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Volumetric and acoustic study of aqueous binary mixtures of quinine hydrochloride, guanidine hydrochloride and quinic acid at different temperatures

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ABSTRACT

In the present communication, we report the fundamental thermodynamic properties like volumetric and compressibility of very important bioactive compounds, *viz.* quinine hydrochloride, guanidine hydrochloride and quinic acid (0.01 to 0.1) $mol \cdot kg^{-1}$ in water at temperatures T = (278.15, 288.15 and 298.15) K. The experimental values of density (ρ) of aqueous solutions and speed of sound (u) in aqueous solutions of the above compounds within the concentration range (0.01 to 0.1) $mol \cdot kg^{-1}$ have been obtained. The apparent molar volumes (V_ϕ), and apparent molar isentropic compressibilities (κ_ϕ) of quinine hydrochloride, guanidine hydrochloride and quinic acid in water have been computed at three different temperatures. Speed of sound values have also been used to calculate the hydration number (n_H) of the solute. The temperature dependence of the apparent molar volume has been used to calculate the thermal expansion coefficient (α^*), apparent molar expansivity (E^0_ϕ) and Hepler's constant $\left(\partial^2 V^0_\phi/\partial T^2\right)$. The derived parameters have been used to interpret the results in terms of (solute + solute)/(ion + ion), (solute + solvent) interactions, structure making and structure breaking tendencies of solutes in water.

1. Introduction

Studies on volumetric and compressibility properties of aqueous solutions of bioactive solutes help in characterizing the structure and properties of solutes in aqueous solutions, which is of great importance in understanding the mechanism of bioactive molecules in the body system. These results can be used to detect various types of interactions, which are helpful in predicting the nature of solute whether the solute modifies or distorts the structure of the solvent. The volumetric properties of an electrolytic solution can provide useful information for insights into interactions that occur in aqueous solution between the ions, the associated electrolyte and the solvent. From the theoretical point of view, the most useful quantities are the limiting values of the apparent molar volume and the apparent molar expansibility, since these only depend on the intrinsic size of the ion and on (ion + solvent) interactions [1,2].

The natural compounds, mainly obtained from cinchona tree have wide applications in the field of medical chemistry. Quinoline methanol, a natural product can be used as an effective antimalarial drug. Quinine is a diacidic base, and it is a methoxy derivative of a companion alkaloid, cinchonine. Quinine contains two basic nitrogen atoms and thus is capable of forming various salts [3]. Guanidine hydrochloride is a well-characterized strong denaturant for proteins and has been frequently applied as the subunit dissociating agent in complex systems. The conformational and thermodynamic aspects of the denaturing action of guanidine hydrochloride have been the subject of extensive study, and the present state of knowledge has been summarized recently [4,5]. Quinic acid is present in free form or as esters [6], such as in cinchona bark, coffee beans, leaves of tobacco, and carrot. Also, it is predominant among the metabolites originating from D-glucose [7]. The quinic acid has five functional groups that can coordinate with metal cations [8] and can yield various kinds of salts. It is an important starting material for the asymmetric multistep synthesis of many natural products and other compounds [9].

Electrolytes influence the stability of biomolecules and play an important role in a living cell. In spite of their extensive medical use, negligible work has been done on thermodynamic studies in aqueous solutions [3–18]. Hence it was thought to study thermodynamic properties of some bioactive compounds at

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different temperatures *i.e.* $T = (278.15,\ 288.15\ \text{and}\ 298.15)$ K. In this communication, we report apparent molar volumes and compressibilities of quinine hydrochloride, guanidine hydrochloride and quinic acid in aqueous solutions at temperatures $T = (278.15,\ 288.15\ \text{and}\ 298.15)$ K within the concentration range (0.01 to 0.1) m. The experimental values of density (ρ) and speed of sound (u) were used to obtain the apparent molar volume (V_ϕ) of solute, isentropic compressibility (κ_s) of solution, apparent molar isentropic compressibility (κ_ϕ) of solute. The limiting values of apparent molar volume (V_ϕ^0), apparent molar isentropic compressibility $\left(\kappa_\phi^0\right)$ and apparent molar expansivity (E_ϕ^0) of solute have also been obtained. The results obtained are interpreted in terms of various interactions, and structure forming and structure destroying abilities of the solute in aqueous medium.

2. Experimental

2.1. Materials and methods

All the solutes used in this work, namely quinine hydrochloride dihydrate, guanidine hydrochloride and quinic acid were of high purity (>0.99 mass fraction) and were used without further purification. Specifications of these bioactive solutes are listed in table 1. Before preparing the solutions, the compounds were dried in a vacuum oven at $T = 343.15$ K till last two values of the weights were constant and kept in a vacuum desiccator over anhydrous fused calcium chloride for more than two days.

The Karl Fischer analysis was done for quinine hydrochloride dihydrate and guanidine hydrochlorides. These results were used during the calculations of solute concentrations. All the solutions were prepared in freshly prepared doubly distilled water, on a molality basis, by using E. Mettler analytical balance with an uncertainty up to ±0.1 mg.

2.2. Density measurements

The densities of all binary systems studied at $T = (278.15,\ 288.15\ \text{and}\ 298.15)$ K were measured by using Lypkin's modified bicapillary pycnometers volume ≈ (31 and 33) cm^3. The pycnometers calibrated by using dilute aqueous NaCl solutions of different concentrations at different temperatures $T = (278.15,\ 288.15\ \text{and}\ 298.15)$ K. The temperature of the experimental liquid bath was maintained constant within (±0.002 K) by circulating coolant liquid (methanol + water) from a MK-70 ultra-cryostat having the accuracy to maintain temperature to ±0.02 K inside the cryostat. The details of density measurements are given elsewhere [19]. The uncertainties in the density measurements were found to be $\pm 5 \cdot 10^{-2}\ \text{kg} \cdot \text{m}^{-3}$ [20]. The combined expanded uncertainty was $U_\rho(\rho) = 0.1\ \text{kg} \cdot \text{m}^{-3}$.

2.3. Speed of sound measurements

Speed of sound measurements of all aqueous binary systems were carried out by using variable path ultrasonic interferometer (Model S1-2M/S Dr. Steeg and Reuter, Germany) at a resonating frequency of 2 MHz (single crystal) and having temperature control ±0.1 K inside the sample holder. Calibration of the interferometer was done by measuring speeds of sound in freshly prepared doubly distilled water at temperatures $T = (278.15,\ 288.15\ \text{and}\ 298.15)$ K [21]. Values of the speed of sound were reproducible within $\pm 0.5\ \text{m} \cdot \text{s}^{-1}$ [22]. The combined expanded uncertainty was $U_u(u) = 1.0\ \text{m} \cdot \text{s}^{-1}$.

3. Results and discussion

3.1. Volumetric properties

3.1.1. Density

In figure 1, the density (ρ) of solution is plotted as a function of molality (m) for the binary systems of (quinine hydrochloride + water), (guanidine hydrochloride + water) and (quinic acid + water) at $T = 278.15$ K. Similar type of graphs are obtained at $T = (288.15\ \text{and}\ 298.15)$ K for all the systems studied. It is seen from the figure that density of the solution increases linearly with rise in concentration of solute in solution. In tables 2–4 are listed the values of densities of all the solutions at different temperatures. From the scrutiny of above tables, it is observed that density of all the studied solutes in aqueous solutions decreases slightly with increase in the temperature of the solution at a particular concentration. Also the plot suggests that the densities are in the order of increasing molar mass *i.e.* guanidine hydrochloride < quinic acid < quinine hydrochloride.

3.1.2. Apparent molar volume

The experimental values of density (ρ) are used to calculate apparent molar volume (V_ϕ) of solute for studied binary systems at different temperatures by using following equation; and are collected in tables 2–4 respectively.

$$V_\phi = \frac{1000(\rho_0 - \rho)}{m\rho\rho_0} + \frac{M}{\rho}, \tag{1}$$

where ρ_0 and ρ are densities of solvent and solution respectively, m and M are the solution molality and molar mass of solute respectively.

Figure 2 shows the plot of variation of $(V_\phi - A_V(m)^{1/2})$ against molality (m) for aqueous solutions of quinine hydrochloride and guanidine hydrochloride (both being 1:1 electrolytes) as a function of molality (m) at $T = 278.15$ K. It is observed from the graph that values of $(V_\phi - A_V(m)^{1/2})$ are higher for quinine hydrochloride and lower for guanidine hydrochloride at a particular concentration. The variation of apparent molar volume of solute (V_ϕ) with molality (m) of quinic acid (being non-electrolyte) at $T = 278.15$ K is depicted in figure 3. It is seen from the above figure that V_ϕ increases continuously with increase in concentration of the solute. Apparent molar volumes of electrolytes and non-electrolyte at infinite dilution (V_ϕ^0) were determined by the extrapolation of $\{(V_\phi - A_V(m)^{1/2}) - m\}$ and $(V_\phi - m)$ curve to zero concentration respectively based on the Redlich–Meyer equations [23].

$$V_\phi = V_\phi^0 + A_V(m)^{1/2} + S_V m, \tag{2}$$

TABLE 1
Provenance and mass fraction purity of materials studied.

Chemical name	Supplier	CAS No.	Mass fraction purity	Analysis method
Quinine hydrochloride dihydrate[b]	E-Merck, India	6119-47-7	⩾0.99	Acidimetry
Guanidine hydrochloride[b]	Sigma Aldrich, USA	50-01-1	⩾0.99	Titration
Quinic acid[b]	Sigma Aldrich, USA	77-95-2	⩾0.975	GC[a]

[a] Gas chromatography.
[b] Structure confirms by I.R.