Studies on molecular interactions of some sweeteners in water by volumetric and ultrasonic velocity measurements at T = (20.0–45.0 °C)

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ABSTRACT

Densities and ultrasonic velocity values for aqueous solutions of two sweeteners viz., maltose monohydrate and acesulfame-K have been measured as a function of concentration at 20.0–45.0 °C and atmospheric pressure. Solutions of acesulfame-K were treated as electrolyte, while maltose was considered as non-electrolyte. The apparent molar and specific volumes, their isentropic apparent molar and specific compressibilities, as well as their compressibility hydration numbers have been calculated and reported. Negative deviations from Debye–Huckel limiting law of apparent molar volume for acesulfame-K was obtained at given temperatures and can be used as a direct measure of the ion–ion and ion–solvent interactions. Furthermore, apparent specific volumes of the solutes were calculated and it was found that these values of the investigated solutes lie on the borderline between the values reported for sweet substances. The partial molar expansibility, its second derivative values, $(\partial^2 V^0/\partial T^2)$ and thermal expansion coefficient have been estimated.

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1. Introduction

The volumetric and acoustical behaviour of electrolytes and non-electrolytes provide useful information for solute–solvent and solute–solute interactions. Of particular importance is the nature of the interaction of water with dissolved species, in particular, ions of non-polar groups, which affect the structural properties of water. Intense sweeteners like acesulfame-K (6-methyl-1,2,3-oxathiazine-4-(3H)-one-2,2-dioxide-K salt) are extensively used due to effectively non-caloric and tooth friendly behavior. Whereas maltose (4-O-α-D-Glucopyranosyl-D-glucose) being used as sweetener and bulking agent in many food products across the world. A new approach to study the mechanism of sweet taste chemoreception is now focused on the role of water (Birch, Karim, Chavez, & Morini, 1993); the interactions of solutes with water may influence their accession to, and binding with receptor sites, affect their taste properties. Therefore, it is very important to understand the origin and nature of sweeteners-water interactions both qualitatively and quantitatively (Darja & Cveto, 2003).

This study concentrates on the thermodynamic properties of biological molecules in aqueous solutions (Birch, 2002; Birch & Parke, 1997). Therefore, the apparent and partial molar volumes,

expansibilities and compressibilities of the solute proven to be very useful tools in elucidating the structural interactions in solution (Cabani, Cants, Metteoli, & Time, 1981; Klofutar, Horvat, & Tasic, 2006; Millero, Surdo, & Shin, 1978). The partial molar and apparent specific volumes of different solutes have been used to distinguish solutes of different molecular weights on the basis of their ion-ion and ion–solvent affinity and in assessing drug potency and sweet taste chemoreception, whereas isentropic compressibility reflects the compactness of the hydration layers around the core of the solutes (Birch, 2002).

In this paper we report the volumetric and acoustical parameters such as apparent molar volumes (ϕ_V), apparent specific volume (ASV), apparent molar isentropic compressibility ($\phi_{K(S)}$), partial molar isentropic compressibility ($\phi_{K°(S)}$), partial molar volumes ($\phi_{V°}$) and their associated constants of sweeteners w.r.t. taste perception, taste quality and intensity to shed more light on such interactions. The behaviour of these parameters will be used to investigate the sensitive structural interactions occurring in solutions.

2. Materials and methods

Sweeteners (acesulfame-K and maltose monohydrate) used in this study were of analytical grade with purity of >99.9% and were procured from Sigma Aldrich, UK and Sherwin Williams Inc. (USA). The sweeteners were kept in vacuum desiccators over P_2O_5 for sus-

tainability. The water used in the experiment was deionized (Ultra-pure water purification system, model GSDI-3007, Daihan Lab Tech, Korea) and degassed prior to making solutions to avoid air intervention. The solutions of investigated sweeteners were prepared on molal concentration scale by using an electronic digital balance (Sartorius CP224S, model SAR CP224S, USA) with an accuracy of ±0.1 mg.

Densities (ρ) and ultrasonic velocities (μ) of aqueous solutions of investigated sweeteners were measured using an Anton Paar density and sound velocity meter (DSA 5000 M) at temperature range 20.0–45.0 °C (±0.05 °C) and atmospheric pressure. The instrument was calibrated once using air and distilled water before the measurement of solution density and sound velocity. Density and sound velocity measurements were accurate to 5×10^{-6} g/cm^3 and 0.5 m/s, respectively and carried out in duplicate to minimize errors.

3. Results and discussion

The values of density ρ (g cm^3) and ultrasonic velocity μ (m/s) for maltose monohydrate and acesulfame-K measured at various temperatures as a function of molality, m (mol kg^{-1}). The density data is used to calculate apparent molar volume ϕ_V (cm^3 mol^{-1}) of investigated sweeteners using Eq. (1) (Harned & Owen, 1958; Iqbal & Verrall, 1989).

$$\phi_V = (1000/m\rho\rho_0)(\rho_0 - \rho) + (M/\rho) \tag{1}$$

where ϕ_V, m, ρ, ρ_o and M are the apparent molar volume, molality of the solution, density of solution, density of the pure solvent and molar mass of the solute, respectively. The uncertainty in the apparent molar volume $\partial\phi_V$ was calculated using the following relation (Harned & Owen, 1958).

$$(\partial\phi_V)^2 = \left[-10^3/m\rho_0\right]^2 (\partial\rho)^2 \tag{2}$$

For both sweeteners the values of $\partial\phi_V$ were almost same which were 0.25–0.01 (cm^3 . mol^{-1}) at lowest and highest studied concentrations respectively. The similar values of $\partial\phi_V$ indicate almost similar solubility of both the sweeteners in water.

Apparent molar volumes, ϕ_V, are larger than molecular volumes and a real measurement of the molecular size of the hydrated molecules in solution. They are larger because the solute molecules actually create a gap between itself and the neighboring solvent molecules. The water molecules do not touch the surface of the solute, but they are held to it by H-bonds. Apparent molar volumes are the sum of the intrinsic volume of the solute, the volume due

to solute–solute interaction and that contributed by solute–solvent interactions (Galema & Hoiland, 1991). Fig. 1A shows that apparent molar volume increases with increasing concentration of the solute as solute–solute interaction replace solute–solvent interaction, and the solutes become less hydrated. Apparent molar volumes generally increase with increasing molecular weight of the solute. It also shows same increasing trend as temperature increases (Anil & Renu, 2013). The maltose is much larger molecule than the acesulfame-K sweetener, in accordance with this effect. However, it is possible for a molecule of large mass to have a smaller apparent molar volume than one of smaller mass (Shamil, Birch, Dinovi, & Rafka, 1989).

Apparent molar volume is therefore a measure of the packing efficiency of sweetener molecules among solvent molecules and is therefore governed by the interaction of sweeteners structure with water structure. It can be thought as a resultant of displacement and electrostrictive forces, the latter being constituted of H-bonds. The heavily hydrated molecules have smaller apparent molar volumes than those which are not. This is because of their greater interaction with water, which causes greater electrostrictive forces and the collapse of water structure around them. A low apparent molar volume indicates better packing characteristics, hence better interaction with water structure. The apparent molar volumes of salts, in this case, the salts of the intense sweetener, is smaller than those of comparable uncharged maltose molecule because salts are completely dissociated in solution and there is a greater electrostrictive effect around the ions (Cohn et al., 1934).

For investigated sweeteners, the concentration-dependence of, ϕ_V, at definite temperature was fitted with an equation of the type (Klofutar, Horvat, & Tasic, 2006).

$$\phi_V = \phi_{V^\circ} + A_v m^{1/2} + B_v m + D_v m^{3/2} \tag{3}$$

The above Eq. (3) represents the partial molar volume, ϕ_{V° (cm^3 mol^{-1}) which is equal to the limiting apparent molar volume of solute at infinite dilution. The increasing trend of ϕ_{V° is due to their hydration behaviour (Anil & Renu, 2013). A_v (cm^3 kg$^{1/2}$ mol$^{-3/2}$) is the Debye–Hückel limiting slopes for the apparent molar volume and B_v (cm^3 kg mol^{-2}) and D_v (cm^3 kg$^{3/2}$ mol$^{-5/2}$) are the empirical constants which depends on solute, solvent and temperature. The parameters ϕ_{V°, A_v and B_v were estimated for acesulfame-K by using least square fit method and the values of parameters of Eq. (3) are given in Table 1.

The data Table 1 represents variable trends for A_v and B_v with the increase in temperature. It was found that sign and magnitude
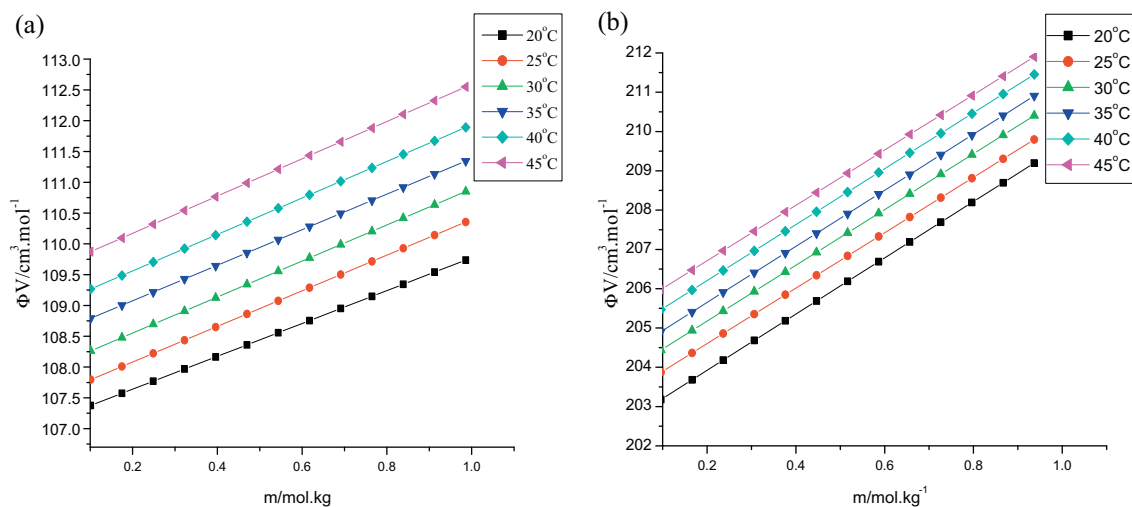

Fig. 1A. Plot of apparent molar volume (ϕ_V) against molality, m, for (a) acesulfame-K and (b) maltose monohydrate at indicated temperatures.