A study of partial molar volumes of citric acid and tartaric acid in water and binary aqueous mixtures of ethanol at various temperatures

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Abstract. Partial molar volumes of citric acid and tartaric acid have been determined in water and binary aqueous mixtures of ethanol (5, 10, 15, 20 and 25% by weight of ethanol) at different temperatures and acid concentrations from the solution density measurements. The data have been evaluated by using Masson equation and the obtained parameters have been interpreted in terms of solute–solvent interactions. The partial molar volumes vary with temperature as a power series of temperature. Structure making/breaking capacities of the organic acids have been inferred from the sign of $[\partial^2 \bar{V}^0/\partial T^2]_p$, i.e. second derivative of partial molar volume with respect to temperature at constant pressure. Both the organic acids behave as structure breakers in water and water + ethanol.

Keywords. Partial molar volumes; citric acid; tartaric acid; water + ethanol mixture; structure breaker.

1. Introduction

Partial molar volumes provide useful information about various types of interactions occurring in solutions.[1,9] These studies are of great help in characterizing the structure and properties of solutions. The solution structure is of great importance in understanding the nature of action of bioactive molecules in the body system. The addition of an organic solvent to water brings about a sharp change in the solvation of ions. The peculiarities of the aqueous–organic mixtures are well reflected in dramatic changes in the reaction rates[10–12] and medium effect or free energies of transfer of ions which can not be explained on the basis of change in the dielectric constants of the solvent mixtures alone. Survey of literature showed that although many studies on thermodynamic properties of various electrolytes have been carried out in single component and in mixed solvent systems, little attention has been paid to the behaviour of organic acids in binary aqueous mixtures of ethanol.

As partial molar volume of a solute reflects the cummulative effects[13] of solute–solvent interactions, it would be of interest to study partial molar volumes of the organic acids viz., citric acid and tartaric acid in binary aqueous mixtures of ethanol. Such data are expected to high light the role of organic acids in influencing the partial molar volumes in mixed solvent systems. These considerations prompted us to undertake the present study.

2. Experimental

Citric acid and tartaric acid (both of Analytical Reagent grade) were used after drying over P_2O_5 in a desiccator for more than 48 h. The reagents were always placed in the desiccator over P_2O_5 to keep them in dry atmosphere. Freshly distilled conductivity water (sp. cond. $\approx 10^{-6}$ ohm^{-1} cm^{-1}) was used as standard solvent and for making binary aqueous mixtures of ethanol (EtOH). Ethyl alcohol was kept over quick lime for about 24 h, refluxed and distilled. The distillate was again treated with magnesium turnings and few crystals of iodine and refluxed for few hours and then distilled. The first and last fractions were discarded and only middle fraction was collected for the present study. The density of ethanol was found to be 0·0780 g cm^{-3} at 30°C and is in good agreement with the literature value[14] (0·0781 g cm^3).

All the binary aqueous mixtures of ethanol as well as the solutions of organic acids were made by weight and the molalities, m, were converted into

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molarities, c, by using the following standard expression:[15]

$$c = 1000 \, dm/(1000 + mM_2), \tag{1}$$

where d is the solution density and M_2 the molecular weight of an organic acid.

For density measurements, an apparatus similar to the one reported by Ward and Millero[16] and described elsewhere[17–19] (accuracy in density measurements, $\pm 0.1 \times 10^{-4} \, g \, cm^{-3}$) was used. The apparent molar volumes (f_v) were calculated from the density data using the following standard expression:[20]

$$f_v = \frac{M_2}{d_0} - \frac{1000}{c} \left[\frac{d - d_0}{d_0} \right], \tag{2}$$

where d_0 and d are the densities of solvent and solution, respectively, c is the molar concentration of acid and M_2 is its molecular weight. The density measurements were carried out in a water-bath ($\pm 0.01°C$).

3. Results and discussion

The densities of both the organic acids viz., citric acid and tartaric acid in water and ethanol + water (5, 10, 15, 20 and 25% by weight of ethanol) measured at 303 K have been used to calculate the apparent molar volumes (f_v) of the solute, using expression (1). The plots of f_v against square root of molar concentration were found to be linear, without scatter, with positive slopes in water and negative slopes in different compositions of EtOH + H$_2$O, reported here. A representative plot for citric acid in different compositions of ethanol + water, at 303 K is shown in figure 1. The partial molar volumes (f_v^0) were calculated using least squares fit to the linear plots of experimental values of f_v vs square root of molar concentration, c, using the following Masson equation:[21]

$$f_v = f_v^0 + S_v c^{\frac{1}{2}}, \tag{3}$$

where $f_v^0 = \bar{V}_2^0$ is the partial molar volume and S_v, the experimental slope. The values of f_v^0, S_v, along with standard errors, obtained in water and in different mixtures of ethanol + water at 303 K, are recorded in table 1.
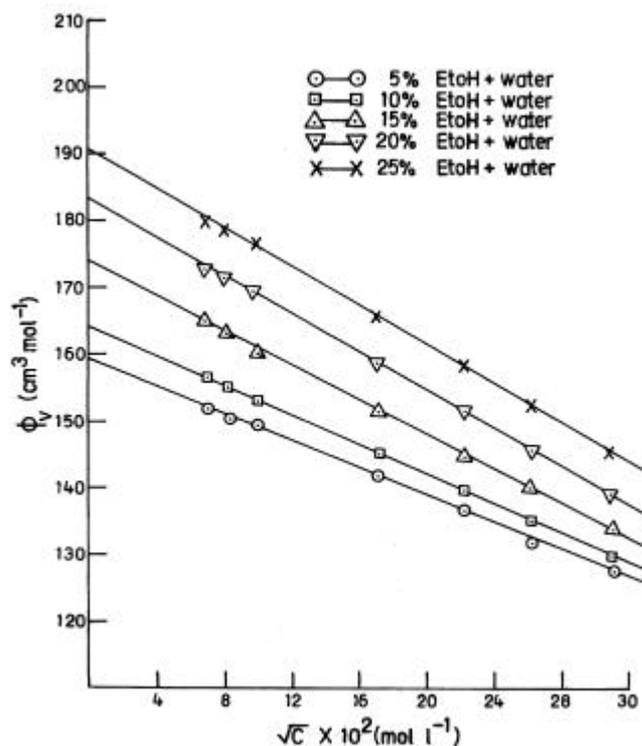

Figure 1. Plots of f_v vs $\sqrt{C}$ for citric acid in different compositions of ethanol + water at 303 K.

It is evident from table 1 that S_v is positive for both the organic acids in water at 303 K but becomes negative, i.e. it changes sign on the addition of ethanol. Further, it is also clear from table 1 that the value of S_v, of course negative, further decreases in magnitude as the composition of ethanol in water increases. From these values of S_v it may be inferred that the solute–solute interactions, which are quite strong in water, are weakened on the addition of ethanol, which are further weakened with the increase in composition of ethanol in water. This may be attributed to the increase in solvation on the addition of ethanol to water for both the organic acids.

A comparison of results obtained in ethanol + water with those obtained in water suggests a possible explanation for the presence of negative S_v values (i.e. negative slopes) for both the organic acids, studied here. Although, at infinite dilution both the organic acids are completely dissociated in all these solvent mixtures, the situation would have been different at higher concentrations of the organic acids. These organic acids remain completely ionized even at fairly high concentrations in ethanol + water mixtures. Therefore, an appreciable interionic penetration occurs and this gives rise to

Table 1. Partial molar volumes (f_v^0), experimental slopes (S_v) and partial molar volumes of transfer ($\Delta \bar{V}_{tr}^0$) for citric acid and tartaric acid in water and binary aqueous mixtures of ethanol at 303 K.

Ethanol + water (% *w/w*)	f_v^0 (cm³ mol⁻¹)	S_v (cm³ lit^½ mol^{-3/2})	$\bar{V}_{tr}^0$ (cm³ mol⁻¹)
Citric acid			
0 (water)	115·90 (1·33)*	153·14 (1·47)*	–
5	160·23 (0·22)	−101·23 (1·11)	44·33
10	163·95 (0·15)	−110·30 (0·76)	48·05
15	173·77 (0·45)	−131·38 (1·34)	57·87
20	183·05 (0·37)	−143·72 (1·91)	67·15
25	190·16 (1·59)	−147·78 (0·83)	74·26
Tartaric acid			
0 (water)	72·72 (0·88)*	170·65 (1·99)*	–
5	120·19 (1·75)	−113·70 (0·90)	47·47
10	133·05 (0·42)	−135·96 (1·14)	60·33
15	138·06 (0·50)	−142·77 (1·55)	65·34
20	144·56 (0·32)	−148·38 (1·67)	71·84
25	153·38 (0·18)	−166·84 (0·93)	80·66

*Standard errors are given in parentheses

negative slope (i.e. weak ion–ion interactions and strong ion–solvent interactions) in the f_v vs $c^{½}$ curves for both organic acids. These negative values of S_v in different compositions of ethanol + water also suggest the presence of cation–anion penetration[22] and this happens due to the competition between the ions to occupy the void space of the large solvent molecules.

It is also clear from table 1 that the f_v^0 values are positive and large for both the organic acids in water as well as in the entire composition of ethanol + water thereby showing the presence of strong solute–solvent interactions. Further the value of f_v^0 increases regularly with the increase of ethanol composition in water, thereby showing that solute–solvent interactions improve on the addition of more and more ethanol in water. It is also clear from table 1 that the values of f_v^0 are quite greater in magnitude than those of S_v values, for both the organic acids, in ethanol + water, thereby showing that solute–solvent interactions dominate over the solute–solute interactions, while the reverse happens in water.

The volumes of transfer ($\Delta \bar{V}_{tr}^0$) were calculated using the following expression:

$$\Delta \bar{V}_{tr}^0 = f_v^0 \, (\text{MS}) - f_v^0 \, (w), \tag{4}$$

and are also recorded in table 1. Here f_v^0 (MS) and f_v^0 (w) are the partial molar volumes of the organic acids in the mixed solvent (ethanol + water) and water, respectively. The increase in f_v^0 and $\Delta \bar{V}_{tr}^0$, for both the acids, may be attributed to the decrease in electrostriction in the presence of ethanol. Thus the electrostriction effect, which brings about the shrinkage in the volume of solvent, is decreased in the mixed solvents as compared with that in pure water. From the values of $\Delta \bar{V}_{tr}^0$ it may also be inferred that the solvation of a particular organic acid increases with the increase in content of ethanol, thereby reducing the strong[23,24] solvent–solvent interactions i.e. between ethanol and water.

3.1 *Effect of temperature*

Since the behaviour of the individual organic acid was found to be linear and identical in different compositions of ethanol + water at 303 K, only 5% ethanol + water composition was selected for studying the effect of temperature. For the comparison of results the effect of temperature was also studied in water. Hence the densities were determined for various concentrations of citric acid and tartaric acid in water and 5% (*w/w*) ethanol + water at different temperatures (298, 303, 308, 313 and 318 K). The linear plots of f_v vs $c^{½}$ have been obtained at different temperatures for individual organic acid. A sample plot is shown in figure 2 for tartaric acid.

Table 2. Partial molar volumes (f_v^0), experimental slopes (S_v) and partial molar volume expansibilities (f_E^0) for citric acid and tartaric acid in water and 5% (*w/w*) ethanol + water at different temperatures.

Temperature (K)	f_v^0 (cm³ mol⁻¹)	S_v (cm³ lit^½ mol⁻³/²)	f_E^0 (cm³ mol⁻¹ K⁻¹)
Water			
Citric acid			
298	94·76 (0·88)	185·81 (1·45)	4·594
303	115·90 (1·33)	153·14 (1·47)	3·860
308	131.28 (1.25)	143.35 (1.25)	3·125
313	145.07 (0.58)	130·63 (1·24)	2·390
318	160.29 (0.32)	99·64 (1·64)	1·655
Tartaric acid			
298	41·85 (0·78)	170·65 (1·99)	7·416
303	72·72 (0·88)	123·07 (2·45)	4·934
308	102·38 (0·15)	60·22 (0·78)	2·252
313	108·43 (0·73)	55·51 (1·71)	0·031
318	117·47 (0·58)	36·45 (1·96)	–2·513
5% (w/w) Ethanol + water			
Citric acid			
298	154·10 (0·44)	–123·44 (1·26)	1·228
303	160·23 (0·22)	–101·23 (1·11)	1·225
308	165·98 (0·33)	–84·87 (1·70)	1·222
313	172·08 (0·36)	–69·39 (1·85)	1·219
318	179·79 (0·43)	–52·38 (1·24)	1·216
Tartaric acid			
298	114·02 (0·43)	–140·84 (1·22)	1·237
303	120·19 (1·75)	–113·70 (0·90)	1·232
308	127·92 (0·43)	–112·68 (1·23)	1·227
313	134·04 (0·35)	–98·83 (1·80)	1·222
318	144·35 (0·17)	–55·49 (0·89)	1·217

Standard errors are given in parentheses

The values of limiting apparent molar volumes (f_v^0) and the experimental slopes (S_v) at different temperatures obtained by using least-square fit to the plots of the experimental values of f_v vs $c^{½}$ (using (3)), along with standard errors, are reported in table 2.

It is evident from table 2 that the values of S_v are positive for both the organic acids in water at all temperatures thereby showing the presence of strong solute–solute interactions. Further it is also clear from table 2 that the values of S_v, for both the organic acids in water, decrease with the rise in temperature thereby suggesting that solute–solute interactions are further reduced with the rise in temperature, which may be attributed to the increase in solvation of individual organic acid in water with the increase in temperature. It is also clear from ta-

ble 2 that the values of S_v are negative for both the organic acids in ethanol + water, studied here, at all temperatures meaning thereby that solute–solute interactions are very weak in the entire temperature range.

The values of f_v^0 increase with the increase in temperature, for both the organic acids, in water as well as ethanol + water, thereby showing that solute–solvent interactions are further strengthened with the increase in temperature. The increase in f_v^0 may be attributed to the increase in solvation.

The temperature dependence of f_v^0 in water for citric acid and tartaric acid can be expressed by the following equations:

$$f_v^0 = -7799·69 + 48·39T - 0·074T^2, \qquad (5)$$
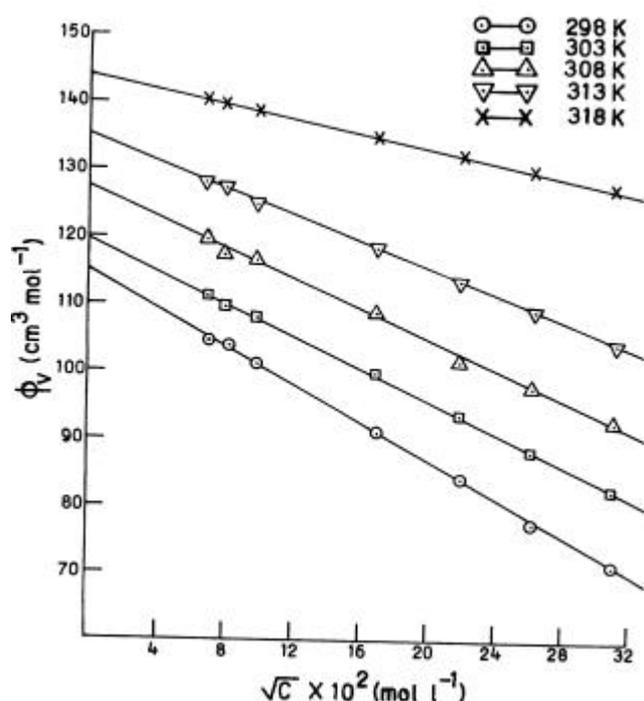$$\text{for citric acid,}$$

Figure 2. Plots of f_v vs $\sqrt{C}$ for tartaric acid in 5% (*w/w*) ethanol + water at different temperatures.

Figure 3. Variation of f_E^0 with temperature in water.

$$f_v^0 = -24211 \cdot 02 + 155 \cdot 36T - 0 \cdot 248T^2, \tag{6}$$

for tartaric acid,

while in 5% (*w/w*) ethanol + water by the following expressions:

$$f_v^0 = -238 \cdot 34 + 1 \cdot 41T - 0 \cdot 0003T^2, \tag{7}$$

for citric acid, and

$$f_v^0 = -298 \cdot 86 + 1 \cdot 54T - 0 \cdot 0005T^2, \tag{8}$$

for tartaric acid.

The temperature T is expressed in Kelvin.

The partial molar volume expansibilities $f_E^0 = [\partial f_v^0 / \partial T]_p$ calculated using expressions (5) to (8) for both the organic acids in water and 5% (*w/w*) ethanol + water are also recorded in table 2. It is evident from table 2 that the value of f_E^0 decreases with the increase in temperature for citric acid and tartaric acid in water as well as 5% (*w/w*) ethanol + water, indicating thereby that the behaviour of both the acids is just like common electrolytes,[23,24] because in common electrolytes the molar expansibilities should decrease with the rise in temperature. The decrease in f_E^0 may be ascribed to the absence of 'caging effect'.[24]
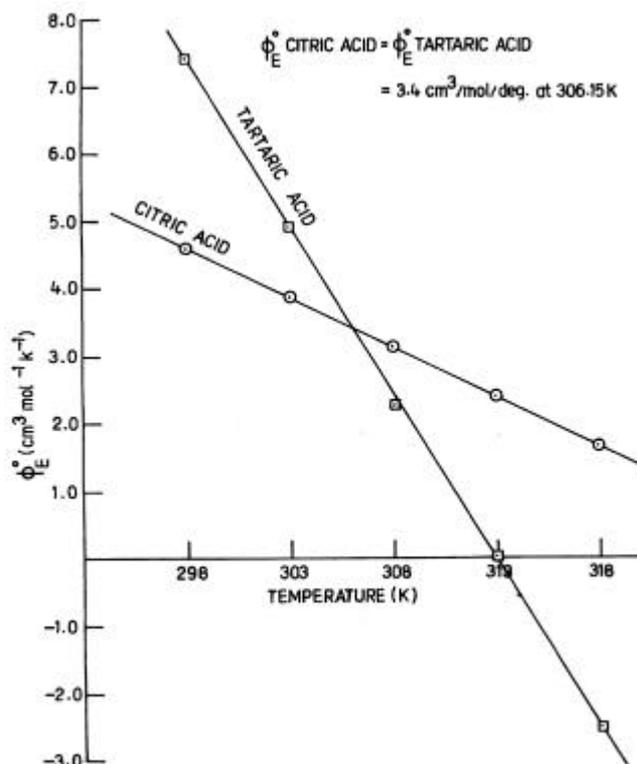
The variation of f_E^0 with temperature for both the organic acids, studied here has been found to be linear in water as well as in 5% (*w/w*) ethanol + water. A sample plot is shown in figure 3 for citric acid and tartaric acid in water. It is clear from figure 3 that the molar expansibilities for citric acid and tartaric acid become the same in water only at 306·15 K, i.e. f_E^0 [citric acid] = f_E^0 [tartaric acid] = $3 \cdot 4$ cm^3 mol^{-1} K^{-1}.

During the past few years, it has been emphasized by number of workers that S_v is not the sole criteria for determining the structure making or breaking nature of any solute. Hepler[25] has developed a technique of examining the sign of $[\partial^2 f_E^0 / \partial T^2]_p$ for various solutes in terms of long range structure making or breaking capacities of the solutes in aqueous solutions using the following general thermodynamic expression:

$$[\partial c_p / \partial P]_T = -[\partial^2 f_E^0 / \partial T^2]_p.$$

On the basis of this expression, it has been deduced that the structure maker solutes should have positive values whereas structure breaker solutes negative values. In the present case it is observed from ex-

pressions (5) to (8) that $[\partial^2 f_E^0/\partial T^2]_p$ for the solutions of citric acid and tartaric acid in water and 5% (w/w) ethanol + water is negative thereby showing that both the organic acids act as structure breakers in both the systems. In other words, the addition of citric acid and tartaric acid to water and ethanol + water causes a decrease in the structure of water as well as ethanol + water.

Acknowledgement

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