

Apparent Molal Volumes and Partial Molar Volumes of Aqueous Solutions of Some Biologically Important Compounds at 308 and 318 K

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Apparent molal volumes (ϕ_v) , partial molar volumes (ϕ_v^0) of aqueous solutions of seven biologically important compounds [glucose, sucrose, urea, citric acid, tartaric acid, ascorbic acid and oxalic acid] in different molality [0.1-1.0 mol/kg] at two different temperatures [308 and 318 K] have been determined. For density measurements sprengel and Ostwald pyknometer has been used. Partial molar volumes (ϕ_v^0) at infinite dilution have been obtained from ϕ_v values using the Masson equation. ϕ_v^0 values are positive for all the compounds studied and apparent molal volumes increase with increase in concentration of ascorbic acid. It decreases with increase in concentrations of other compounds [glucose, sucrose citric acid, tartaric acid and oxalic acid]. Variations in ϕ_v values with change in solute concentrations are discussed in terms of solute-solvent interactions and electrostriction.

Key Words: Apparent molal volume, Partial molar volume, Density, Masson equation, Electrostriction, Glucose, Sucrose, Urea, Citric acid, Tartaric acid, Ascorbic acid, Oxalic acid.

INTRODUCTION

The reaction medium plays an important role in determining reactivity, which is reflected in thermodynamic, transport and spectral properties^{1,2}. In order to gain insight into the mechanism of such interactions, thermodynamic and transport studies involving solute in mixed solvent systems are highly useful. The volumetric and viscometric studies of electrolytes at infinite dilution in solvent systems have contributed to our knowledge about electrolyte-non electrolyte-water interactions. By examining the apparent molal volumes and partial molar volumes of solutes as a function of size, nature, temperature and composition of the mixed solvent, it is possible to study the effect of these parameters on solute- water interactions in solutions.

The importance of carbohydrates³⁻⁶ to living things can hardly be over emphasized. The energy stores of most animals and plants are both carbohydrates and lipid in nature. Carbohydrates are generally available as an immediate energy source, whereas lipids act as a long-term energy resource and tend to be utilized at a slower rate.

Urea plays an important role⁷ in the metabolism of nitrogen containing compounds by animals and is the main nitrogen containing substance in the urine of mammals.

Carboxylic acids are very important biologically active compounds⁷. They have long chains of carbon atoms attached

to them are called fatty acids. They are important in the formation of fat in the body. Many carboxylic acids are present in the foods and drinks we ingest. Ascorbic acid is a water soluble antioxidant. Body requires vitamin C for normal physiological functions. It helps in the metabolism of tyrosine, folic acid and tryptophan.

Apparent molal volumes and partial molar volumes of aqueous solutions of glucose, sucrose, urea, citric acid, tartaric acid, ascorbic acid and oxalic acid at two different temperatures (308 and 318 K) have not been reported so far and hence need for the title investigation.

EXPERIMENTAL

All the compounds (AR, Qualigens) of highest purity grade were used without further purification. However they were dried in an oven and kept over anhydrous calcium chloride for 48 h before use. The solutions were prepared in doubly distilled deionized water having specific conductance less than 1×10^{-6} ohm⁻¹ cm⁻¹ and it was degassed before use. All the solutions were prepared by weight using Mettler balance having an accuracy of ± 0.01 mg.

Sprengel and Ostwald pyknometer⁸ which was essentially a U-tube in shape with side arms being made up of small bore capillary used to measure the densities of solutions. Measurements were done in a water thermostat having an accuracy of ± 0.01 K.

RESULTS AND DISCUSSION

Apparent molal volumes (ϕ_v) of the various solutes in water at 308 and 318 K were calculated from the experimentally measured densities from the following equation.

$$\varphi_{v} = \frac{1000}{\text{mdd}_{0}} \times (d_{0} - d) + \frac{M}{d}$$

where M = molecular mass of the solute, m = molality (mol kg⁻¹) of the solution, d and d₀ are the densities (kg m⁻³) of solution and solvent, respectively. The concentration 'C' on the molal scale was used (Tables 1 and 2). The plots of ϕ_v against square root of concentration were found to be linear with negative slopes for glucose, sucrose, urea, citric, tartaric

and oxalic acids. The positive slope was obtained for ascorbic acid. The partial molar volumes (ϕ_v^{0}) were calculated by plotting the experimental values of ϕ_v against the square root of molal concentration (C) using Masson's equation^{9,10}.

$$\phi_{v} = \phi_{v}^{0} + S_{v}^{*}C^{1/2}$$

where φ_v^0 = partial molar volume at infinite dilution and S_v^* = experimental slope. The values of φ_v^0 and S_v^* along with standard errors are listed in Table-3. It is evident that S_v^* is negative for all the solutes except ascorbic acid in aqueous mixtures at 308 K. These results indicate that the above solutes mix ideally with water and there is a perfect solvation of these molecules resulting into the absence of solute-solute interactions¹¹⁻¹³.

| TABLE-1 | | | | | | | | | | | | |
|---|------------------------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--|
| MOLALITIES (m), DENSITIES (d), APPARENT MOLAL VOLUMES (ϕ_v) FOR THE CHOSEN SOLUTES IN WATER AT 308 K | | | | | | | | | | | | |
| Glucose | Molality (m) | 0.1034 | 0.2060 | 0.3038 | 0.4051 | 0.5047 | 0.5964 | 0.6957 | 0.7962 | 0.8721 | 0.9801 | |
| | Density (d) | 1.0015 | 1.0081 | 1.0143 | 1.0204 | 1.0274 | 1.0321 | 1.0379 | 1.0433 | 1.0483 | 1.0536 | |
| | Apparent molal volume (ϕ_v) | 118.76 | 116.29 | 115.34 | 114.10 | 112.96 | 112.00 | 111.24 | 110.50 | 110.20 | 109.10 | |
| | Molality (m) | 0.1006 | 0.2029 | 0.3016 | 0.4033 | 0.5075 | 0.6081 | 0.7088 | 0.7594 | 0.8065 | 0.9639 | |
| Sucrose | Density (d) | 1.0077 | 1.0194 | 1.0312 | 1.0416 | 1.0539 | 1.0645 | 1.0731 | 1.0788 | 1.0837 | 1.0976 | |
| | Apparent molal volume (ϕ_v) | 217.30 | 216.30 | 215.20 | 217.64 | 214.51 | 213.99 | 213.40 | 213.30 | 212.80 | 212.40 | |
| | Molality (m) | 0.1023 | 0.2062 | 0.2907 | 0.4012 | 0.5003 | 0.6012 | 0.7081 | 0.8041 | 0.9172 | 0.9954 | |
| Urea | Density (d) | 0.9968 | 0.9988 | 1.0008 | 1.0018 | 1.0027 | 1.0044 | 1.0065 | 1.0068 | 1.0081 | 1.0098 | |
| | Apparent molal volume (ϕ_v) | 44.49 | 44.00 | 43.70 | 43.45 | 43.20 | 42.95 | 42.70 | 42.45 | 42.25 | 42.15 | |
| Citria | Molality (m) | 0.1008 | 0.2041 | 0.3050 | 0.4063 | 0.5046 | 0.6086 | 0.7100 | 0.8096 | 0.9064 | 1.0169 | |
| Citric acid | Density (d) | 1.0046 | 1.0086 | 1.0162 | 1.0220 | 1.0301 | 1.0362 | 1.0399 | 1.0491 | 1.0543 | 1.0619 | |
| aciu | Apparent molal volume (ϕ_v) | 141.10 | 140.10 | 139.36 | 138.90 | 138.10 | 137.47 | 137.46 | 136.66 | 136.30 | 135.82 | |
| Assarbia | Molality (m) | 0.1010 | 0.2010 | 0.3054 | 0.4079 | 0.4984 | 0.6132 | 0.7038 | 0.8096 | 0.9060 | 1.0230 | |
| Ascorbic acid | Density (d) | 1.0115 | 1.0187 | 1.0244 | 1.0310 | 1.0365 | 1.0438 | 1.0489 | 1.0553 | 1.0603 | 1.0666 | |
| aciu | Apparent molal volume (ϕ_v) | 64.95 | 72.50 | 78.15 | 85.21 | 89.60 | 92.44 | 94.83 | 96.22 | 101.10 | 103.50 | |
| Textexia | Molality (m) | 0.1016 | 0.2034 | 0.3024 | 0.4076 | 0.5063 | 0.6071 | 0.7048 | 0.8150 | 0.9121 | 1.0149 | |
| Tartaric acid | Density (d) | 1.0022 | 1.0049 | 1.0127 | 1.0165 | 1.0237 | 1.0290 | 1.0346 | 1.0409 | 1.0457 | 1.0490 | |
| aciu | Apparent molal volume (ϕ_v) | 93.10 | 92.55 | 92.20 | 91.70 | 91.36 | 91.49 | 90.78 | 90.50 | 90.33 | 90.20 | |
| Ovelic | Molality (m) | 0.1029 | 0.2060 | 0.3065 | 0.4102 | 0.5156 | 0.6180 | 0.7157 | 0.8191 | 0.9224 | 1.0258 | |
| Oxalic acid | Density (d) | 0.9830 | 0.9872 | 0.9915 | 0.9959 | 1.0002 | 1.0042 | 1.0079 | 1.0112 | 1.0152 | 1.0183 | |
| aciu | Apparent molal volume (ϕ_v) | 105.80 | 104.50 | 103.00 | 102.50 | 101.00 | 102.20 | 99.50 | 98.84 | 97.50 | 96.00 | |

| TABLE-2 | | | | | | | | | | | |
|---|------------------------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| MOLALITIES (m), DENSITIES (d), APPARENT MOLAL VOLUMES (qv) FOR THE CHOSEN SOLUTES IN WATER AT 318 K | | | | | | | | | | | |
| | Molality (m) | 0.1009 | 0.2035 | 0.3031 | 0.4052 | 0.5074 | 0.6026 | 0.7042 | 0.8108 | 0.9115 | 1.0026 |
| Glucose | Density (d) | 0.9900 | 0.9969 | 1.0038 | 1.0125 | 1.0159 | 1.0211 | 1.0263 | 1.0315 | 1.0349 | 1.0418 |
| | Apparent molal volume (ϕ_v) | 141.30 | 139.00 | 137.20 | 135.57 | 134.40 | 134.14 | 132.30 | 131.05 | 131.80 | 128.10 |
| | Molality (m) | 0.1016 | 0.2039 | 0.3034 | 0.4054 | 0.5042 | 0.6093 | 0.7093 | 0.8104 | 0.9095 | 1.0126 |
| Sucrose | Density (d) | 0.9902 | 0.9943 | 0.9978 | 1.0030 | 1.0073 | 1.0113 | 1.0150 | 1.0183 | 1.0223 | 1.0254 |
| | Apparent molal volume (ϕ_v) | 317.00 | 315.00 | 313.50 | 312.10 | 311.30 | 310.00 | 309.61 | 308.02 | 306.90 | 306.50 |
| | Molality (m) | 0.1017 | 0.2071 | 0.3043 | 0.4097 | 0.4977 | 0.6071 | 0.7032 | 0.8086 | 0.9137 | 1.0250 |
| Urea | Density (d) | 0.9932 | 0.9952 | 0.9969 | 0.9986 | 0.9996 | 1.0004 | 1.0014 | 1.0021 | 1.0038 | 1.0058 |
| | Apparent molal volume (ϕ_v) | 61.40 | 60.35 | 57.40 | 55.90 | 54.70 | 53.90 | 52.61 | 51.38 | 50.41 | 49.80 |
| Citatia | Molality (m) | 0.0999 | 0.2082 | 0.3122 | 0.4074 | 0.5073 | 0.6069 | 0.7067 | 0.8175 | 0.9167 | 1.0126 |
| Citric acid | Density (d) | 0.9883 | 0.9952 | 1.0021 | 1.0056 | 1.0142 | 1.0211 | 1.0297 | 1.0384 | 1.0436 | 1.0488 |
| aciu | Apparent molal volume (ϕ_v) | 178.80 | 172.40 | 168.00 | 164.80 | 161.20 | 160.00 | 156.44 | 151.23 | 150.52 | 149.65 |
| A | Molality (m) | 0.1032 | 0.2028 | 0.3041 | 0.4076 | 0.5035 | 0.6125 | 0.7081 | 0.7845 | 0.9105 | 1.0148 |
| Ascorbic acid | Density (d) | 0.9934 | 0.9986 | 1.0073 | 1.0125 | 1.0211 | 1.0246 | 1.0315 | 1.0367 | 1.0418 | 1.0470 |
| aciu | Apparent molal volume (ϕ_v) | 126.10 | 125.20 | 123.70 | 122.80 | 121.87 | 123.00 | 120.81 | 118.62 | 119.70 | 119.24 |
| Texterie | Molality (m) | 0.1005 | 0.2047 | 0.3050 | 0.3897 | 0.5072 | 0.6093 | 0.7099 | 0.8097 | 0.9073 | 1.0162 |
| Tartaric acid | Density (d) | 0.9798 | 0.9952 | 1.0004 | 1.0055 | 1.0142 | 1.0176 | 1.0228 | 1.0297 | 1.0331 | 1.0366 |
| aciu | Apparent molal volume (ϕ_v) | 118.40 | 115.80 | 115.00 | 112.60 | 110.87 | 111.19 | 108.55 | 107.40 | 104.65 | 105.30 |
| Oralia | Molality (m) | 0.0972 | 0.2032 | 0.3021 | 0.4062 | 0.5020 | 0.6060 | 0.7077 | 0.8129 | 0.9145 | 1.0212 |
| Oxalic acid | Density (d) | 0.9330 | 0.9952 | 0.9986 | 1.0021 | 1.0056 | 1.0090 | 1.0107 | 1.0159 | 1.0211 | 1.0246 |
| aciu | Apparent molal volume (ϕ_v) | 114.10 | 112.10 | 110.60 | 109.30 | 108.10 | 107.00 | 106.50 | 105.19 | 104.15 | 103.90 |

| | TABLE-3 | | | | | | | | | | | | | | |
|--------------|---|--------|---------|--------|--------|--------|--------|-------------|--------|---------------|--------|---------------|--------|-------------|--------|
| | PARTIAL MOLAR VOLUMES (ϕ^0_{ν}) AND EXPERIMENTAL SLOPES (S [*] _v) FOR THE CHOSEN SOLUTES AT 308 AND 318 K | | | | | | | | | | | | | | K |
| | | Glu | Sucrose | | U | Urea | | Citric acid | | Ascorbic acid | | Tartaric acid | | Oxalic acid | |
| | | 308 K | 318 K | 308 K | 318 K | 308 K | 318 K | 308 K | 318 K | 308 K | 318 K | 308 K | 318 K | 308 K | 318 K |
| | 10 0 | 122.97 | 147.00 | 220.12 | 322.10 | 45.60 | 66.70 | 143.6 | 192.00 | 46.5 | 129.3 | 94.5 | 124.30 | 109.40 | 118.9 |
| ϕ^0_{v} | (0.20*) | (0.24) | (0.76) | (1.15) | (0.03) | (0.06) | (1.08) | (0.21) | (0.05) | (1.14) | (0.02) | (0.01) | (0.11) | (0.13) | |
| | S_v^* | -13.98 | -18.33 | -7.72 | -15.22 | -3.46 | -17.14 | -7.83 | -43.64 | 55.88 | -10.00 | -4.5 | -20.00 | -12.5 | -15.00 |
| | *Standard error given in parenthesis | | | | | | | | | | | | | | |

*Standard error given in parenthesis

It is evident from Table-3 that ϕ_v^0 values are positive for all the solutes in various molal mixtures of water at 308 K, thereby showing the presence of very strong solute-solvent interactions¹⁴. The relative values of ϕ_v^0 in case of sucrose are much larger as compared to all the other solutes thereby suggesting that solute-solvent interactions are much stronger in case of sucrose as compared with those of other solutes.

The positive slope obtained for ascorbic acid in aqueous mixtures at 308 K, indicate the decrease in electrostriction¹⁵ which brings about shrinkage in the volume of solvent. Electrostriction primarily reflects electrolyte solvent interactions. The values of φ_v^0 are positive and large for all the solutes in various molal mixtures of water at higher temperature 318 K, showing the presence of very strong solute-solvent interactions which are further strengthened with the rise in temperature attributed to the increase in solvation^{16,17}.

Apparent molal volumes, partial molar volumes, viscosities, adiabatic compressibilities of various biologically important compounds such as galactose, fructose, succinic acid and malic acid in water and in various solvents is under investigation.

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