



Acoustical and thermodynamical properties of lactose in mixed aqueous electrolytic solutions at 298.15K

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ABSTRACT

Ultrasonic velocity (U), viscosity (η) and density (ρ) of lactose of (0.5m) in three aqueous electrolytic solutions of guanidine hydrochloride (GuHCl), barium chloride (BaCl_2) and strontium chloride (Sr Cl_2) have been measured at 298.15 K. The derived acoustical parameters namely adiabatic compressibility (β), apparent molal compressibility (ϕ_K), apparent molal volume (ϕ_V), limiting apparent molal compressibility (ϕ_K^0), limiting apparent molal volume (ϕ_V^0), and their constant (S_K , S_V), viscosity B -coefficient and hydration number (n_H) have been computed from the experimental data. The variation of these parameters with respect the molality of solute has been discussed in terms of solute-solvent and solute-co-solute interactions.

Keywords: Ultrasonic velocity, adiabatic compressibility, hydration number, apparent molal compressibility, apparent molal volume.

INTRODUCTION

Ultrasonic investigations provide an extensive application in characterising acoustical and thermodynamic behaviour of electrolytic mixtures. The measurement of ultrasonic speed enables the accurate determination of some useful acoustical parameters which are highly sensitive to molecular interactions. Ultrasonic velocities and their related thermodynamic properties have been used to study the physico-chemical behaviour and molecular interactions in electrolytes. Ultrasonic study of binary and ternary mixtures containing electrolytes is of considerable theoretical and industrial importance.

The study of carbohydrates/disaccharides has become a subject of increasing interest, because of the multidimensional, physical, biochemical and industrially useful properties of these compounds. In addition to their importance to the food, pharmaceutical and chemical industries, the simple saccharides have received considerable attention for their ability to protect biological macromolecules. Saccharide molecules have several hydroxyl groups interact with metal ions to produces a variety of metal saccharide complexes. These complexes are weak, but the interactions are specific¹.

In recent years, the study of acoustical properties of aqueous mixed electrolytic solutions has been found to be useful in understanding the specific ion-ion and ion-solvent interaction in solutions. The accurate measurement of density, viscosity, sound velocity and hence the derived parameters such as adiabatic compressibility and apparent molal volume will give significant information regarding the state of affairs in a solution. Such studies on binary electrolytes have been made by many researchers²⁻³. However, ultrasonic velocity studies on ternary electrolytes have not received as much attention as that of binary electrolytes. Currently the studies on carbohydrates have become an interesting topic of research from which their physico-chemical properties could be assessed. Since physico-chemical studies of binary electrolytes cannot be so useful to get a definite conclusion regarding the structural properties and the type of interaction involved the study of ternary electrolytes is gaining much importance now-a-days. Ionic association and electrostatic interactions are the prime factors that must be considered in these electrolytes. It is evident from the prevailing literature that very few attempts have been made to study the molecular interactions among the carbohydrates in aqueous electrolytic solutions through ultrasonic velocity measurements.

Owing to these considerations an attempt has been made to elucidate the molecular associations / interactions of lactose in three aqueous electrolytic solution (0.5m) of guanidine hydrochloride, barium chloride and strontium chloride solutions at 298.15K by measuring ultrasonic velocity (U), density (ρ) and viscosity (η). From the experimental values the acoustical parameters such as adiabatic compressibility (β), apparent molal compressibility (ϕ_k), apparent molal volume (ϕ_v), limiting apparent molal compressibility (ϕ_k^0), limiting apparent molal volume (ϕ_v^0) and their constants (S_K, S_V), viscosity B-coefficient of Jones-Dole equation and molal hydration number (n_H) have been computed to shed more light on such interactions.

MATERIALS AND METHODS

Experimental Technique

All the chemicals used in this present research work are spectroscopic reagent (SR) and analytical reagent (AR) grades of minimum assay of 99.9% obtained from E-Merck, Germany and Sd Fine chemicals, India, which are used as such without further purification. Doubly distilled deionised water has been used for preparing 0.5m of aqueous electrolytic solution namely guanidine hydrochloride, barium chloride and strontium chloride. The required quantity of lactose for given molality was dissolved in aqueous electrolytic solution and similar procedure has been adopted for different molalities of lactose. All the solutions were prepared by weight using an electronic digital balance having an accuracy of ± 0.1 mg. (Model: SHIMADZU AX-200). The density was determined using a specific gravity bottle by relative measurement method with an accuracy of ± 0.1 kg·m⁻³. An Ostwald's viscometer (10ml capacity) was used for the viscosity measurement and efflux time was determined using a digital chronometer within ± 0.01 s. An ultrasonic interferometer having the frequency 3 MHz (Mittal Enterprises, New Delhi, Model: F81) with an overall accuracy of $\pm 0.1\%$ has been used for velocity measurement. An electronically digital operated constant temperature bath (RAAGA Industries) has been used to circulate water through the double walled measuring cell made up of steel containing the experimental solution at the desired temperature. The accuracy in the temperature measurement is ± 0.1 K.

Theory and Calculations

Various acoustical and thermodynamical parameters are calculated from the measured data such as *Adiabatic Compressibility*

$$\beta = \frac{1}{U^2 \rho} \quad \dots(1)$$

The apparent molal compressibility has been calculated from relation,

$$\varphi_K = \frac{1000}{m\rho_0} (\rho_0\beta - \rho\beta_0) + \left(\frac{\beta_0 M}{\rho_0} \right) \quad \dots(2)$$

where β , ρ and β_0 , ρ_0 are the adiabatic compressibility and density of solution and solvent respectively, m is the molal concentration of the solute, and M the molecular mass of the solute. φ_K is the function of m as obtained by Gucker⁴ from Debye Huckel theory⁵ and is given by

$$\varphi_K = \varphi_K^0 + S_K m^{1/2} \quad \dots(3)$$

where φ_K^0 is the limiting apparent molal compressibility at infinite dilution and S_K is a constant. φ_K^0 and S_K of equation (3) have been evaluated by the least square method.

The apparent molal volume φ_V has been calculated using the relation

$$\varphi_V = \left(\frac{M}{\rho} \right) - \frac{1000(\rho - \rho_0)}{m\rho\rho_0} \quad \dots(4)$$

The apparent molal volume φ_V has been found to differ with concentration according to Masson⁶ empirical relation as

$$\varphi_V = \varphi_V^0 + S_V m^{1/2} \quad \dots(5)$$

where φ_V^0 is the limiting apparent molal volume at infinite dilution and S_V is a constant and these values were determined by least square method.

The viscosity A and B coefficients for the lactose in aqueous electrolytic solutions are calculated from the Jones-Dole equation⁷.

$$\frac{\eta}{\eta_0} = 1 + Am^{1/2} + Bm \quad \dots(6)$$

where, η and η_0 are the viscosities of the solution and solvent respectively and m is the molal concentration of the solute. A is determined by the ionic attraction theory of Falkenhagen-Vernon and therefore also called Falkenhagen coefficient⁸, B or Jones-Dole coefficient is an empirical constant determined by solute-solvent interactions.

The molal hydration number has been computed using the relation,

$$n_H = \left(\frac{n_1}{n_2} \right) \left(1 - \frac{\beta}{\beta_0} \right) \quad \dots(7)$$

where β and β_0 are adiabatic compressibilities of solution and solvent respectively, n_1 and n_2 are number of moles of solvent and solute respectively.

RESULTS AND DISCUSSION

The experimental values of density, viscosity and ultrasonic velocity for different molal concentration of lactose in (0.5m) of the three aqueous electrolytic solution viz. guanidine hydrochloride, barium chloride and strontium chloride are shown in Table 1. The values of adiabatic compressibility (β), apparent molal compressibility (φ_K), apparent molal volume (φ_V), limiting apparent molal compressibility (φ_K^0), limiting apparent molal volume (φ_V^0), and their

constants (S_K , S_V), the values of A and B co-efficients of Jones-Dole equation and hydration number (n_H) are given in Tables 2&3.

In all the three systems the values of density and ultrasonic velocity (Table 1) are increases with increase in molal concentration of lactose. This increasing behaviour suggests, a moderate strong electrolytic nature in which the solute tends to attract the solvent (aqueous electrolytic solutions) molecules. Generally the values of ultrasonic velocities are smaller in aqueous guanidine hydrochloride solution than other two systems. Molecular association is thus responsible for the observed increase in ultrasonic velocity in these mixtures. The increase in ultrasonic velocity in these solutions may be attributed to the cohesion brought about by the ionic hydration.

The decrease in adiabatic compressibility (Table 2) observed in aqueous electrolytic solutions with lactose in the present study generally confirms that conclusion drawn from the velocity data. The decrease in compressibility imply that there is enhanced molecular associations in these system on increase in solute content, as the new entities (formed due to molecular association) become compact and less compressible. The interaction between the solute and the water molecules in the solvent is termed as hydration. The positive values of hydration number indicate an appreciable solvation of solutes⁹. This is an added support for the structure intensifying property of the solutes as well as the presence of appreciable dipole-dipole interaction between solute and water molecules. This also suggests that compressibility of the solution will be less than that of solvent. As a result, solutes will gain mobility and have more probability of contacting solvent molecules. This may enhance the interaction between solute and solvent molecules. From Table 2 it is observed that the values of n_H decreases with increasing the concentration of lactose in all the three systems studied. This shows that aqueous electrolytic solutions have a dehydration effect on the lactose.

The following observations have been made on ϕ_K and ϕ_V (Table 2) of the lactose in aqueous electrolytic solutions.

- (i) the values of ϕ_K and ϕ_V are all negative over the entire range of molality and the same increases with increase in concentration of solute in all the three systems
- (ii) The maximum value of ϕ_V obtained in all the systems is in the order guanidine hydrochloride > barium chloride > strontium chloride.

The increasing values of ϕ_K reveals that strengthening of solute-solvent interactions exist in these mixtures. The negative values of ϕ_V indicate electrostrictive solvation of ions¹⁰. From the magnitude of ϕ_V , it can concluded that, strong molecular association is found in strontium chloride solution than the other two solutions and hence strontium chloride is a more effective structure maker than others.

ϕ_K^0 provides information regarding solute – solvent interactions and S_K , that of the solute – co-solute interactions in the mixtures. From the Table 3 it is observed that ϕ_K^0 and ϕ_V^0 values are negative in all the three systems studied. Appreciable negative value of ϕ_K^0 for all the systems reinforce our earlier view that existence of solute-solvent interaction. The values of S_K and S_V exhibits in negative in all the systems studied which indicates the existence of ion-solute interactions. Further the magnitude of ϕ_V^0 is in the order: $\text{SrCl}_2 < \text{BaCl}_2 < \text{GuHCl}$.

Table 1: Values of density (ρ), viscosity (η) and ultrasonic velocity (U) of lactose in aqueous electrolytic solution (0.5m) at 298.15 K for

Molality m/(mol. kg ⁻¹)	ρ /(kg.m ⁻³)	η /($\times 10^{-3}$ Nsm ⁻²)	U/(ms ⁻¹)
System I : water+GuHCl+lactose			
0.00	1009.7	0.9139	1531.8
0.02	1012.4	0.9259	1558.2
0.04	1015.5	0.9413	1581.0
0.06	1017.0	0.9539	1599.0
0.08	1018.2	0.9683	1611.1
0.10	1019.7	0.9825	1618.1
System II : water+BaCl₂+lactose			
0.00	1048.4	0.9659	1542.2
0.02	1051.1	0.9874	1568.6
0.04	1053.7	1.0093	1591.4
0.06	1055.6	1.0282	1609.4
0.08	1056.9	1.0494	1621.5
0.10	1058.4	1.0709	1628.5
System III : water+SrCl₂+lactose			
0.00	1054.3	0.9842	1550.5
0.02	1055.6	1.0087	1576.9
0.04	1058.0	1.0274	1599.8
0.06	1059.2	1.0494	1617.8
0.08	1060.0	1.0677	1630.2
0.10	1061.8	1.0899	1637.4

Table 2 : Values of adiabatic compressibility (β), hydration number (n_H), apparent molal compressibility (ϕ_K) and apparent molal volume (ϕ_V) of lactose in aqueous electrolytic solution (0.5m) at 298.15 K for

Molality m/(mol. kg ⁻¹)	β /($\times 10^{-10}$ m ² N ⁻¹)	(n_H)	ϕ_K /($\times 10^{-8}$ m ² N ⁻¹)	ϕ_V /(m ³ mol ⁻¹)
System I : water+GuHCl+lactose				
0.00	4.221
0.02	4.068	9.66	-8.21	-136.18
0.04	3.940	8.88	-7.63	-133.45
0.06	3.846	7.90	-6.75	-111.91
0.08	3.784	6.90	-5.91	-105.35
0.10	3.745	6.01	-5.18	-99.73
System II : water+BaCl₂+lactose				
0.00	4.011
0.02	3.867	20.66	-26.38	-2052.15
0.04	3.748	13.80	-16.43	-1088.96
0.06	3.657	10.97	-12.60	-758.82
0.08	3.599	9.08	-10.24	-584.34
0.10	3.563	7.67	-8.61	-482.92
System III : water+SrCl₂+lactose				
0.00	3.9452
0.02	3.8097	23.67	-30.16	-2347.79
0.04	3.6930	15.20	-18.25	-1236.78
0.06	3.6073	11.17	-13.67	-857.37
0.08	3.5498	9.66	-11.02	-658.25
0.10	3.5126	8.16	-9.26	-542.05

From the Table 1 it is observed that the values of viscosity are increases with increase in concentration of lactose in aqueous electrolytic solutions viz., GuHCl, BaCl₂ and SrCl₂. This increasing trend indicates the existence of molecular interaction occurring in these systems. In

order to shed more light on this, the role of viscosity B-coefficient has been obtained from the Table 3, it is observed that the values of A are negative in all systems studied and B co-efficient are positive. Since A is a measure of ionic interaction¹¹, it is evident that there is a weak ion-solute interaction in the mixtures studied, which is indicated by the smaller magnitude of A values. B-coefficient is also known as measure of order and disorder introduced by the solute into the solvent. It is also a measure of solute-solvent interaction and relative size of the solute and solvent molecules. The behaviour of B-coefficient in all the three systems suggests the existence of strong solute-solvent interaction. The magnitude of B values is in the order of $\text{SrCl}_2 > \text{BaCl}_2 > \text{GuHCl}$. This conclusion is an excellent agreement with that drawn from S_V and ϕ_v^0 data and the larger values of B indicate structure intensifying property of the solute. The higher magnitude of B in the case of SrCl_2 and BaCl_2 suggest that the interactions between $\text{Sr}^{2+}/\text{Ba}^{2+}$ ions and saccharide are stronger as compared with GuHCl .

Table 3 : Values of limiting apparent molal compressibility (ϕ_k^0), limiting apparent molal volume (ϕ_v^0), constants S_K and S_V and A and B coefficients of Jones-Dole equation of lactose in aqueous electrolytic solutions (0.5m) at 298.15 K

Aqueous Electrolytic Solutions	$-\phi_k^0 / (\times 10^{-8} \text{ m}^2 \text{ N}^{-1})$	$-S_k / (\times 10^{-8} \text{ N}^{-1} \text{ m}^{-1} \text{ mol}^{-1})$	$-\phi_v^0 / (\text{m}^3 \cdot \text{mol}^{-1})$	$-S_v / (\text{m}^3 \text{ l}^{1/2} \cdot \text{mol}^{-3/2})$	$-A / (\text{dm}^{3/2} \cdot \text{mol}^{-1/2})$	$B / (\text{dm}^3 \cdot \text{mol}^{-1})$
GuHCl	1.70	2.48	2.67	438.44	27.3	0.74
BaCl ₂	5.97	5.00	47.68	3184.50	8.88	2.06
SrCl ₂	6.88	5.49	54.63	3607.47	12.40	2.40

CONCLUSION

From the above study, it may be concluded that the existence of intermolecular interaction of ionic, hydrophilic and hydrophobic nature exist in the system studied. Derived acoustical and thermodynamical parameters suggest that strong interactions exist between the saccharides and co-solutes ($\text{SrCl}_2 / \text{BaCl}_2/\text{GuHCl}$). But, in which the solute and cosolute interactions are dominating over the solute-solvent interactions. The existence of molecular interaction is in the order of $\text{SrCl}_2 > \text{BaCl}_2 > \text{GuHCl}$. This suggests that divalent cations interact strongly than monovalent cations with the saccharides.

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