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Ultrasonic Characterization of Ferrous Ammonium Sulphate in Aqueous Galactose Solutions

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Ultrasonic velocities and densities of aqueous ternary solutions containing ferrous ammonium sulphate (0.0 to 1.0 M) and aqueous galactose (0.0, 0.5 and 1.0 M) at 308 K have been measured using ultrasonic interferometric and pyknometric techniques. The experimental data have been used to calculate several ultrasonic parameters *viz.*, adiabatic compressibility (β_s), inter molecular free length (L_f), molar sound velocity (R), specific acoustic impedance (Z) and hydration number (H_n). The results have been interpreted in terms of structure making (SM) and structure breaking (SB) properties of ferrous ammonium sulphate in aqueous galactose solutions.

Key Words: Ferrous ammonium sulphate, Ultrasonic velocity, Adiabatic compressibility, Inter molecular free length, Specific acoustic impedance, Molar sound velocity, Hydration number, Structure maker, Structure breaker.

INTRODUCTION

The ammonium salts play significant role in several fields of chemistry *viz.*, medicinal chemistry, explosive chemistry, industrial chemistry, *etc.* and are, also, used as a micro-cosmic salts as laboratory reagent for testing silica as well as in manufacturing of crackers, fertilizers, dyes, *etc*. On the other hand, the role of biomolecules such as polyols and carbohydrates on thermodynamic characteristics of ternary and quaternary solutions and their interactions with electrolytes are biologically and physico-chemically significant. In recent years, the interactions and thermodynamic characteristics of ternary system consisting of electrolytes and non-electrolytes have been subjected to several physico-chemical investigation[1-3] because of their physico-chemical importance.

Studies on interactions of polyhydroxy compounds with electrolytes in different solvents are very significant for investigating structure making and breaking behaviour of non-electrolytes. Robinson and Strokes[4,5] carried out extensive studies on electrolytes-solvent-non-electrolytes systems. Such studies have also been undertaken conductometrically[1-6] and viscometrically[7,8]. Conway and Verrall[9] have reported the compressibility behaviour tetra alkyl ammonium and ammonium salts in water.

Ultrasonic techniques have not been used for studying such systems. It is recently developed technique for investigating intermolecular interactions, structural characteristics and hydration of polyhydroxy compound in biomolecular solutions. Jasra and Ahluwalia[10] have been reported solute-co-solute interactions in sorbitol and NaCl mixture.

The present paper reports the study of aqueous ternary solutions of ferrous ammonium sulphate and galactose using ferrous ammonium sulphate as a solute and aqueous galactose solution as a solvent for investigating the concentration effects of electrolytes on different ultrasonic parameters as well as structural characteristics of ferrous ammonium sulphate. Extensive survey of literature on ammonium salts and their interactions with biomolecules reveals that the ultrasonic characterization of double ammonium salts has rarely been reported. No comprehensive and systematic approach to investigate interactions between ammonium salts and biomolecules as well as thermodynamic characteristics of ammonium salts in biomolecular solutions has so far been made by ultrasonic technique.

EXPERIMENTAL

All chemical used in this work were either Sarabhai, M. Chemicals or CDH or BDH of A.R. grade with minimum assay 99.8%. They were used as such without further purification. Galactose solution of concentration 0.0, 0.5 and 1.0 M were prepared by weight dilution method using doubly distilled deionized water (K = 2.48 μ mho, pH = 7.8) of high dielectric constant (D) = 78 at 25 °C. Ferrous ammonium sulphate solutions of different molarities were prepared using aqueous galactose solution as solvents. A digital balance (Citizen, made in Germany) of accuracy 10^{-4} g was used to prepare different solutions.

Ultrasonic interferometer has been used for measuring ultrasonic velocity of solutions at a constant temperature of 308 K in present study. Single crystal ultrasonic interferometer (Mittal enterprises, New Delhi Model F-81) was used at a fixed frequency of 1.5 MHz.

The densities of water and different solutions of ferrous ammonium sulphate in aqueous galactose solution were measured at 308 K by calibrated bicapillary pyknometer in conventional way. Density data were found to be accurate with ± 0.02 %. The constant temperature of solution was maintained by using electronically controlled water thermostat using mercury contact thermometer of accuracy ± 0.1 K.

Various ultrasonic parameters were computed from the ultrasonic velocity (u) and density (ρ) data using the following equations 1-5:

Adiabatic compressibility (β_s) : $\beta_s = 1/u^2\rho$ (1)

Inter molecular free length (L_f): $L_f = K^* \beta_s^{-½}$ (Jacobson's empirical equation) where, K is Jacobson's constants (2)

Molar sound velocity (R): $R = (M/e)\cdot u^{1/3}$ (3)
where M = Effective molecular weight

Specific acoustic impedance (Z): $Z = \rho^*e$ (4)

Hydration number (Hn): $H_n = n_o/n\ (1-\beta_s/\beta_s^o)$ (5)

where u is the ultrasonic velocity, ρ is density of solution, β_s and β_s^o are the compressibility of the solution and solvent, n and n_o are the number of moles of solute and solvent, respectively. M is the effective molecular weight of ternary solution given by:

$$M = (n_1M_1 + n_2M_2 + n_3M_3)/(n_1 + n_2 + n_3)$$

where n_1, n_2 and n_3 are the number of moles of ferrous ammonium sulphate (1), water (2) and galactose (3) and M_1, M_2 and M_3 are their respective molecular weights.

RESULTS AND DISCUSSION

Ferrous ammonium sulphate ($FeSO_4.(NH_4)_2SO_4.6H_2O$) is a double salt. Its aqueous solution is slowly hydrolyzed and so the ultrasonic velocity has been measured using the freshly prepared aqueous ferrous ammonium sulphate solution. The plots of ultrasonic velocity *versus* ferrous ammonium sulphate molarities (M) in water and in aqueous galactose solution of different molarities are shown in Fig. 1. Normally, in presence of electrolyte, sound velocity and compressibility show a linear behaviour with molar concentrations. However, non-linearity, too, has been observed. In present case, these plots display almost linearity which perhaps indicates the presence of short-range weak interactions in present system. Increase in velocity has also been found in presence of ferrous ammonium sulphate with increasing aqueous galactose concentrations.

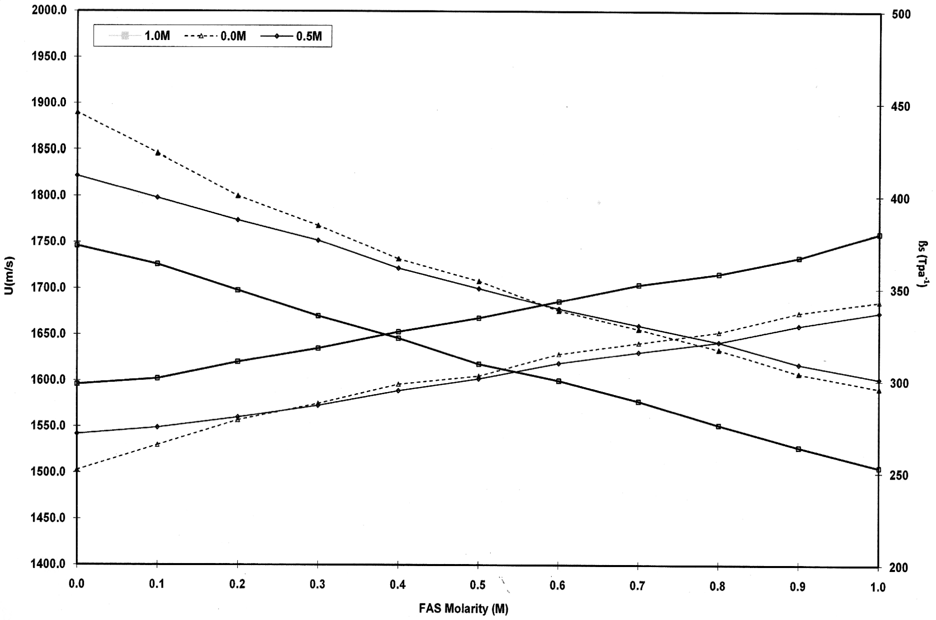

Fig. 1. Ultrasonic velocity (u) and adiabatic compressibility (βs) profiles of ferrous ammonium sulphate (FAS) with its molarity (M) in aqueous glactose solution of different molarities (0.0, 0.5 and 1.0 M)

The variation of ultrasonic velocity with concentration can also be expressed in terms of concentration derivative of density and compressibility by following equation[11]:

$$du/dc = -u/2\ (1/\rho * d\rho/dc + 1/\beta_s * d\beta_s/dc)$$

The velocity change depends on the sign of the concentration derivatives of density (dρ/dc) and compressibility ($d\beta_s/dc$) which have got opposite sign. The former quantity is positive while latter is negative. Velocity is found to increase with ferrous ammonium sulphate concentration in present system while compressibility decreases with ferrous ammonium sulphate concentration. The compressibility factor appears to be dominant for velocity change[12].

Erying *et al.*[13] pointed out that the sound velocity is infinite within the molecule and is equal to gas kinetic velocity in intermolecular space. According to this idea, the increase in the free length of solution due to process of mixing results in decrease of ultrasonic velocity. This indicates that intermolecular free length and sound velocity are correlated. Formation of hydrogen bond results in decrease in free length. Structure-making and breaking (hydrogen bond formation and destruction) property of solute can be co-related with variation in sound velocity. Solute which increases the ultrasonic velocity, therefore, acts as structure maker (SM) and those decreasing the ultrasonic velocity as a structure breaker (SB). Variation of ultrasonic velocity in terms of structural properties of ions have also been discussed by Nambinarayan and Srinivasan Rao[14] who have correlated the decrease in velocity with structure breaking property of ion. It is well known that large monovalent ion have generally structure breaking effect. In present study, the ultrasonic velocity of ferrous ammonium sulphate solution increases in water as well as in aqueous galactose solutions with increasing ferrous ammonium sulphate concentration which reveals that ferrous ammonium sulphate is structure maker in water and also in aqueous galactose solution.

The adiabatic compressibility (β_s) is most significant thermodynamic and acoustic parameter related to ultrasonic velocity. The compressibility profile of ferrous ammonium sulphate in aqueous galactose solution of different molar concentration (0.0, 0.5 and 1.0 M) are displayed in Fig. 1. Linearity of these plots also supports the presence of short range weak interactions in the system being studied. Compressibility in water is greater than that in aqueous galactose solutions and decreases with the increasing aqueous galactose concentration as shown in Fig. 1. Compressibility change may also be interpreted in terms of structural properties of ferrous ammonium sulphate.

Inter molecular free length (L_f) is correlated with adiabatic compressibility (β_s) by Jacobson's empirical eqn. 2. Since, inter molecular free length is directly proportional to β_s, its behaviour should therefore be similar to that of compressibility. Variation of inter molecular free length with ferrous ammonium sulphate molarity is found to be similar to that of compressibility in present system as shown in Fig. 2. The validity of Jacobson equation can be tested from the plot of L_f^2 *versus* β_s. The linearity of such plots would show its validity. Fig. 3 exhibits the linearity of plot which reveals the validity of Jacobson's empirical equation.

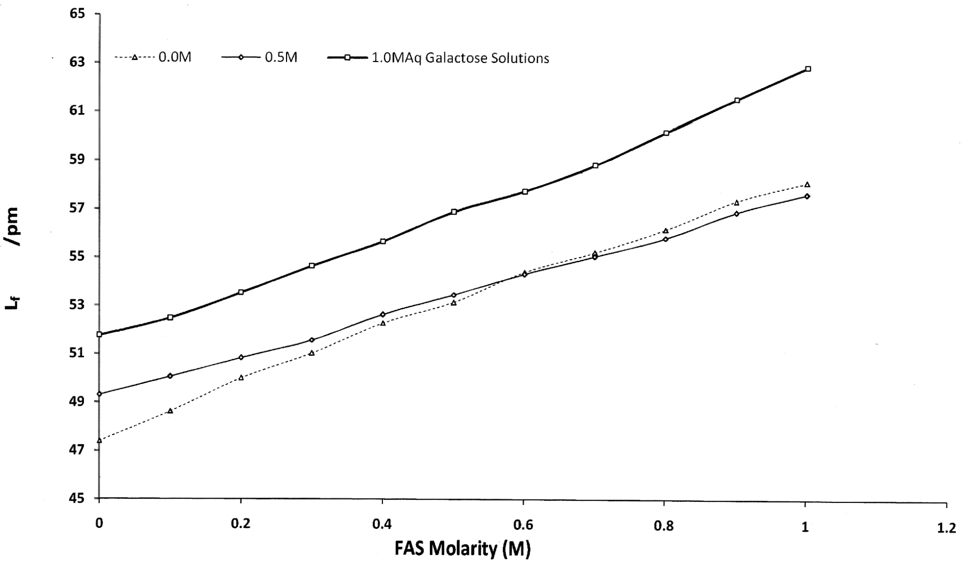

Fig. 2. Variation of inter molecular free length (L_f) of ferrous ammonium sulphate (FAS) with its molarity (M) in aqueous glactose solution of different molarities (0.0, 0.5 and 1.0 M) at 308 K

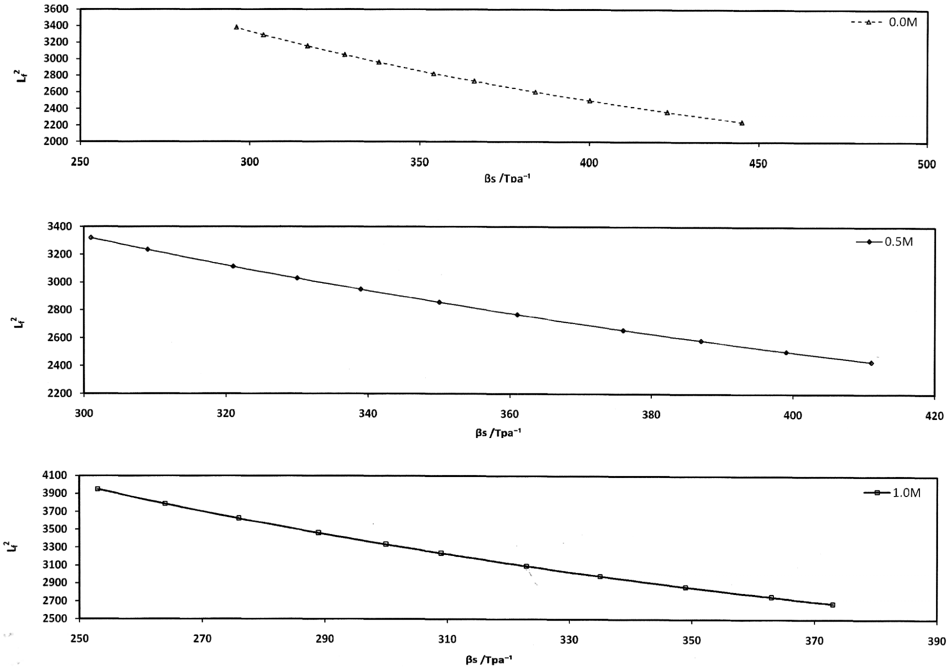

Fig. 3. Test for validity of Jacobson's empirical equation at different molarity

Hydration number (Hn) is a solution parameter related to adiabatic compressibility (β_s) of a solution. The hydration number of ferrous ammonium sulphate in water and in different aqueous galactose solutions have been computed from the adiabatic compressibility using eqn. 5. Fig. 4 displays plots of hydration number (Hn) *vs*. FAS molarity (M). Ferrous ammonium sulphate containing Fe^{2+}, NH_4^+ and SO_4^{2-} ions in an aqueous solution is extremely get hydrated. Fig. 4 reveals that the hydration number (Hn) of ferrous ammonium sulphate in water is greater than that in aqueous galactose solution and is found to be gradually decreasing with increasing ferrous ammonium sulphate concentration. Increasing the concentration of aqueous galactose solution brings about a decrease in hydration number (Hn). Change may be described as a change of the secondary hydration into primary hydration[16-21]. It appears that electrolyte concentration has no pronounced effect on ferrous ammonium sulphate hydration.

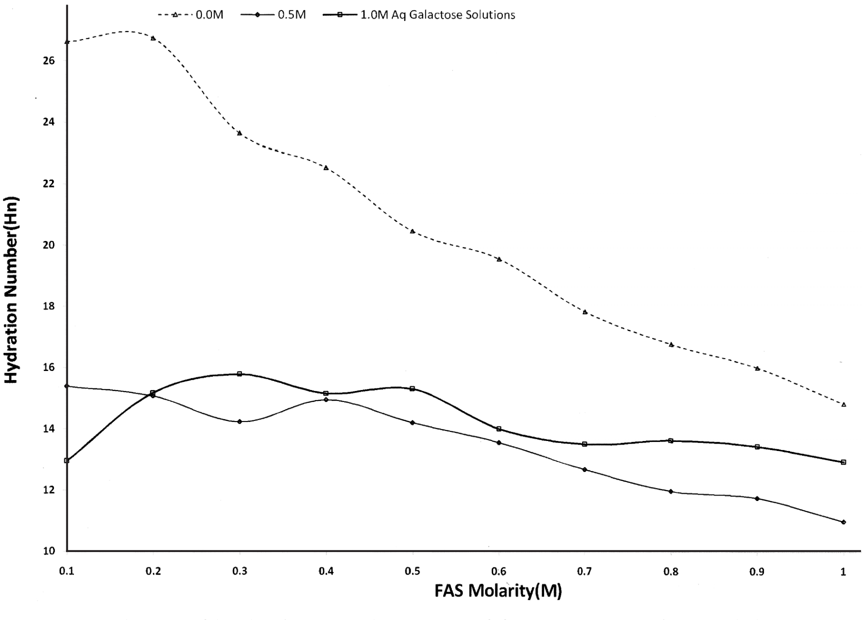

Fig. 4. Dependence of hydration number (Hn) of ferrous ammonium sulphate (FAS) on its molarity (M) in aqueous glactose solution of different molarities (0.0, 0.5 and 1.0 M) at 308 K

The validity of Bachem's relation[22] given below:

$$(\beta_s - \beta_s^o)/C = A + B\sqrt{C}$$

where, β_s and β_s^o are the adiabatic compressibility of solution and solvent respectively. C is the molar concentration of solute and A & B are constant, can also be tested by plotting (β_s-βs^o/C) *versus* $\sqrt{C}$. Such plots in present system are found to be linear which shows that compressibility of ferrous ammonium sulphate in aqueous galactose solution obeys Bachem's empirical relation.

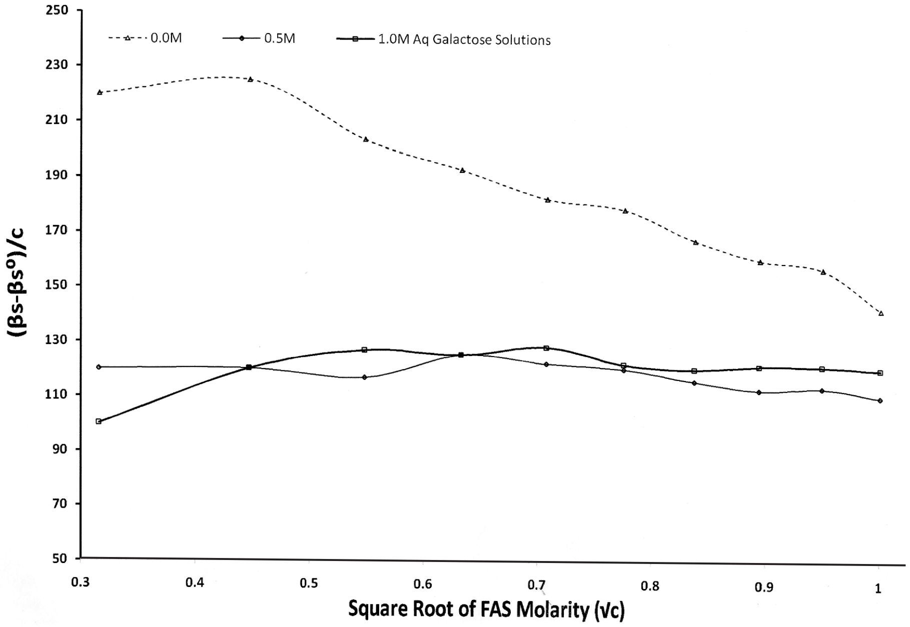

Fig. 5. Test of validity of Bachem's empirical equation

The molar sound velocity (R) is another ultrasonic parameter correlated with ultrasonic velocity (u) and molar volume (v).The molar sound velocity (R) of ferrous ammonium sulphate in different aqueous glactose solutions has been calculated from ultrasonic velocity data and effective molar volume of solutions using eqn. 3.

The specific acoustic impedance (Z) is yet another acoustical parameter related to ultrasonic velocity (u) and density (ρ) of ferrous ammonium sulphate in aqueous galactose solution using eqn. 4. Molar ferrous ammonium sulphate (R) and specific acoustic impedance (Z) are smallest in water and these are found to increase with increasing ferrous ammonium sulphate molarity and also with increasing galactose concentration as shown in Figs. 6 and 7.

The increase in these parameters may be due to greater increase in effective molar volume and density respectively than the decrease in ultrasonic velocity. The structural properties of solute can be analyzed in terms of ferrous ammonium sulphate (R) and specific acoustic impedance (Z) in the similar way as in the case of other ultrasonic parameters.

It may, finally, be concluded that:

(**1**) There are short range weak interactions in the present system.

(**2**) Ferrous ammonium sulphate and galactose are structure maker (SM).

(**3**) There is no appreciable change in hydration number (Hn) of ferrous ammonium sulphate in aqueous galactose solutions of different molarities. These data may be of great theoretical and physico-chemical significance in the field of solution chemistry, molecular biology, physical sciences, bio-sciences, *etc.*

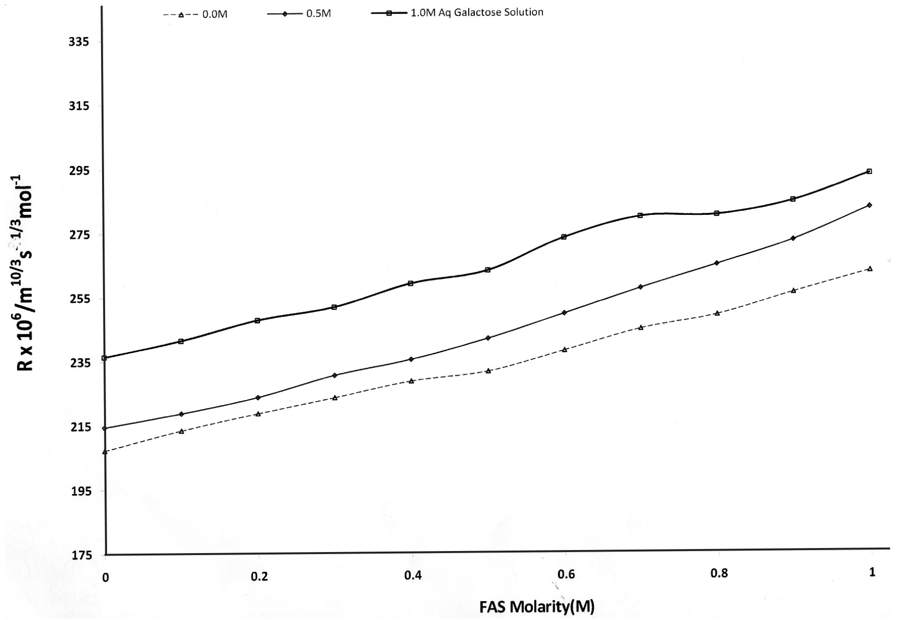

Fig. 6. Variation of molar sound velocity (R) of ferrous ammonium sulphate (FAS) with its molarity (M) in aqueous galactose solution of diffeent molarities (0.0, 0.5 and 1.0 M) at 308 K

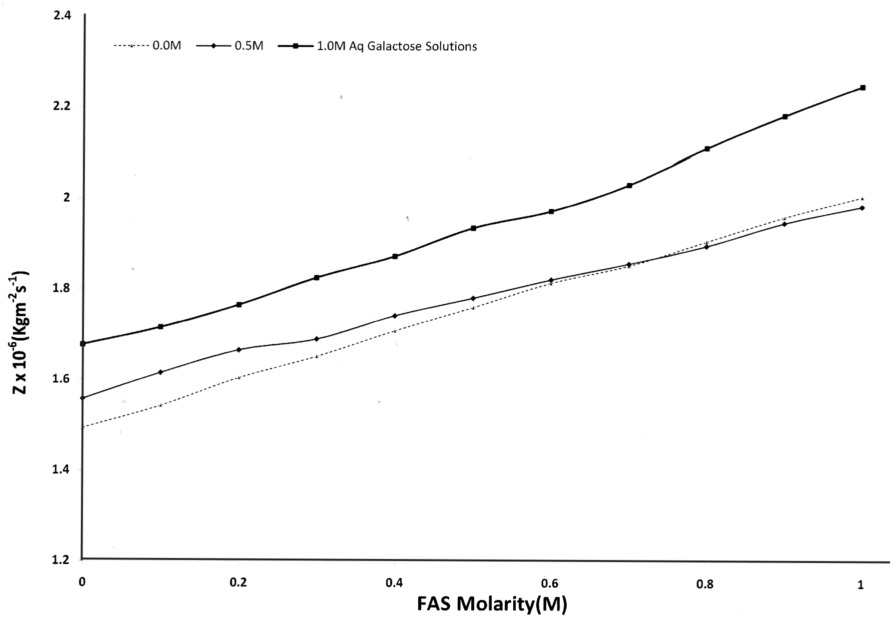

Fig. 7. Variation of specific acoustic impedance (Z) of ferrous ammonium sulphate (FAS) with its molarity (M) in aqueous galactose solution of diffeent molarities (0.0, 0.5 and 1.0 M) at 308 K

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