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Volumetric properties of ascorbic acid (vitamin C) and thiamine hydrochloride (vitamin B_1) in dilute HCl and in aqueous NaCl solutions at (283.15, 293.15, 298.15, 303.15, 308.15, and 313.15) K

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Abstract

Apparent molar volumes and apparent molar isentropic compressibilities of ascorbic acid (vitamin C) and thiamine hydrochloride (vitamin B_1) were determined from accurately measured density and sound velocity data in water and in aqueous NaCl solutions at (283.15, 293.15, 298.15, 303.15, 308.15, and 313.15) K. These volume and compressibility data were extrapolated to zero concentration using suitable empirical or theoretical equations to determine the corresponding infinite dilution values. Apparent molar expansibilities at infinite dilution were determined from slopes of apparent molar volume *vs*. temperature plots. Ionization of both ascorbic acid and thiamine hydrochloride were suppressed using sufficiently acidic solutions. Apparent molar volumes at infinite dilution for ascorbic acid and thiamine hydrochloride were found to increase with temperature in acidic solutions and in the presence of co-solute, NaCl. Apparent molar expansibility at infinite dilution were found to be constant over the temperature range studied and were all positive, indicating the hydrophilic character of the two vitamins studied in water and in the presence of co-solute, NaCl. Apparent molar isentropic compressibilities of ascorbic acid at infinite dilution were positive in water and in the presence of co-solute, NaCl, at low molalities. Those of thiamine hydrochloride at infinitive dilution were all negative, consistent with its ionic nature. Transfer apparent molar volumes of vitamins at infinite dilution from water solutions to NaCl solutions at various temperatures were determined. The results were interpreted in terms of complex vitamin–water–co-solute (NaCl) interactions.

Keywords: Apparent molar volume; Apparent molar isentropic compressibility; Ascorbic acid; Thiamine hydrochloride; Transfer molar volume

1. Introduction

Vitamins are organic compounds needed by cells and organs to maintain their functions and developments. They take role in enzymic processes either as co-enzymes or their precursors and in genetic regulation processes. They may also act as antioxidants. Most vitamins cannot be synthesized by the body, thus must be taken through the diet. Vitamins are classified as water soluble and fat soluble vitamins. Ascorbic acid (vitamin C) and thiamine hydrochloride (vitamin B_1) are water soluble. It is necessary to study aqueous solution properties of these vitamins in order to understand the mechanisms of their actions in detail. Volumetric properties are important tools in studying the solution behaviors of solutes and reveal valuable information about solute–solvent interactions. They include apparent molar volume, apparent molar expansibility which is the derivative of volume with respect to temperature and apparent molar compressibility which is the derivative of volume with respect to pressure. In our earlier works, we utilized one or more of these properties in obtaining information about solution behaviors of various groups of solutes. Studies on hydration behaviors of sulfur and chlorine oxy-anions [1], hydration and ionization of a series of organic bases and their conjugate ions [2], denaturation of bovine serum albumin by urea [3], ionic hydration volumes in relation to solution properties and ionic

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adsorption [4] are examples of such works. A close correlation was also found between volumetric properties and adsorption characteristics of various aromatic heterocyclic compounds [5].

Studies on volumetric properties of solutions of food components gained interest in recent years. Zhou *et al.* [6] determined the volumetric properties of interaction of monosaccharides with NaI in water; Rudan-Tasic *et al.* [7] examined the correlation between volumetric properties of cyclohexylsulfamates and their sweetening effect. The later correlation had previously been searched by Birch and Catsoulis [8]. Ayranci and Akgul [9] and Akgul *et al.* [10] measured the volumetric properties of some fatty acids and their triglycerides in non-aqueous solvents and predicted the aqueous solution properties of these compounds by analogy. There are very limited number of works in the literature for the volumetric properties of vitamins and their interpretations in terms of vitamin–water or vitamin–water–co-solute interactions. Kundu and Kishore [11] reported the apparent molar volumes and heat capacities of nicotinamide (vitamin B_3). Apparent molar volumes of ascorbic acid in water at 298.15 K were determined by Apelblat and Manzurola [12] without considering the ionization which is expected to be significant especially at low concentrations. Kaulgud *et al.* [13] reported apparent molal volume and compressibility of dilute aqueous solutions of ascorbic acid. These workers also examined the effect of presence of NaCl on ascorbic acid–water interactions. The volumetric and thermochemical properties of L-ascorbic acid in water at three temperatures (288.15, 298.15, and 308.15) K were investigated by Hakin *et al.* [14].

The purpose of present study is to determine the apparent molar volume, compressibility and expansibility of two vitamins; ascorbic acid (vitamin C) and thiamine hydrochloride (vitamin B_1) in water at various temperatures (283.15, 293.15, 298.15, 303.15, 308.15, and 313.15) K. Investigation of the effect of presence of NaCl at various molalities and interpretation of all the results in terms of vitamin–water and vitamin–water–NaCl interactions were also aimed.

2. Experimental

2.1. Materials

L(+)Ascorbic acid was obtained from ABCR, thiamine hydrochloride from Sigma and NaCl from Merck. HCl was reagent grade. Deionized water was used in all experiments. The structures of L(+)ascorbic acid and thiamine hydrochloride are given in figure 1.

2.2. Density and sound velocity measurements

Apparent molar volumes were determined from accurate density measurements whereas apparent molar compressibilities were determined from accurate sound velocity and density measurements. Densities and sound velocities were measured by an Anton Paar DSA 5000 model high precision vibrating tube digital densimeter and sound velocity measuring device, with automatic viscosity corrections. The instrument has a built-in thermostat to maintain the temperature between 0 °C and 70 °C with a precision of ±0.005 °C. The calibration of the instrument was made with degassed and bidistilled water at 20 °C. The instrument required a liquid volume of about 2.5 mL and measured the density and sound velocity simultaneously after a thermal equilibration period of about 5 min to 10 min.

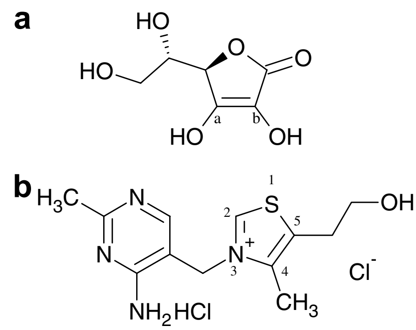

FIGURE 1. The structures of L(+)ascorbic acid (a) and thiamine hydrochloride (b).

Density and sound velocity measurements were carried out for solutions of ascorbic acid and thiamine hydrochloride in water and in NaCl solutions of 0.1 m to 5.0 m at (283.15, 293.15, 298.15, 303.15, 308.15, and 313.15) K. In order to suppress the ionization of both solutes in water, ascorbic acid solutions were prepared in 0.01 M HCl and thiamine hydrochloride solutions in 0.001 M HCl. These HCl concentrations were determined on the basis of simple analytical calculations using the pK_a values of 4.04 for ascorbic acid and 4.8 for thiamine hydrochloride [15].

3. Treatment of data

Apparent molar volumes, V_Φ, were determined from the measured densities of solvent, ρ_o, and of solution, ρ, using the following equation [16]:

$$V_\Phi = [1000(\rho_o - \rho)/(m\rho\rho_o)] + M_2/\rho = [1000(\rho_o - \rho)/(c\rho_o)] + M_2/\rho_o, \quad (1)$$

where m is the molality, c is the molarity of the solution and M_2 is the molecular weight of the solute, ascorbic acid or thiamine hydrochloride. Solvent was taken as 0.01 M HCl solution for ascorbic acid and 0.001 M HCl solution for thiamine hydrochloride. For the determination of V_Φ of vitamins in the presence of NaCl, the solvent was taken as the solution containing HCl, either at 0.01 M or at 0.001 M, and NaCl at various molalities.

Apparent molar volumes at infinite dilution, V°_Φ, were determined by extrapolating V_Φ *vs.* concentration data to zero concentration. For ascorbic acid, being a nonelectrolyte, this extrapolation was made on the basis of the following empirical equation [16]: