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Density, speed of sound, viscosity and refractive index properties of aqueous solutions of vitamins B_1.HCl and B_6.HCl at temperatures (278.15, 288.15, and 298.15) K

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ABSTRACT

The experimental values of density (ρ), speed of sound (u), absolute viscosity (η) and refractive index (n_D) properties are reported for aqueous solutions of thiamine hydrochloride (vitamin B_1.HCl) and pyridoxine hydrochloride (vitamin B_6.HCl) within the concentration range (0.01 to 0.55) mol · kg^{-1} at three different temperatures, *viz.* T/K = 278.15, 288.15, and 298.15. Using experimental data, different derived parameters such as the apparent molar volume of solute (ϕ_V), isentropic compressibility of solution (β_S), apparent molar isentropic compressibility of solute (ϕ_{KS}) and relative viscosity of solution (η_r) have been computed. The limiting values of apparent molar volume (ϕ_V^0) and apparent molar isentropic compressibility (ϕ_{KS}^0) have been obtained. The limiting apparent molar expansivity (ϕ_E^0) of solute, coefficient of thermal expansion (α^*) and hydration numbers (n_h) of above vitamins in the aqueous medium have also been estimated. The experimental values of relative viscosity are used to calculate the Jones–Dole equation viscosity *A* and *B* coefficients for the hydrochlorides. The temperature coefficients of *B i.e.* (dB/dT) for these solutes have been used to study water structure making and breaking effects due to cations. Further, a discussion is made on the basis of solute–solute and solute–solvent interactions.

1. Introduction

Vitamins are small organic molecules that can perform chemical functions (often in enzyme catalysis) that cannot be performed by chemistry of ordinary amino acids, sugars or lipids. These are essential nutrients that the human body needs in small amounts to tune biological processes properly. It is known that these are not produced in the body and have to be supplemented from outside [1]. In general, the functionality and classification are based on solubility in water or bio-fluids. Important vitamins such as pyridoxine and thiamine are known to cure diseases like tuberculosis and beriberi. Vitamins are in general organic compounds which have limited solubility in water. It is found that very few systematic studies of the properties of such compounds in water are being made although the vitamin B complex have been explored to understand the chemistry of functional groups associated with it [2–7]. It is felt that a systematic study on volumetric and compressibility properties of these molecules is needed to understand ion–ion, ion–solvent and solvent–solvent interactions [8–14]. This information is of fundamental importance for understanding of reaction rates and chemical equilibria involving dissolved electrolytes. The viscosity of aqueous solution has gained importance among the other transport properties. As the body fluid is always circulating, it is interesting to study the transport properties of vitamins in aqueous solutions at different temperatures.

In this communication, we report results for density (ρ), speed of sound (u), viscosity (η) and refractive indices (n_D) of (thiamine hydrochloride + water) and (pyridoxine hydrochloride + water) at temperatures T = (278.15, 288.15, and 298.15) K within the concentration range (0.01 to 0.55) mol · kg^{-1}. The data are used to obtain derived properties, apparent molar volume (ϕ_V) of solute, limiting apparent molar volume (ϕ_V^0), isentropic compressibility of solution (β_S), apparent molar isentropic compressibility of solute (ϕ_{KS}), limiting apparent molar isentropic compressibility (ϕ_{KS}^0), limiting apparent molar expansivity (ϕ_E^0), hydration number (n_h), coefficient of thermal expansion (α^*), relative viscosity (η_r), Jones–Dole equation viscosity *A* and *B* coefficients and temperature coefficient of *B i.e.* (dB/dT). The concentration and temperature dependence observed are examined from the point of view of solute–solvent and solute and solute–solute interactions (ion–ion).

2. Materials and methods

Thiamine hydrochloride (CAS No. 67-03-8) and pyridoxine hydrochloride (CAS No. 58-56-0) were supplied by E-Merck, India.

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Both the vitamins were of analytical reagent grade and used without further purification. The specifications of these compounds are listed in table 1. These compounds were dried in a vacuum oven at $T = 353.15$ K and were kept in a vacuum desiccators over anhydrous fused calcium chloride for more than two days till complete drying. All the solutions were prepared in freshly prepared doubly distilled water on a molality basis. For weighing purpose, an E. Mettler balance having uncertainty to weigh ±0.1 mg was used.

In the present work, densities of aqueous solutions of binary systems of Thiamine hydrochloride and Pyridoxine hydrochloride at temperatures $T = (278.15, 288.15, \text{and } 298.15)$ K were measured by using modified Lypkin's bicapillary pycnometer. The temperatures of the experimental water bath were maintained constant up to ±0.002 K by circulating the thermostatted liquid from Julabo cryostat which maintains the temperature constant to ±0.01 K in the cryostat. The density of pure water at different temperatures was taken from literature [15] and was used to obtain radius of the capillary and volume of the pycnometers. The volumes of the pycnometers used in the present work were found to be $\approx 26\ \text{cm}^3$ and $\approx 28\ \text{cm}^3$ respectively. Pycnometers were calibrated by measuring the densities of aqueous solutions of sodium chloride at $T/\text{K} = 298.15$ in the low concentration range. The density values agreed well with the literature up to $\pm 0.05\ \text{kg} \cdot \text{m}^{-3}$ [16]. Thus the combined expanded uncertainty was $U_\rho(\rho) = 0.1\ \text{kg} \cdot \text{m}^{-3}$. The details of density measurement are given elsewhere [17].

The speed of sound was measured in aqueous solutions of both the vitamins using an ultrasonic interferometer (model SI-2 M/s Dr. Steeg and Reuter, Germany) at a fixed frequency of 2 MHz and having temperature control ±0.1 K. The temperature was maintained constant by circulating coolant liquid from the MLW MK-70 ultracryostat (Germany). The details are given elsewhere [18]. The interferometer was calibrated by measuring speed of sound in freshly prepared doubly distilled water. The uncertainty in speed of sound measurement was of the order of $\pm 0.5\ \text{m} \cdot \text{s}^{-1}$ [19]. Thus the combined expanded uncertainty was $U_u(u) = 1.0\ \text{m} \cdot \text{s}^{-1}$.

The viscosities of aqueous binary solutions of both vitamins *i.e.* Thiamine hydrochloride and Pyridoxine hydrochloride were determined at all studied temperatures $T = (278.15, 288.15, \text{and } 298.15)$ K by using the Ostwald viscometer. The viscometer was suspended in an experimental bath (capacity $\approx 35\ \text{dm}^3$) having a glass window to observe the meniscus of the liquid. The temperature in an experimental water bath was maintained constant (±0.002 K) by circulating coolant liquid from the MLW MK-70 ultracryostat (uncertainty ± 0.02 K). The flow time measurements for aqueous binary mixtures of vitamins were made in triplicate. The average of the flow time was used to calculate viscosity of the solution. The measurements of flow time were made with a "ROCAR" stopwatch having uncertainty of ±0.1 s. The viscometer was calibrated by measuring viscosity of aqueous NaCl solutions of different concentrations at $T = 298.15$ K. Our values of relative viscosity (η) agreed well with the literature [20] within ±0.1% and thus the combined expanded uncertainty was $U_\eta(\eta) = 0.2\%$.

Refractive index measurements were made for sodium light using Abbe's Refractometer (Carl Ziess, Germany) having an assembly for the temperature control of the sample holder by circulating liquid from the cryostat. The temperature of the liquid was maintained constant ±0.02 K by circulating coolant from the MK-70 ultracryostat (Germany). The details are given elsewhere [21]. The refractometer was calibrated using doubly distilled water. The uncertainty in the refractive index measurements was of the order of ±0.0001 [22] and thus the combined expanded uncertainty was $U_{n_\text{D}}(n_\text{D}) = 0.0002$.

TABLE 1
Provenance and purity of chemical samples.

Chemical name	Source	Mass fraction purity	Analysis method
Thiamine hydrochloride	E-Merck, India	$\geqslant 0.995$	LC-MS[a]
Pyridoxine hydrochloride	E-Merck, India	$\geqslant 0.995$	LC-MS[a]

[a] Liquid chromatography, mass spectrometry.

3. Calculations of derived parameters

The densities (ρ) of aqueous solutions of both vitamins *i.e.* thiamine hydrochloride and pyridoxine hydrochloride at all temperatures *i.e.* $T = (278.15, 288.15, \text{and } 298.15)$ K were calculated using relationship:

$$\rho = \frac{W}{V_\text{P} - \pi r^2 dh}, \tag{1}$$

where, W is the weight of solution, V_P is the volume of pycnometer at that temperature, r is the radius of capillary of pycnometer used and dh is the difference in the height of meniscus of solution in the pycnometer.

The isentropic compressibility (β_S) of the solutions has been computed using data of density (ρ) and speed of sound (u) of aqueous solutions of both vitamins at different temperatures using the well-known Newton–Laplace equation, assuming the absorption of wave is negligible,

$$\beta_\text{S} = -\frac{1}{V} \cdot \left(\frac{\partial V}{\partial P}\right)_\text{S} = \frac{1}{\rho . u^2}. \tag{2}$$

The apparent molar volume (ϕ_V) of solute and apparent molar isentropic compressibility (ϕ_KS) of solute in aqueous solutions at different temperatures were calculated using the following expressions:

$$\phi_\text{V} = \frac{M_2}{\rho} + \left[\frac{1000(\rho_1 - \rho)}{m.\rho.\rho_1}\right], \tag{3}$$

$$\phi_\text{KS} = \left[\frac{1000.(\rho_1 . \beta_\text{S} - \rho . \beta_0)}{m.\rho.\rho_1}\right] + \left[\frac{M_2 . \beta_\text{S}}{\rho}\right], \tag{4}$$

where ρ and ρ_1 are the density of solution and solvent, respectively, m is the molality of the solution, M_2 is the molar mass of the solute, and β_S and β_0 represent the values of isentropic compressibility of solution and pure solvent, respectively.

Apparent molar volumes of solute *i.e.* electrolytes at infinite dilution (ϕ_V^0) were determined by the extrapolation of $\phi_\text{V} - A_\text{V}\sqrt{m}$ against m curve to zero concentration based on the Redlich–Meyer equation [23]:

$$\phi_\text{V} = \phi_\text{V}^0 + A_\text{V} \cdot \sqrt{m} + S_\text{V} m \tag{5}$$

where S_V is the experimental slope of ($\phi_\text{V} - A_\text{V}\sqrt{m}$)-$m$ curve and A_V is the Debye–Hűckel limiting slope which changes with temperature. The values of A_V for 1:1 electrolyte at $T = (278.15, 288.15, \text{and } 298.15)$ K have been taken as $1.529\ \text{cm}^3 \cdot \text{mol}^{-3/2} \cdot \text{dm}^{3/2}$, $1.697\ \text{cm}^3 \cdot \text{mol}^{-3/2} \cdot \text{dm}^{3/2}$ and $1.868\ \text{cm}^3 \cdot \text{mol}^{-3/2} \cdot \text{dm}^{3/2}$ respectively [24].

Values of the limiting apparent molar isentropic compressibility (ϕ_KS^0) of the solute in aqueous medium have been obtained by smooth extrapolation of $\phi_\text{KS} - \sqrt{m}$ curves to the zero concentration [3].

The limiting apparent molar expansivity (ϕ_E^0) of the solute at infinite dilution in aqueous medium has been obtained at $T/\text{K} = (283.15 \text{ and } 293.15)$ by using the following relation: