes (ϕ_v) of oxalic acid and its salts. The plots of ϕ_v against the square-root of molar concentration ($c^{1/2}$) were found to be linear with positive slopes for oxalic acid and its salts at all temperatures. The limiting apparent molar volumes (ϕ_v^0) were calculated using the least-square treatment to the plots of ϕ_v vs $c^{1/2}$, using Masson's equation,

$$\phi_v = \phi_v^0 + S_v c^{1/2} \quad (1)$$

where ϕ_v^0 is the partial molar volume at infinite dilution and S_v the experimental slope. The values of ϕ_v^0 and S_v along with standard errors, are listed in Table 1.

It is evident from Table 1 that the values of S_v are positive but smaller in magnitude, for oxalic acid and its salts, at different temperatures. Since S_v is a measure of solute-solute/ion-ion interactions, these results indicate the presence of specific solute-solute/ion-ion interactions. It is also clear from Table 1 that the value of S_v decreases with the

Table 1. Partial molar volumes (ϕ_v^0), experimental slopes (S_v) for oxalic acid, ammonium oxalate, sodium oxalate and potassium oxalate in water at various temperatures

Temp. (K)	ϕ_v^0 (cm ³ mol ⁻¹)	S_v (cm ³ dm ^{3/2} mol ^{-3/2})
Oxalic acid		
298.15	52.853 (0.379)*	0.865 (0.019)*
303.15	64.648 (0.288)	0.718 (0.015)
308.15	71.422 (0.113)	0.554 (0.006)
313.15	77.529 (0.100)	0.422 (0.005)
318.15	84.245 (0.206)	0.249 (0.036)
Ammonium oxalate		
298.15	52.129 (0.104)*	0.775 (0.005)*
303.15	65.710 (0.112)	0.653 (0.006)
308.15	72.888 (0.165)	0.645 (0.008)
313.15	78.194 (0.010)	0.590 (0.005)
318.15	86.743 (0.073)	0.430 (0.004)
Sodium oxalate		
298.15	8.525 (0.045)*	0.352 (0.002)
303.15	14.460 (0.038)	0.323 (0.002)
308.15	17.322 (0.045)	0.295 (0.002)
313.15	21.530 (0.031)	0.280 (0.002)
318.15	26.180 (0.053)	0.204 (0.001)
Potassium oxalate		
298.15	15.769 (0.293)*	1.516 (0.015)*
303.15	28.043 (0.092)	1.514 (0.005)
308.15	38.213 (0.202)	1.009 (0.010)
313.15	47.301 (0.122)	0.968 (0.006)
318.15	70.640 (0.122)	0.653 (0.006)

*Standard errors are given in parentheses.

rise in temperature for oxalic acid and individual salt in water thereby showing that the solute-solute interactions decrease with the rise in temperature, which may be attributed to the increase in solvation of individual solute in water with the increase of temperature.

These results of oxalic acid, ammonium oxalate, sodium oxalate and potassium oxalate at different temperatures suggest a possible explanation for the absence of the negative S_v values (i.e. negative slope) for oxalic acid and its salts in water. Although at infinite dilution oxalic acid and its salts are completely dissociated in water at different temperatures, the situation would be different at higher concentrations. The oxalic acid and its salts are not completely ionized such that interionic penetration does not occur which may give rise to positive slope in ϕ_v versus $c^{1/2}$ curves.

Since ϕ_v^0 is a measure of solute-solvent/ion-solvent interactions (as solute-solute/ion-ion interactions vanish at infinite dilution), therefore, it is evident from Table 1 that the values of ϕ_v^0 are positive and large for oxalic acid and its salts in water at different temperatures, indicating the presence of strong solute-solvent/ion-solvent interactions. These interactions are further strengthened with the rise in temperature for oxalic acid and its salts. The increase in ϕ_v^0 with the increase in temperature for oxalic acid and individual salt, may be attributed to increase in solvation.

The temperature dependence of ϕ_v^0 , for oxalic acid and its salts, can be expressed by the following relations :

$$\phi_v^0 = -5790.24 + 36.56 T - 0.057 T^2 \quad (2)$$

for oxalic acid,

$$\phi_v^0 = -1479.16 + 8.97 T - 0.013 T^2 \quad (3)$$

for ammonium oxalate,

$$\phi_v^0 = -1862.76 + 11.57 T - 0.017 T^2 \quad (4)$$

for sodium oxalate, and

$$\phi_v^0 = -3823.75 + 23.24 T - 0.035 T^2 \quad (5)$$

for potassium oxalate.

Here the temperature T is expressed in Kelvin (K).

The partial molar expansibilities, $\phi_E^0 = (\partial\phi_v^0/\partial T)_p$, were calculated from relations (2) to (5) for oxalic acid and its salts at different temperatures. The variation of ϕ_E^0 with temperature for oxalic acid and its salts is linear as shown in Fig. 1. It is evident that ϕ_E^0 decreases in magnitude with the increase in temperature, suggesting thereby that the behaviour of oxalic acid and its salts is just like common salts, because in the case of common salts the molar expansibility should decrease with the increase in temperature². The negative decrease in ϕ_E^0 with the increase in temperature for oxalic acid and its salts may be ascribed to the

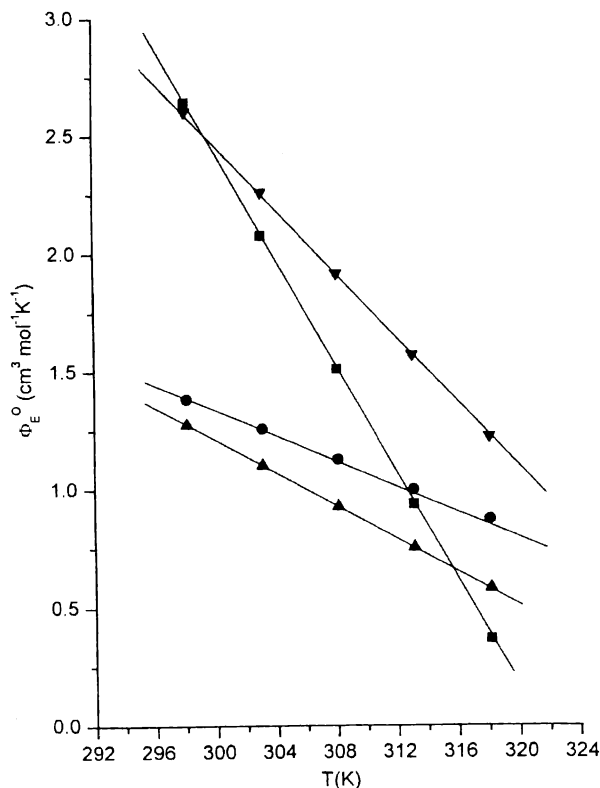


Fig. 1. Variation of ϕ_E^0 with temperature in water : (■) oxalic acid, (●) ammonium oxalate, (▲) sodium oxalate, (▼) potassium oxalate.

absence of "caging effect"³.

However, S_v is not the sole criterion for determining the structure making-breaking nature of any solute.

On the basis of the expression $[\partial C_p/\partial P]_T = -[\partial^2\phi_v^0/\partial T^2]_p$ it has been observed that positive and negative values are related with structure making-breaking properties. In the present system it is observed from expressions (2) to (5) that $[\partial^2\phi_v^0/\partial T^2]_p$ is negative for oxalic acid, ammonium oxalate, sodium oxalate and potassium oxalate in water indicating oxalic acid and its salts behave as structure breakers in water. In other words, the addition of oxalic acid and its salts to water modify the structure of water.

Experimental

AnalaR quality oxalic acid, ammonium oxalate, sodium oxalate and potassium oxalate were used after drying over P_2O_5 . Doubly distilled water was always prepared afresh. All the solutions were made by weight and conversion of molality m , into molar concentration, c , was done by using the standard expression⁴ $c = 1000 d m / (1000 + mM_2)$ where

d is the solution density and M_2 molecular weight of the solute. Density was measured by an apparatus of the Ward and Millero⁵ and the accuracy in density measurement was of $\pm 1.10^{-5} \text{ g cm}^{-3}$. The apparent molar volumes (ϕ_v) were calculated from the density data using the following standard expression.

$$\phi_v = \frac{M_2}{d_0} - \frac{1000}{c} \left[\frac{d - d_0}{d_0} \right] \quad (6)$$

where d_0 is the solvent density⁶. The density measurements were carried out in a water bath ($\pm 0.01\text{K}$).

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