Apparent Molal Volume, Apparent Molal Compressibility & Transport Properties of Dilute Aqueous Solutions of Ascorbic Acid

M. V. KAULGUD, H. G. DOLE & K. S. M. RAO
Department of Chemistry, Nagpur University Campus, Nagpur 440010

Received 31 January 1978; accepted 3 April 1978

Apparent molal volume ($\phi_v$), apparent molal compressibility ($\phi_k$) and $B$-coefficients of ascorbic acid in dilute aqueous solutions are reported. The same properties are studied in 0.06 m sodium chloride solution to see the effect of NaCl on ascorbic acid-water interactions. Hydrations numbers are calculated from both $B$-coefficients and compressibility. These properties are also compared with those of glucose and the results are discussed in the light of possible effect of ascorbic acid on the structure of water.

Biochemists and clinicians are probing into the role of ascorbic acid in body chemistry. Though the exact role of ascorbic acid in cellular process is not known, it is believed that it either promotes the secretion of enzymes or creates suitable molecular environments for the enzymes to act effectively. Absorption of small doses of ascorbic acid into the blood stream produces in turn very dilute solution of the same in body fluid. One possible way in which such dilute solutions could influence the molecular environments is by modifying or affecting the solvent structure suitably or by preferential hydration. Franks et al. studied the volumetric and compressibility properties of dilute solutions of glucose and other polyhydroxy carbohydrates and showed that these properties depend upon the conformation of sugars in solution. Their results show that the apparent molal adiabatic compressibility at infinite dilution, $\phi_k$, for these compounds are generally negative, lying between $-13 \times 10^{-10}$ and $-61 \times 10^{-10}$ cm$^3$ dyne$^{-1}$ mole$^{-1}$ depending upon their structure in aqueous solutions. Negative values of $\phi_k$ would mean introduction of order in solvent structure by the solute molecules and Franks believes that $\phi_k$ is a measure of protection that the solute molecule gives to the solvent water. A study of $\phi_k$ would thus give information regarding the structural interactions taking place in ascorbic acid solution. Since ascorbic acid is structurally not very dissimilar to glucose, it was felt that a comparative study of volumetric and compressibility properties of ascorbic acid is meaningful. The study of its transport properties is also important as the body fluid is always circulating. The body fluid contains isotonic solutions of sodium chloride (0.06 m) and so it was worthwhile to examine its behaviour in NaCl medium also, to see if it shows a different behaviour. With this object in view we have undertaken the study of apparent molal volumes, adiabatic compressibilities and viscosities of aqueous ascorbic acid solutions at 25°C.

Materials and Methods

All the measurements were carried out in solutions of ascorbic acid (GR, 99.8% pure) in water and NaCl (AR) solutions (0.06 m) as solvent. The solutions were prepared fresh in doubly distilled water.

Density measurements — Densities of dilute solutions of ascorbic acid were determined by the differential float balance assembled in this department (see Fig. 1). Two identical glass plungers S, S (volume $\approx$ 180 ml weighted by mercury) are hung from the beam of a two-pan balance B (± 0.1 mg) with nylon threads. The balance is kept on a massive anti-vibration concrete bench. The plungers are dipped in two glass jars $J_1$, $J_2$ (capacity 1 litre) kept in a well insulated and covered water-bath (capacity 30 litres) whose temperature was kept...
constant by circulating liquid from a MK-70 cryostat (range -30 to +30°C). The cryostat is capable of maintaining temperature with an accuracy of ± 0.02°C. Owing to the large heat capacity of the bath the temperature fluctuations in the bath were much less (± 0.001°C) as read on the Beckman thermometer B2 (0.1°C range, ± 0.001°C). To begin with distilled water was added on either side and weighed amounts of pure ascorbic acid added to one and the change in buoyancy due to the change in the density read on the optical scale OS of the balance. In order to balance the pans and to know the exact change in buoyancy before the next addition of the solute, the offset of the balance was brought back to near zero using calibrated platinum loop weights (5-50 mg) specially obtained for this purpose from M/s Ravindra Haerans, Bombay. The small offset from zero were read on the optical scale OS. To prevent oxidation of ascorbic acid care was taken to flush water with nitrogen at the beginning as well as by keeping an atmosphere of nitrogen over the solution during the measurements. It was possible to obtain differences in the densities up to ± 5 ppm. From the densities thus obtained apparent molal volumes were calculated using standard formulae.

Sound velocity measurement — Since very dilute solutions were being handled, conventional methods like secondary interferences, diffraction and interferometry were not found adequate as the differences in the sound velocity from that of water were very small (1-2 m/sec). Hence differential phase comparison interferometer technique proposed by Schaaffs and Kalweit which was suitably modified and used by Kaulgud for handling problems of dilute aqueous solutions of electrolytes, was also employed in the present work. Details of the measurements have been described earlier. From the values of sound velocity and density which together give adiabatic compressibility β, apparent molal compressibility φb was calculated from the relation (1)

\[ \phi_b = \frac{1000 (d_b \beta - \beta_0 d) + \beta M_s}{md_0} \]  

where \( \beta, \beta_0 \) are the adiabatic compressibilities of solution and solvent respectively and \( d, d_0 \) are the respective densities. The sound velocities are considered to be accurate to ± 0.0015% which coupled with densities of ± 5 ppm gave values of \( \phi_b \) accurate to ± 0.5 units at the moderate concentration (0-025 m).

Viscosity measurement — An Ubbelohde viscometer with flow time 400 sec for water was used for obtaining the relative viscosity of ascorbic acid solutions at 25°C in the concentration range 0-01 to 0-05 M, using the same thermostatic arrangement described above. An accuracy of 0-2% in the relative viscosity could be obtained.

Results and Discussion

The viscosity variations of \( \phi_c, \phi_b \) and sound velocity with the concentration of ascorbic acid in both water and NaCl solutions are shown in Fig. 2. The results were analysed by Jones-Dole equation (2)

\[ \eta/\eta_0 = 1 + A \sqrt{C} + BC \]  

where \( A \) is a constant related to the ionic interactions and \( B \) is the viscosity \( B \)-coefficient representing the solute-solvent interactions. The \( pH \) values (4-2 and 11-6) show that even at the lowest concentration the number of ions present is negligible (<2%). Hence ascorbic acid has been regarded as undissociated species and the Jones-Dole equation is rewritten as:

\[ \eta/\eta_0 = 1 + BC \]  

The \( B \)-coefficient was calculated by plotting \( (\eta/\eta_0 - 1) \) against \( C \) (Fig. 3). The hydration numbers were calculated from \( B \)-coefficients using the modified form of the Einstein equation

\[ \eta/\eta_0 = 1 + a_1 \phi \]  

where \( a_1 \) is a constant defined by the axial ratio of the molecule and \( \phi \) is volume fraction occupied by the solute particle.

The axial ratio of ascorbic acid molecule has been taken to be equal to that of glucose (2-5 : 1) since the structure of ascorbic acid is not very dissimilar to that of glucose. For this axial ratio the value of \( a_1 \) in Eq. (4) is calculated to be equal to 2-85 from the variation of log \( a_1 \) with log \( R \) where \( R \) is the axial ratio.

Using relations (3) and (4) and writing \( \phi \) as

\[ \phi = CV_a \]  

where \( C \) is the concentration, and \( V_a \) is the molar volume of solute including the attached solvent, one can obtain \( V_a \) from \( B \)-values. The apparent molal volume \( \phi_0 \) obtained from density measurements are less than \( V_a \). Assuming that this difference..
arises due to the water molecules held firmly around solute molecules one can obtain hydration number by dividing \( V_s - \phi_b \) by molar volume of water.

Table 1 gives the values of various parameters at infinite dilution for ascorbic acid at 25° as found in this work. No significant differences in \( \phi_b \) values are observed in aqueous and NaCl solutions of ascorbic acid. The value of \( \phi_b \) for ascorbic acid in aqueous solution appears to be slightly more negative than the value observed in NaCl solution. This would suggest that ascorbic acid gives less protection to water compared to NaCl solution. Table 1 also gives values of hydration numbers calculated from B-coefficient and compared with those calculated from compressibility measurements. The differences in the hydration numbers obtained by both these methods may be due to the fact that viscosity is a transport property whereas compressibility is an equilibrium property. Moreover, we assume that the solute molecules are incompressible hard spheres and compressibility of hydration water is equal to that of ice which is not true in all the cases. Nevertheless the general trend is that the hydration number in NaCl solution is less than that in aqueous solution. This might be due to the stronger electrostatic attraction between the ions and water molecules resulting in the suppression of interactions between water and ascorbic acid molecules. It was shown that \( \phi_b \) for carbohydrates is function of number of \( -OH \) groups and their positions (axial or equatorial) in the molecule. Table 2 shows a comparison of the values of \( \phi_b, \phi_a \) and B-coefficient values of ascorbic acid and glucose at 25°.

TABLE 1 — HYDRATION NUMBERS OF L-ASCORBIC ACID IN WATER AND NaCl SOLUTION AT 25°

<table>
<thead>
<tr>
<th>Solute</th>
<th>( \phi_b )</th>
<th>( \phi_b \times 10^{10} )</th>
<th>B-coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>WATER</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>105.4 ± 1.0</td>
<td>-7 ± 0.5</td>
<td>0.383</td>
<td>1.6</td>
</tr>
<tr>
<td>NaCl SOLUTION</td>
<td></td>
<td>105.3 ± 1.0</td>
<td>-6 ± 0.5</td>
</tr>
</tbody>
</table>

TABLE 2 — COMPARISON BETWEEN \( \phi_b, \phi_a \) AND B-COEFFICIENTS FOR L-ASCORBIC ACID AND GLUCOSE

<table>
<thead>
<tr>
<th>Solute</th>
<th>( \phi_b )</th>
<th>( \phi_b \times 10^{10} )</th>
<th>B-coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>L-Ascorbic acid</td>
<td>105.4</td>
<td>-7 ± 0.5</td>
<td>0.383</td>
</tr>
<tr>
<td>Glucose</td>
<td>111.9</td>
<td>-16 ± 5.0</td>
<td>0.448</td>
</tr>
</tbody>
</table>

Further work in this direction is in progress.

Acknowledgement

This work was supported by the UGC, New Delhi through a special research grant. Two of the authors (H.G.D. and K.S.M.R.) are thankful to the UGC, New Delhi, for the award of junior research fellowships.
References