SHORT COMMUNICATIONS

ULTRASONIC STUDIES IN AQUEOUS SOLUTIONS OF NON-ELECTROLYTES WITH ALKALI HALIDES

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SEVERAL ultrasonic studies were carried out on aqueous solutions of alkali halides and aqueous solutions of non-electrolytes with alkali halides[1-5] Studies on aqueous solutions of non-electrolytes like sucrose, glucose and fructose with alkali halides NaF and NaCl revealed very interesting features on the nature of molecular interactions between the constituents in these solutions[6]. In the present communication, ultrasonic investigations on the effect of alkali halides on aqueous sugar solutions are reported. In intravenous transfusion of fluids, a certain amount of flow rate is to be maintained and it is interesting to study whether the flow rate changes with the alkali halide impurities as the water used may contain some alkali halide impurities. Literature survey shows that no such studies are carried out on sugar solutions with KF, KCl and LiCl except for the effect of K^+ ion on 0.2 M solutions of D-Glucose[7].

In the present investigation, sugars and alkali halides used are of AR/BDH/SM quality. The sucrose, glucose and fructose solutions were prepared by dissolving a known amount of the substance in double-distilled water to obtain 0.059 M, 0.175 M and 0.292 M concentrations of the sugar. The ultrasonic velocity (C) of the sugar solutions was determined by using ultrasonic interferometer 2 MHz (Mittal, Delhi) with an accuracy of 0.1% and the density of solutions was determined by using a pyknometer with an estimated accuracy of 0.001%. The experiment was repeated by adding potassium fluoride, potassium chloride and lithium chloride in the concentration range 0.1 M to 0.6 M. The temperature was maintained at 30±0.1°C by using a water thermostat. The values of ultrasonic velocity and density, the adiabatic compressibility (β_s), hydration number (h) and the apparent molal compressibility (ϕ_k) are calculated using the standard formulae[4,8]. The hydration number (h) is also

computed by limiting the values of ϕ_k as the concentration of alkali halide tends to zero through Wada's relation

$$\phi_k \underset{\text{Lim conc} \to 0}{} = \beta_s^0 V_h,$$

where β_s^0 is the compressibility of the solvent and V_h the hydration volume. The hydration numbers (mean values) of the alkali halides in sugar solutions are presented in table 1 along with figures indicating the hydration numbers as computed from Wada's relation. The values of mean apparent molal compressibility ϕ_k of various sugar solutions with alkali halides are presented in table 2.

Table 1 *Mean hydration numbers of alkali halides in various sugar solutions*

Conc. moles	Electro-lyte	Sucrose	Glucose	Fructose
0.059	KF	6.61 (5.66)	8.19 (7.44)	8.43 (7.59)
	KCl	6.39 (5.03)	6.84 (5.39)	7.43 (6.04)
	LiCl	4.33 (3.12)	5.18 (3.91)	5.26 (3.93)
0.175	KF	6.89 (6.01)	6.25 (5.39)	7.49 (6.55)
	KCl	5.48 (3.76)	6.00 (4.46)	6.13 (4.30)
	LiCl	4.68 (3.46)	4.71 (3.49)	5.34 (3.99)
0.292	KF	6.66 (5.92)	6.75 (6.08)	7.92 (7.37)
	KCl	5.04 (3.38)	5.76 (4.31)	5.49 (3.90)
	LiCl	4.49 (3.32)	4.98 (3.96)	5.32 (4.12)

Figures in brackets indicate the hydration numbers as computed from Wada's relation.

Table 2 *Mean apparent molal compressibility of sugar solutions with alkali halides*

Conc. moles	Electro-lyte	Sucrose	Glucose	Fructose
0.059	KF	4.39	5.85	5.98
	KCl	3.90	4.23	4.75
	LiCl	2.42	3.07	3.09
0.175	KF	4.55	4.15	5.06
	KCl	2.85	3.43	3.32
	LiCl	2.62	2.68	3.08
0.292	KF	4.36	4.61	5.59
	KCl	2.49	3.26	2.96
	LiCl	2.44	3.00	3.12

It is observed that the ultrasonic velocities in sucrose, glucose and fructose solutions are higher than that of water. As the concentration of sugar is increased the ultrasonic velocity is also increased. Ultrasonic velocities in sucrose solutions are higher than those in glucose and fructose solutions for the same molar concentration. Increase in ultrasonic velocity in solution is an indication of the association of sucrose, glucose and fructose molecules with water molecules. The association may be due to ionic hydration of the solute[9] or through hydrogen bonding between solute and solvent molecules[10,11]. The association in sugar solutions, may be due to hydrogen bonding among hydroxyl groups of sucrose, glucose and fructose with water molecules. Conductivity studies of sucrose solutions[12,13] also suggest hydrogen bonding in sucrose solutions. A greater ultrasonic velocity observed in sucrose solutions in comparison with glucose and fructose solutions, may be due to the larger number of OH groups in the sucrose than in glucose and fructose. The addition of KF, KCl and LiCl to sucrose, glucose and fructose solutions further increased the ultrasonic velocity. This increase in ultrasonic velocity may be attributed to the ionic hydration. As the concentration of KF, KCl and LiCl is increased, ultrasonic velocity increased perhaps due to the increased association. The ultrasonic velocities observed due to addition of KF are greater than those due to the addition of KCl. This is in accordance with the ultrasonic studies of Ramabrahmam[9] and Satyanarayanamurthy[14] whose studies showed that the ultrasonic velocity in aqueous solutions of metalic salts in general decreased with increase of atomic weight of the anion or cation when the other ion is fixed. The ionic radii of F^- and Cl^- are 1.36 Å and 1.81 Å respectively. The relatively small ions like F^- induce higher order in water structure[15]. Higher order means lower compressibility and higher ultrasonic velocity which is observed in the present studies. Higher ultrasonic velocity due to the addition of KF may also be attributed to fluorine which forms very strong hydrogen bonds in comparison with oxygen and chlorine. The smaller ultrasonic velocities with K^+ when compared to Na^+ are in agreement with earlier studies[9]. The computed values of compressibilities of sucrose, glucose and fructose solutions with alkali halides also support the conclusions drawn on velocity data. It can be seen from table 1 that for 0.059 M glucose and fructose solutions, the hydration number for any alkali halide concentration studied is greater as compared to the corresponding ones in the sucrose

solution. This is because glucose and fructose molecules have lesser number of hydroxyl groups per molecule than sucrose. Thus glucose and fructose may bring about a stabilization of water structure to a smaller extent and a large number of free monomer water molecules may exist. Thus the dissolved KF, KCl or LiCl molecules get themselves fully hydrated. It can be seen from table 1 that for the sugar solutions of all concentrations studied, the hydration number for KF is greater as compared to KCl and LiCl. This may be due to the strong electronegativety of fluorine. For all the sugar solutions the hydration numbers of LiCl are in general relatively small as compared to the hydration numbers of KF and KCl (table 1). A greater hydration number for KF or KCl may be due to the larger ionic radius of potassium in comparison with lithium. The ionic radii[16] of potassium and lithium are 1.33 Å and 0.60 Å respectively. The hydration numbers computed for KF, KCl and LiCl are based on the compressibility data and are in good agreement with the most probable integral values of primary hydration numbers[17]. Table 1 also shows that the compressibility data agree with the numbers reported by Wada. The observation that LiCl has smaller hydration numbers compared to KF and KCl may also be due to the fact that the lattice energy of LiCl (202 kcal/mole) is larger compared to the lattice energies of KF and KCl (190 and 167 kcal/mole)[18]. It is likely that in LiCl the disassociated Li^+ and Cl^- ions may recombine with greater probability thereby setting up a dynamic equilibrium between the ions and LiCl molecules. The exchange between these species may be responsible for the smaller hydration number observed in aqueous sugar solutions containing LiCl. The lower hydration number observed in aqueous sugar solutions containing LiCl also indicates that the positive ionic charge alone is not responsible for hydration. Since a smaller number of electrons circulate around the Li^+ ion, the positive charge is more exposed. If positive charge alone is responsible for hydration, one would expect a greater hydration number for the positive charge of potassium. The present studies therefore indicate that electronic charges may also play a significant role in hydration in the solutions. The mean values of apparent molal compressibilities of sugar solutions with alkali halides are shown in table 2. The behaviour is found similar to the hydration numbers. These studies indicate that the presence of halide impurities alter the flow characteristics of aqueous sugar solutions some of which are used in intravenous transfusion.

Hence it is necessary that the water in these solutions should be free from even the trace impurities of alkali halides.

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IRIDIUM ENRICHMENT AT CRETACEOUS/TERTIARY BOUNDARY IN MEGHALAYA

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EXCESS iridium has been observed to occur at the Cretaceous/Tertiary (K/T) boundary at sevei il locations on the earth. The source of iridium is believed to be extraterrestrial such as asteroids[1] or comets[2] or the earth's mantle from where it emanated during large scale volcanism that occurred in peninsular India[3]. We report here results of a geochemical study in a marine section in the eastern Tethys across the K/T boundary. The results confirm enhanced iridium levels of 12 ppb at the boundary in Um Sohryngkew river section in Meghalaya, which is correlated with high concentration of several elements such as Fe, Co, Ni, rare earths etc, whereas calcium and barium show depletion at the boundary. The results are compared with geochemical behaviour observed at other sites.

Marine sections preserving K/T boundary are exposed on the eastern margin of the Indian shield, in the Cauvery basin and in Cherrapunji area of the southern Shillong plateau[4]. The Um Sohryngkew river section in Meghalaya is believed to have uninterrupted sedimentation having principal litho units of Cretaceous-Paleocene age which includes the Mahadeo, Langpar, Therria and Lakadong formations. The K/T boundary, based on the studies of planktonic foraminifera lies about 10 meters below the Mahadeo/Langpar contact in light to medium grey shales, characterized by a brown limonitic and nodular shale about 1.5 cm thick and turning more brownish in the Paleocene

The foraminiferal shows an abrupt break in the planktonic constituents across the boundary although quite a few benthic types remain unaffected. The typical assemblages in the cretaceous include Globotruncana-Globigerina eugubina zone[4]

Samples at about 10 cm intervals, across the boundary were collected in 1985, and based on the observation of excess iridium in one sample, a fine sampling at intervals of 0.5–5 cm was done in May 1986, in a 30 cm thick section.

Concentration of iridium, rare earths and several other elements of interest was measured by in-