Journal of Molecular Liquids 123 (2006) 68 – 71

journal of MOLECULAR LIQUIDS

www.elsevier.com/locate/molliq

Studies on the effect of chlorides of magnesium, calcium, strontium and barium on the temperature of the sound velocity maximum of water

G. Venktaramana [1], E. Rajagopal, N. Manohara Murthy *

Department of Physics, Sri Krishnadevaraya University, Anantapur 515 003, India

Received 11 October 2004; accepted 15 February 2005
Available online 13 September 2005

Abstract

The effect of chlorides of magnesium, calcium, strontium and barium on the temperature of the sound velocity maximum (TSVM) of water, T_w, has been studied by determining the ultrasonic velocity using a single crystal variable path interferometer working at 3 MHz. The accuracy in ultrasonic velocity measurement is ± 0.05 m s^{-1}. The ultrasonic velocity measurements were carried out at $\simeq 2$ °C intervals over a range of 5 °C to either side of TSVM of the solutions. The accuracy in fixing TSVM is ± 0.2 °C. The shifts in TSVM of water due to the addition of $MgCl_2$ and $CaCl_2$, (ΔT_{obs}), are found to be positive at low concentrations becoming maxima around the weight fraction $w \simeq 2.3 \times 10^{-2}$ for $MgCl_2$ and $w \simeq 3.8 \times 10^{-2}$ for $CaCl_2$ and becoming negative around $w \simeq 5.6 \times 10^{-2}$ for $MgCl_2$ and $w \simeq 3.8 \times 10^{-2}$ for $CaCl_2$. (ΔT_{obs}) for $MgCl_2 > CaCl_2 > SrCl_2 > BaCl_2$ indicating that the strength of the structural interactions in modifying the hydrogen-bonded structure of water is in the order $Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$. The results are explained in the light of the structural properties of the anions and cations in the solutions in modifying the three dimensional hydrogen-bonded structure of water.

Keywords: Ultrasonic velocity; Temperature; Aqueous electrolytes; Structure

1. Introduction

The temperature of the sound velocity maximum (TSVM) observed for pure water at 74 °C and similar other extrema like density maximum at 3.98 °C, adiabatic compressibility minimum at 64 °C, isothermal compressibility minimum around 45 °C and heat capacity minimum around 35 °C can be explained on the basis of the two-state model for water, common to many theories on the structure of water [1–6]. At any given temperature there exists an equilibrium between the hydrogen-bonded clusters and non-hydrogen-bonded monomers of water. Rise in temperature produces volume expansion of both the species and an equilibrium shift between the two species resulting in an increase in the population of non-hydrogen-bonded water molecules. Volume expansion of both the species results in a negative temperature coefficient of sound velocity as where an increase in the population of monomers of water leads to the positive temperature coefficient of sound velocity. The maximum in ultrasonic velocity at 74 °C corresponds to the balance between these two opposing effects. The presence of an electrolyte changes the hydrogen-bonded structure of water due to the ion–solvent interactions there by affecting the temperature of the sound velocity maximum. The cations and anions may be classified as structure makers; that is, promoting or stabilizing the hydrogen-bonded structure of water against thermal collapse or structure breakers, i.e., destabilization of the hydrogen-bonded structure of water leading to the creation of monomers of water, depending whether the shift in TSVM is towards higher temperature or lower temperature.

Tamm and Haddenhorst [7], Mikhailov and coworkers [8–10], Marks [11], Pancholy and Singal [12] and Gnanamba and Ramachandra Rao [13] studied the effect of different electrolytes on TSVM of water, wherein the accuracy in fixing TSVM ranged from 2 to 5 °C. This large error in fixing TSVM led to ambiguity in delineating the structure-breaking or -making nature of the ions. With improved accuracy in ultrasonic velocity measurement, Subramanyam and Raghavan [14] studied the effect of LiCl, LiBr, LiI, NaCl, KCl and RbCl on

* Corresponding author.
E-mail address: nmanoharamurthy@yahoo.co.in (N. Manohara Murthy).
[1] Present address: Department of Physcis, Sri Lakshmi Sreenivasa Degree College, Pullareddy Peta, Kadapa 516175, India.

0167-7322/$ - see front matter © 2005 Published by Elsevier B.V.
doi:10.1016/j.molliq.2005.02.008

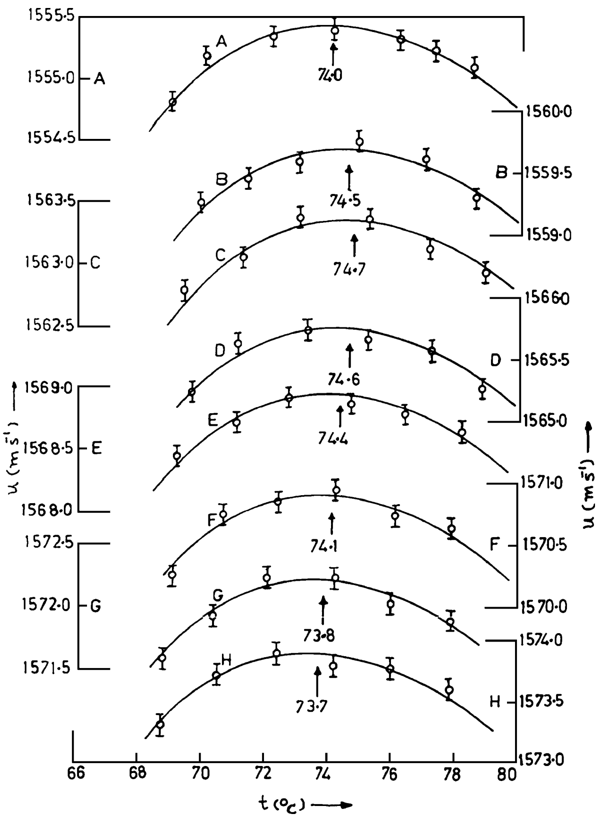

Fig. 1. Ultrasonic velocity (u) versus temperature (t) in aqueous magnesium chloride at different weight fractions. A — pure water; B — w=0.0091; C — w=0.0142; D — w=0.0283; E — w=0.0342; F — w=0.0484; G — w=0.0540; H — w=0.0661.

TSVM of water and the accuracy in fixing TSVM was ±0.2 °C. They could successfully classify the ions as structure makers (Li^+, Na^+) and structure breakers. (Rb^+, Cl^-, Br^-, I^-). Achari et al. [15] studied the effect of lithium carbonate, ammonium phosphate, ammonium acetate and strontium phosphate on TSVM of water. The effect of alkali fluorides, iodides, acetates, formates and nitrates on TSVM of water was studied by Sivakumar [16]. Venkataramana et al. [17,18] studied the effect of sulphates of lithium, sodium, potassium, ammonium and magnesium and halides of ammonium on TSVM of water and could delineate the structural propensities of the ions precisely as a result of improved accuracy in fixing TSVM. In the present work, the authors studied the effect of chlorides of magnesium, calcium, strontium and barium on TSVM of water with improved accuracy in fixing TSVM and the results are reported here.

2. Experimental

Ultrasonic velocities in pure water and in dilute solutions of $MgCl_2$, $CaCl_2$, $SrCl_2$ and $BaCl_2$ were determined using a single crystal variable path interferometer working at 3 MHz with an accuracy of ±0.05 m s^{-1}. The details of mechanical assembly, electronic circuitry employed and accuracy obtainable in ultrasonic velocity measurement are presented in our earlier communication [18]. For each solution, ultrasonic velocity measurements were made in the temperature range 68 to 80 °C at ~2 °C intervals. Solutions of the desired concentration of the electrolytes studied were prepared by weight using triple distilled degassed water.

3. Results and discussion

The measured ultrasonic velocities as a function of temperature at different concentrations of the aqueous electrolyte solutions of $MgCl_2$, $CaCl_2$, $SrCl_2$ and $BaCl_2$ are presented in Figs. 1–4. The ultrasonic velocity temperature curves for all the solutions studied have the same shape as the curve for pure water, and hence, a transparent template of the ultrasonic velocity–temperature curve for pure water was used to fix the TSVM of the solution. The accuracy in fixing TSVM is ±0.2 °C.

The temperature of the sound velocity maximum, T_s, and the observed shift in the TSVM of water, T_w, due to the addition of an electrolyte ΔT_{obs} ($=T_s-T_w$) at different weight fractions of $MgCl_2$, $CaCl_2$, $SrCl_2$ and $BaCl_2$ are presented in Table 1. Due to the non-availability of experimental data on the temperature dependence of the elastic constants of $MgCl_2$, $CaCl_2$, $SrCl_2$ and $BaCl_2$ in the literature, the authors could not evaluate the values of T_{id}, the ideal value of TSVM of the solution and hence the structural shifts as was done in the case of other electrolytes studied [17,18]. ΔT_{obs} versus weight fraction w, of $MgCl_2$, $CaCl_2$, $SrCl_2$ and $BaCl_2$ are presented graphically in Fig. 5. An examination of the data presented in Fig. 5 indicates that the values of ΔT_{obs} for $MgCl_2$ and $CaCl_2$ are positive at low concentrations becoming maxima around $w \simeq 2.3\times10^{-2}$ for $MgCl_2$ and $w \simeq 1.9\times10^{-2}$ for $CaCl_2$ and becoming negative around $w \simeq 5.6\times10^{-2}$ for $MgCl_2$ and $w \simeq 3.8\times10^{-2}$ for

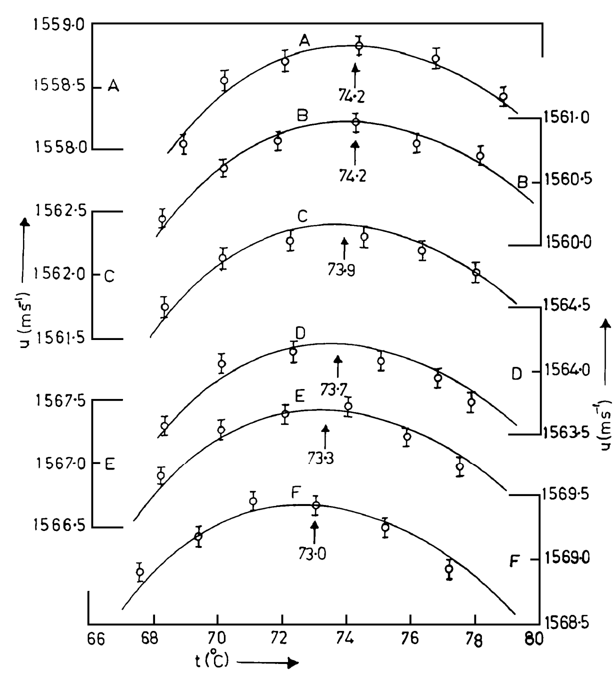

Fig. 2. Ultrasonic velocity (u) versus temperature (t) in aqueous calcium chloride at different weight fractions. A — w=0.0142; B — w=0.0257; C — w=0.0351; D — w=0.0440; E — w=0.0536; F — w=0.0646.