Studies on Apparent Molal Compressibility and Molal Volume of ZnSO₄ in Aqueous Saccharides Mixed Solvent Systems: A Comparative Study

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Abstract. Different metal ions as well as carbohydrates play vital role in human metabolism. The present investigation emphasizes on zinc sulphate (ZnSO₄) in galactose and its comparative study with lactose in aqueous medium at 303.15, 308.15, 313.15K temperature and at 1.0 atmospheric pressure. Different physical quantities such as density, viscosity and speed of sound have been measured as function of concentrations and temperatures for these multi-component solutions. These quantities were further used to evaluate various thermo-acoustic parameters like acoustic impedance, isentropic compressibility, partial molal compressibility, partial molal volume, internal pressure etc., The results were analyzed to assess the type and extent of association among the components. Moreover, both Zn²⁺ and SO₄²⁻ are in the Hofmeister series and there is a possibility of ion-macro molecule interactions in aqueous solution. The breaking of the structure and the solvation of the solute by changing the temperature in mixed solvents are the point of discussion in the present study. Interestingly, the ion-solvation of zinc ion is comparatively more favorable in galactose than in lactose-water mixed solvent systems.

Keywords: Speed of sound; thermo-acoustic parameters; apparent molal volume; structure breaking effect; galactose, saccharides.

Resumen. Diferentes iones metálicos, así como carbohidratos juegan un papel vital en el metabolismo humano. La presente investigación centra su atención sobre el sulfato de zinc (ZnSO₄) en galactosa y un estudio comparativo con lactosa en soluciones acuosas a las temperaturas 303.15, 308.15, 313.15K y 1 atm de presión. Se midieron diferentes cantidades físicas como densidad, viscosidad y velocidad del sonido como función de la concentración y la temperatura de las soluciones. Posteriormente, estas cantidades se utilizaron para evaluar distintos parámetros termoacústicos como impedancia acústica, compresibilidad isoentrópica, compresibilidad molal parcial, volumen molal parcial, presión interna, etc. Los resultados se analizaron para evaluar el tipo y grado de la asociación entre los componentes. Mas aún, tanto Zn²⁺ como SO₄²⁻ están en las series de Hofmeister y hay una posibilidad de presencia de interacciones ión-macromolécula en la solución acuosa. Un punto de discusión en el presente estudio es el rompimiento de la estructura y la solvatación del soluto debidos al cambio de la temperatura de las soluciones. Es interesante hacer notar que la solvatación de los iones de zinc es comparativamente mas favorable en las soluciones acuosas de galactosa que de lactosa.

Palabras clave: Velocidad del sonido; parámetros termoacústicos; volúmenes molales aparentes; efecto de rompimiento de estructuras; galactosa; sacáridos.
Introduction

The carbohydrates, commonly known as saccharides are the energy suppliers to all living organisms. They are utilized in the pharmaceutical industries for the manufacture of drugs and are also important in the field of chemicals, bio-chemicals and foods industries. Presently, the monosaccharide galactose and the disaccharide lactose have been considered for the investigation, where galactose is supposed to be the building blocks for the preparation of lactose. This saccharide is quite abundant in human diets and responsible for various functions inside the body. According to Hussain et al. [1] galactose with certain properties is involved in biological processes. Similarly, lactose is considered as the milk sugar and it is exclusively present in milk apart from medicines and culture media. It is also responsible for the development of brain as it is the essential element for the formation of cerebral galactolipids. Besides, absorption of lactose depends on the enzyme lactase, which enhances the absorption of metals like calcium, magnesium, and zinc. Zinc ion is one amongst the transition metals that is essential for the biological functions in all living organisms [2,3]. This metal is present in bones, muscles, liver and brain [4] and the deficiency of zinc ion is responsible for the chronic age-related diseases like neurological disorders and Alzheimer's [5]. Zinc ion is also an important metal ion in the preparations of various drugs and especially, ZnSO\(_4\) is supposed to be a better supplement for chronic diarrhea [6]. Moreover, media of certain drugs needs appropriate amounts of different saccharides. Therefore, it is important to investigate the association of this metal with different saccharides.

Intermolecular interaction studies have been reported for different zinc salts [7-9] and saccharides [10-13] as solutes in aqueous solvents. Besides, many other solutes have also been investigated in various aqueous-saccharides as mixed solvents [14-18]. However, inter-molecular interactions of biologically important transition metal ions in presence of aqueous galactose and lactose are quite rare in the literature. Furthermore, certain anions and cations are responsible for some specific ionic effect like ion-pair formation in aqueous solutions. This is recognized as a Hofmeister effect where specific ions or solute affect the structure of water upon addition. Such type of effects has been reported in biological activities [19-21]. Paul S Cremer and his group have studied the effect of Hofmeister cations, where Zn\(^{2+}\) is coming under the ions that tend to increase the solubility [22]. As per the Hofmeister series, the behaviors of anions are more pronounced than cations and SO\(_4^{2-}\) ion is considered as a kosmotrope. This ion is believed to be strongly hydrated and a ‘water structure maker’. Above all, it is a stabilizing ion, having salting-out effect on macromolecules like proteins [23]. Harold studied the nature of interactions between water and functional groups in proteins [24]. Roy et al., reported the interaction between vitamins and aqueous cysteine [25]. Most of the functions of human metabolic systems involve aqueous media and also carbohydrates have significant role in this process. It is, therefore, essential to study the interactions of such systems.

In continuation of our previous work with lactose [26], this would be an extension to compare between two saccharides, where only aqueous galactose mixed solvent has been presented and was compared with our earlier reported data of lactose [26].

Experimental

Chemicals

The zinc sulphate heptahydrate and the galactose of high purity (mass fraction more than 99.9) used in the present investigation were acquired from Qualigen Chemicals. All these chemicals were used without further purifications and were kept in desiccator at room temperature to avoid any possible moisture absorption.
Solution preparation

Mixed aqueous solvents were prepared from galactose for four different concentrations (2.5, 5.0, 7.5, 10.0%) in double distilled water having density $0.9960 \times 10^3 \text{kg m}^{-3}$ (w/V) at room temperature. Series of ZnSO$_4$ solutions of varying concentration from 0.01 to 0.1 mole.dm$^{-3}$ were made by taking the above prepared mixed solvents. The solutions were kept acquiring different temperature for 30 minutes in a thermostat with an accuracy of 0.01 K. Systems containing ZnSO$_4$ with aqueous lactose solvents have been studied and reported earlier [26].

Apparatus and Procedure

The solutions were prepared in glass volumetric vials using a Vibra Make HTR-220E analytical balance. The densities of all solutions were measured by a bicapillary pycnometer with a reproducibility of $\pm 3 \times 10^{-3} \text{kg.m}^{-3}$. The viscosity of the solutions was measured by using a calibrated Ostwald viscometer, where it was immersed in a water bath to maintain constant temperature. The temperature was maintained within $\pm 0.01$ K. The speed of sound in all the solutions was measured by a single crystal variable-path ultrasonic interferometer operating at 3MHz frequency (Mittal make, India). Constant temperature was maintained by circulating water from a thermostatically regulated water bath maintained within $\pm 0.01$ K around the sample holder. The reproducibility for speeds of sound measurements was $\pm 5 \times 10^{-1}\text{ms}^{-1}$.

Results and discussion

The experimentally measured values of density, $\rho$, viscosity, $\eta$ and speed of sound, $U$, of ZnSO$_4$ in different concentrations of aqueous galactose as mixed solvents have been listed in Tables. Few parameters are also represented in figures. The respective values of ZnSO$_4$ in lactose solutions have been presented elsewhere [26] and certain parameters are presented here in figures for comparison.

Our results reveal that the speed of sound increases with the concentration of ZnSO$_4$ in both mixed solvents as well as with the concentration of galactose (Table 1) and lactose in water [(Fig. 1) Representative 3-D plot of ZnSO$_4$ in galactose-water mixed solvent at different temperatures]. This enhancement is indicative of cohesive forces by ionic hydration suggesting molecular association. However, the speed of sound is comparatively larger in galactose systems than in the lactose systems (Fig. 2). This reveals the compactness of ZnSO$_4$ in aqueous galactose than that in lactose. The higher values of density for ZnSO$_4$ in aqueous galactose than lactose further supports this finding. This also suggests the existence of ion-solvent interactions and the structure making tendency by H-bonding of solvent [27]. As per the literature, the increase of density indicates the enhancement of solvent-solvent and solute-solvent interactions, whereas the decreasing values indicate less
interactions [28]. The increase in density can be assumed to be the shrinkage in the volume, which in turn is due to the presence of solute molecules. This might also be interpreted to the structure-maker of the solvent due to the addition of solute. Similarly, the decrease in density is indicative of structure-breaker of the solvent [29]. However, variation of density refers to the gap between the components in the solution, whereas that of viscosity to the thinness or thickness of the fluids. Both these parameters are affected by the temperature. Presently, viscosity increases with the increase in the concentrations of both ZnSO₄ as well as that of galactose and lactose. However, it shows decreasing trends with increase in temperature for all systems. The increase in viscosity can be explained by the presence of solute particles across the fluid streamlines, which tend to rotate and absorb energy, thus are responsible for the enhancement [30,31].

Fig. 1. 3-D Representative plot of ultrasonic velocity, U vs Concentration (mole kg⁻¹) of ZnSO₄ in 2.5% Galactose-water mixed solvent at T = (303.15K, 308.15K, 313.15K).

Fig. 2. Variation of speed of sound, U vs. Concentration (mole kg⁻¹) of ZnSO₄ in Galactose-water and Lactose-water mixed solvent at 303.15K.
Table 1. Experimentally determined density, $\rho$, viscosity, $\eta$, and ultrasonic velocity, $U$, of ZnSO$_4$ in 2.5%, 5.0%, 7.5% and 10% Galactose-water mixed solvent at 303.15K, 308.15K and 313.15K temperature.

| C mol.kg$^{-1}$ | $\rho \times 10^3$ kg.m$^{-3}$ | $\eta \times 10^3$ kg.m$^{-1}$.s$^{-1}$ | $U$ m.s$^{-1}$ |
|----------------|--------------------------------|--------------------------------------|----------------|
|                | 303.15 K                        | 308.15 K                             | 313.15 K       |                   |
| 0.00           | 1.0066                          | 1.0052                               | 1.0040         | 0.8548 0.7738 0.7054 | 1513.2 1524.5 1535.2 |
| 0.01           | 1.0088                          | 1.0072                               | 1.0059         | 0.8629 0.7805 0.7124 | 1515.5 1526.0 1536.4 |
| 0.02           | 1.0109                          | 1.0090                               | 1.0076         | 0.8709 0.7869 0.7200 | 1516.4 1527.2 1537.6 |
| 0.04           | 1.0146                          | 1.0127                               | 1.0110         | 0.8797 0.7982 0.7288 | 1517.4 1528.4 1539.0 |
| 0.06           | 1.0175                          | 1.0157                               | 1.0143         | 0.8895 0.8067 0.7370 | 1520.3 1530.4 1540.2 |
| 0.08           | 1.0205                          | 1.0190                               | 1.0176         | 0.9041 0.8218 0.7461 | 1523.2 1532.5 1541.8 |
| 0.10           | 1.0237                          | 1.0223                               | 1.0199         | 0.9197 0.8369 0.7605 | 1525.5 1534.4 1544.2 |

|                | 308.15 K                        | 308.15 K                             | 308.15 K       |                   |
| 0.00           | 1.0170                          | 1.0156                               | 1.0139         | 0.9010 0.8191 0.7433 | 1522.6 1532.8 1541.8 |
| 0.01           | 1.0190                          | 1.0173                               | 1.0159         | 0.9087 0.8266 0.7505 | 1524.8 1534.6 1543.5 |
| 0.02           | 1.0207                          | 1.0189                               | 1.0173         | 0.9164 0.8342 0.7582 | 1526.7 1536.1 1545.5 |
| 0.04           | 1.0240                          | 1.0221                               | 1.0206         | 0.9322 0.8430 0.7670 | 1528.2 1537.5 1546.9 |
| 0.06           | 1.0273                          | 1.0252                               | 1.0238         | 0.9473 0.8519 0.7756 | 1530.7 1539.8 1548.7 |
| 0.08           | 1.0306                          | 1.0283                               | 1.0269         | 0.9634 0.8611 0.7908 | 1533.4 1541.5 1550.9 |
| 0.10           | 1.0332                          | 1.0312                               | 1.0298         | 0.9788 0.8766 0.8061 | 1536.6 1543.3 1553.3 |

|                | 313.15 K                        | 313.15 K                             | 313.15 K       |                   |
| 0.00           | 1.0268                          | 1.0251                               | 1.0234         | 0.9661 0.8706 0.7878 | 1532.4 1542.0 1552.4 |
| 0.01           | 1.0287                          | 1.0271                               | 1.0254         | 0.9740 0.8783 0.7954 | 1534.0 1543.7 1553.7 |
| 0.02           | 1.0303                          | 1.0287                               | 1.0270         | 0.9883 0.8862 0.8031 | 1535.4 1545.6 1555.2 |
| 0.04           | 1.0337                          | 1.0322                               | 1.0305         | 0.9979 0.9014 0.8122 | 1537.5 1547.1 1556.7 |
| 0.06           | 1.0370                          | 1.0354                               | 1.0336         | 1.0085 0.9106 0.8206 | 1540.1 1549.4 1558.6 |
| 0.08           | 1.0400                          | 1.0385                               | 1.0368         | 1.0230 0.9200 0.8361 | 1543.0 1551.7 1560.6 |
| 0.10           | 1.0431                          | 1.0416                               | 1.0399         | 1.0390 0.9294 0.8518 | 1545.6 1554.2 1562.8 |

|                | 303.15 K                        | 308.15 K                             | 313.15 K       |                   |
| 0.00           | 1.0365                          | 1.0351                               | 1.0336         | 1.0322 0.9296 0.8462 | 1542.6 1552.7 1559.3 |
| 0.01           | 1.0385                          | 1.0372                               | 1.0353         | 1.0396 0.9371 0.8533 | 1544.4 1554.3 1562.0 |
| 0.02           | 1.0402                          | 1.0387                               | 1.0369         | 1.0483 0.9452 0.8616 | 1546.2 1556.2 1564.6 |
| 0.04           | 1.0436                          | 1.0421                               | 1.0401         | 1.0630 0.9550 0.8706 | 1548.6 1558.8 1567.1 |
| 0.06           | 1.0465                          | 1.0451                               | 1.0432         | 1.0738 0.9658 0.8798 | 1550.0 1562.2 1569.0 |
| 0.08           | 1.0496                          | 1.0482                               | 1.0463         | 1.0900 0.9798 0.8950 | 1552.7 1564.1 1571.6 |
| 0.10           | 1.0526                          | 1.0512                               | 1.0492         | 1.1072 0.9963 0.9111 | 1555.1 1566.6 1574.0 |
Isentropic compressibility and molal compressibility

Isentropic compressibilities, $\beta_s$, of solutions were obtained using the following Laplace equation [32]:

$$\beta_s = \frac{1}{\rho U^2}$$

where $\rho$ and $U$ are the density and ultrasonic velocity for the fluid samples. As per Sadeghi et al., this compressibility is the sum of two contributions, $\beta_s^{\text{solute intrinsic}}$ and $\beta_s^{\text{solvent intrinsic}}$ [33]. The compressibility resulting from the compression of solvent molecules (galactose and lactose) is $\beta_s^{\text{solvent intrinsic}}$ whereas that of due to the compression of the hydration shell of ions is known as $\beta_s^{\text{solute intrinsic}}$ [34]. Perusal of tables and figures shows that isentropic compressibility decreases with increase in concentrations of both ZnSO$_4$ as well as the carbohydrates contents in the solvents (Table 2). This type of variation confirms the presence of ion-solvent interactions through ion-dipole type between zinc ion and surrounding water molecules. This even supports the increasing number of H-bonding in carbohydrates. Compressibility of solvent is generally found to be higher than that of solution and it reduces with the increase in concentration of the solution [27]. The closeness of the components in solutions also results in the decrease in compressibility. Again, increase in compressibility with temperatures can be attributed to the thermal expansion of the solutions resulting in a less compressible liquid [18] [Representative 3-D plots for ZnSO$_4$ in both aqueous galactose and lactose at different temperatures (Figs. 3 and 4)]. The $\beta_s$ values decrease with an increase in temperature for each binary system at a fixed composition due to an increase in thermal agitation. This happens by the release of solvent molecules from the solute and the resulting increase in solution volume. According to Bahadur et al. the decrease in isentropic compressibilities with increase in concentration of the solute is the consequence of the combined effect of solvation of ions and breaking of the structure of solvent molecules and also because of the dominating nature of $\beta_s^{\text{solute intrinsic}}$ over the $\beta_s^{\text{solvent intrinsic}}$ effect [35]. In addition, another compressibility factor such as the apparent molal compressibility, $\phi_k$ was also studied, which can be determined by using the formula [36]:

$$\phi_k = \frac{1000(\beta_s \rho_0 - \beta_s^0 \rho)}{c \rho_0} + \frac{\beta_s M}{\rho}$$

where $\rho$ and $\beta_s^0$ are the density and isentropic compressibility of the solvent (aqueous-galactose), $\rho$ and $\beta_s$ are those of solution, respectively; $c$ and $M$ are the molarity of the solution and the molar mass of the solute (zinc sulphate), respectively. Observing the variations of $\phi_k$ from figures 5 and 6, it reveals that $\phi_k$ values decrease when increasing the concentrations of both Zn ions and carbohydrates. It also shows negative values and decreasing trends with increase in temperature. According to Bahadur et al, negative values of $\phi_k$ are attributed to strong attractive interactions between the solute and solvent due to solvation of the solute [34]. It has also been reported that the negative values are indicative of electrostrictive solvation of ions [37]. Again, the apparent molal compressibility of ZnSO$_4$ in galactose-water systems is comparatively more than that of ZnSO$_4$ in lactose-water for few systems. This shows that the ion-solvent interactions are slight more important in the former systems.
**Fig. 3.** 3-D Representative plots of $\beta_s$ vs Concentration (mole kg$^{-1}$) of ZnSO$_4$ in Galactose-water mixed solvent at $T = (303.15K, 308.15K, 313.15K)$.

**Fig. 4.** 3-D Representative plots of $\beta_s$ vs Concentration (mole kg$^{-1}$) of ZnSO$_4$ in Lactose-water mixed solvent at $T = (303.15K, 308.15K, 313.15K)$. 
Fig. 5. Variation of apparent molar compressibility, $\phi_k$ vs Concentration (mole kg$^{-1}$) of ZnSO$_4$ in Galactose-water and Lactose-water mixed solvent at 303.15K.

Fig. 6. Variation of apparent molar compressibility, $\phi_k$ of ZnSO$_4$ in 2.5% Galactose-water and Lactose-water vs. Temperature (303.15K, 308.15K, 313.15K).
Table 2. Calculated values of isentropic compressibility, $\beta_s$, Internal pressure, $\pi_i$, free volume, $V_f$ of ZnSO$_4$ in 2.5%, 5.0%, 7.5% and 10% Galactose-water mixed solvent at 303.15K, 308.15K and 313.15K temperature.

| C mol.kg$^{-1}$ | $\beta_s \times 10^{10}$ N$^{-1}$m$^2$ | $\pi_i \times 10^9$ Pa | $V_f \times 10^6$ m$^3$mol$^{-1}$ |
|-----------------|-----------------|-----------------|-----------------|
|                 | 303.15 K        | 308.15 K        | 313.15 K        | 303.15 K        | 308.15 K        | 313.15 K        |
|                 |                 |                 |                 |                 |                 |                 |
| 0.00            |                 |                 |                 |                 |                 |                 |
| 0.01            |                 |                 |                 |                 |                 |                 |
| 0.02            |                 |                 |                 |                 |                 |                 |
| 0.04            |                 |                 |                 |                 |                 |                 |
| 0.06            |                 |                 |                 |                 |                 |                 |
| 0.08            |                 |                 |                 |                 |                 |                 |
| 0.10            |                 |                 |                 |                 |                 |                 |

Free volume and partial molal volume

The free volume, $V_f$, internal pressure, $\pi_i$, relaxation time, $\tau$, and relative association, $R_A$ are other parameters that were calculated using the following relations [38-41].

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\[
V_f = \left( \frac{M_{\text{eff}} U}{K \eta} \right)^{3/2}
\]

(3)

\[
\pi_i = bRT \left( \frac{K \eta}{U} \right)^{\frac{1}{2}} \rho^{2/3} \left( \frac{\rho}{M_{\text{eff}}} \right)^{7/6}
\]

(4)

\[
\tau = \frac{4 \eta}{3 \rho U^2}
\]

(5)

\[
R_A = \left( \frac{P}{\rho_0} \right) \left( \frac{U_0}{U} \right)^{1/3}
\]

(6)

where, \( M_{\text{eff}} \) is the effective molecular mass and \( K \) is a constant equal to \( 4.28 \times 10^9 \), independent of temperature for all types of liquids; \( b \) is the space packing factor, generally 2 for liquids, \( R \) is the gas constant, \( T \) is the absolute temperature. Presently, \( V_f \) values decrease with the concentration of \( \text{ZnSO}_4 \) as well as that of galactose and lactose (Figs. 7 and 8) and increase with temperature. As per the literature, the higher values are indicative of less solute-solvent interaction [42].

The relative association, \( R_A \), is found to be increasing regularly with the concentration of \( \text{ZnSO}_4 \) in both galactose and lactose systems (Fig. 9). But hardly any distinct variation was observed with temperature. However, it decreases slowly with the concentration of galactose and increases with lactose concentration. According to Jahagirdar et al., \( R_A \) is influenced by two factors, such as breaking of associated solvent molecules on addition of solute or electrolyte and the solvation of solute molecules. It has been reported that the former leads to decrease and the later to an increase in \( R_A \) with solute concentration [43]. The relaxation time, \( \tau \), is found to be increasing with the concentrations of \( \text{ZnSO}_4 \) as well as carbohydrates (Table 3) and shows a decreasing trend with temperature [Representative 3-D plots for \( \text{ZnSO}_4 \) in aqueous galactose mixed solvent at different temperatures (Fig. 10)]. It has been reported earlier that the decrease in relaxation time is indicative of a structure breaking tendency, whereas linear or non-linear increment with concentration indicates structure formation [44]. Kannappan et al. also reported a similar observation [42]. The internal pressure, considered as the cohesive energy is supposed to be caused by the attractive and repulsive forces between the molecules [45]. Presently, it increases with \( \text{ZnSO}_4 \) as well as with galactose and lactose concentrations. However, the values are little higher in case of \( \text{ZnSO}_4 \) in galactose than in lactose systems (Fig. 11). This enhancement is due to the strong cohesive forces that appear during the structure making of solvents in presence of solute [46]. The values of internal pressure decrease with temperature for all the systems studied (Fig. 12). This happens due to the dispersion of solute molecules with temperature and hence there is decrease in cohesive force.

The apparent molal volumes, \( \phi_v \), of \( \text{ZnSO}_4 \) have been calculated from the measured values of densities of mixed solvents and solutions using the following relation:

\[
\phi_v = \frac{1000(\rho_0 - \rho)}{c \rho_0} + \frac{M}{\rho}
\]

(7)

where, \( \rho_0 \) and \( \rho \) are the densities of mixed solvents (aqueous-galactose, -lactose) and solutions, respectively; \( c \) is the molality of the solutions, \( M \) is the molar mass of the solute (\( \text{ZnSO}_4 \)). This is the shrinkage of the solution volume after mixing of the components, where same numbers of molecules are accommodated into comparatively smaller volume than the total volumes of the components. Presently, values of \( \phi_v \) for \( \text{ZnSO}_4 \) in
aqueous-galactose and lactose mixed solvent are positive and mostly increasing with concentrations (Fig. 13). According to Gupta G and his group, the positive values of $\phi_v$ is indicative of strong solute-solvent interaction [55]. However, the values are not in a regular increasing trend with the concentration of lactose. This type of variation suggest that the galactose molecules interact more constructively with water to strengthen the H-bonded network in the mixed solvent systems than that of lactose [47]. In the literature there are reports showing that a higher value of $\phi_v$ is due to strong solute-solvent interaction [48].

**Fig. 7.** Variation of free volume, $V_f$ vs. Concentration (mole kg$^{-1}$) of ZnSO$_4$ in Galactose-water and Lactose-water mixed solvent at 303.15K.

**Fig. 8.** Variation of free volume, $V_f$ of ZnSO$_4$ in 2.5% Galactose-water and Lactose-water vs. Temperature (303.15K, 308.15K, 313.15K).
Table 3. Calculated values of Relative association, $R_A$, viscous relaxation time, $\tau$, Gibbs’ free energy change, $\Delta G$ of ZnSO$_4$ in 2.5%, 5.0%, 7.5% and 10% Galactose-water mixed solvent at 303.15K, 308.15K and 313.15K temperature.

| C mol.kg$^{-1}$ | $R_A$ | $\tau \times 10^{13}$ s | $\Delta G \times 10^{-21}$ k.J.mol$^{-1}$ |
|-----------------|-------|-------------------|----------------------|
|                 | 303.15 K | 308.15 K | 313.15 K | 303.15 K | 308.15 K | 313.15 K | 303.15 K | 308.15 K | 313.15 K |
| 0.00            | 1.0017 | 1.0006 | 1.0016 | 4.9449 | 4.4163 | 3.9748 | 3.8307 | 3.5275 | 3.2409 |
| 0.01            | 1.0036 | 1.0032 | 1.0031 | 4.9637 | 4.4370 | 4.0004 | 3.8464 | 3.5451 | 3.2657 |
| 0.02            | 1.0070 | 1.0066 | 1.0061 | 4.9954 | 4.4708 | 4.0299 | 3.8687 | 3.5740 | 3.2940 |
| 0.04            | 1.0093 | 1.0091 | 1.0092 | 5.0209 | 4.4988 | 4.0581 | 3.8876 | 3.5976 | 3.3208 |
| 0.06            | 1.0116 | 1.0120 | 1.0121 | 5.0430 | 4.5214 | 4.0840 | 3.9040 | 3.6166 | 3.3454 |
| 0.08            | 1.0142 | 1.0148 | 1.0139 | 5.0913 | 4.5786 | 4.1125 | 3.9395 | 3.6642 | 3.3721 |
| 0.10            | 1.0171 | 1.0178 | 1.0176 | 5.1474 | 4.6361 | 4.1694 | 3.9804 | 3.7116 | 3.4251 |
|                 | 303.15 K | 308.15 K | 313.15 K | 303.15 K | 308.15 K | 313.15 K | 303.15 K | 308.15 K | 313.15 K |
| 0.00            | 1.0015 | 1.0013 | 1.0016 | 5.0953 | 4.5770 | 4.1120 | 3.9425 | 3.6629 | 3.3717 |
| 0.01            | 1.0027 | 1.0025 | 1.0026 | 5.1140 | 4.6004 | 4.1345 | 3.9561 | 3.6822 | 3.3927 |
| 0.02            | 1.0057 | 1.0054 | 1.0055 | 5.1359 | 4.6263 | 4.1604 | 3.9721 | 3.7036 | 3.4168 |
| 0.04            | 1.0083 | 1.0079 | 1.0083 | 5.1974 | 4.6520 | 4.1875 | 4.0165 | 3.7245 | 3.4418 |
| 0.06            | 1.0110 | 1.0106 | 1.0108 | 5.2475 | 4.6729 | 4.2114 | 4.0522 | 3.7415 | 3.4637 |
| 0.08            | 1.0128 | 1.0131 | 1.0132 | 5.3497 | 4.7588 | 4.3258 | 4.1241 | 3.8105 | 3.5669 |

Fig. 9. Variation of Relative association, $R_A$ vs Concentration (mole kg$^{-1}$) of ZnSO$_4$ in Galactose-water and Lactose-water mixed solvent at 303.15K.
### ZnSO₄ in 7.5% Galactose – Water

|        | 303.15 K | 308.15 K | 313.15 K | 303.15 K | 308.15 K | 313.15 K | 303.15 K | 308.15 K | 313.15 K |
|--------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| 0.00   | 5.3423   | 4.7624   | 4.2589   | 4.1190   | 3.8134   | 3.5069   |          |          |          |
| 0.01   | 1.0015   | 1.0016   | 1.0017   | 5.3649   | 4.7846   | 4.2845   | 4.1347   | 3.8310   | 3.5299   |
| 0.02   | 1.0028   | 1.0027   | 1.0029   | 5.4253   | 4.8083   | 4.3109   | 4.1764   | 3.8497   | 3.5536   |
| 0.04   | 1.0056   | 1.0058   | 1.0060   | 5.4450   | 4.8647   | 4.3365   | 4.1900   | 3.8940   | 3.5765   |
| 0.06   | 1.0082   | 1.0084   | 1.0086   | 5.4669   | 4.8846   | 4.3576   | 4.2049   | 3.9095   | 3.5951   |
| 0.08   | 1.0105   | 1.0110   | 1.0113   | 5.5087   | 4.9057   | 4.4149   | 4.2334   | 3.9258   | 3.6454   |
| 0.10   | 1.0130   | 1.0134   | 1.0139   | 5.5595   | 4.9252   | 4.4718   | 4.2676   | 3.9408   | 3.6947   |

### ZnSO₄ in 10.0% Galactose – Water

|        | 303.15 K | 308.15 K | 313.15 K | 303.15 K | 308.15 K | 313.15 K | 303.15 K | 308.15 K | 313.15 K |
|--------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| 0.00   | 5.5799   | 4.9668   | 4.4895   | 4.2812   | 3.9727   | 3.7100   |          |          |          |
| 0.01   | 1.0015   | 1.0017   | 1.0011   | 5.5960   | 4.9865   | 4.5041   | 4.2920   | 3.9877   | 3.7225   |
| 0.02   | 1.0028   | 1.0027   | 1.0021   | 5.6205   | 5.0100   | 4.5259   | 4.3083   | 4.0056   | 3.7411   |
| 0.04   | 1.0055   | 1.0054   | 1.0046   | 5.6632   | 5.0287   | 4.5445   | 4.3365   | 4.0196   | 3.7569   |
| 0.06   | 1.0080   | 1.0076   | 1.0072   | 5.6946   | 5.0489   | 4.5678   | 4.3571   | 4.0348   | 3.7766   |
| 0.08   | 1.0104   | 1.0102   | 1.0096   | 5.7434   | 5.0945   | 4.6177   | 4.3889   | 4.0689   | 3.8184   |
| 0.10   | 1.0128   | 1.0125   | 1.0119   | 5.7994   | 5.1491   | 4.6734   | 4.4251   | 4.1093   | 3.8647   |

**Fig. 10.** 3-D Representative plots of Relaxation time, \( \tau \) vs Concentration (mole kg⁻¹) of ZnSO₄ in 2.5% Galactose-water mixed solvent at \( T = (303.15K, 308.15K, 313.15K) \).
Fig. 11. Variation of internal pressure, $\pi_i$ vs Concentration (mole kg$^{-1}$) of ZnSO$_4$ in Galactose-water and Lactose-water mixed solvent at 303.15K.

Fig. 12. Variation of internal pressure, $\pi_i$ vs Concentration (mole kg$^{-1}$) of ZnSO$_4$ in 2.5% Galactose-water and Lactose-water vs. Temperature (303.15K, 308.15K, 313.15K).
Fig. 13. Variation of apparent molal volume, $\bar{v}$ vs. Concentration (mole kg$^{-1}$) of ZnSO$_4$ in Galactose-water and Lactose-water mixed solvent at 303.15K.

**Solvation number**

The speed of sound measurement is used to evaluate solvation number, $S_n$. It was suggested by Passynski and is studied to assess the mode of association. [49]

$$S_n = \frac{n_0}{n_i} \left( 1 - \frac{\beta_s}{\beta_s^0} \right)$$

where, $n_0$ and $n_i$ are the moles of solvent and solute, respectively. As per the literature, there are basically two solvation sheaths, primary and secondary. These can be studied with the help of speed of sound measurements [50]. The association of solvent molecules with the ion is a strong co-ordination bond type and occurs in the primary sheath of solvation. On the other hand, in the secondary sheath, there are weak forces of attraction between solute and solvent molecules. However, the solvation indicates the association among solute with solvent molecules. $S_n$ values are found to be positive for all systems and such variation is due to appreciable solvation of solute in solution [51]. It decreases with the concentrations of both ZnSO$_4$ and galactose (Table 4 and Fig. 14). This is due to the reduction of size of the secondary sheath of solvation. $S_n$ values are also in a decreasing trend with temperature (Fig. 15). This can be attributed to the weakening of solute-solvent interaction. Marcus reported that $S_n$ depends on both the ion and solvent as well as on the concentration through the interactions of this ion with other ions [52]. Again, the non-linear variation with the concentration of ZnSO$_4$ indicates the increase in ion-solvent interactions [53].
Fig. 14. Variation of Solvation number, $S_n$ vs. Concentration (mole kg$^{-1}$) of ZnSO$_4$ in Galactose-water and Lactose-water mixed solvent at 303.15K.

Fig. 15. Variation of Solvation number, $S_n$ vs Concentration (mole kg$^{-1}$) of ZnSO$_4$ in 2.5% Galactose-water and Lactose-water vs Temperature (303.15K, 308.15K, 313.15K).
Table 4. Calculated values of apparent molar compressibility, $\phi_K$, apparent molar volume, $\phi_v$, solvation number, $Sn$ of ZnSO$_4$ in 2.5%, 5.0%, 7.5% and 10% Galactose-water mixed solvent at 303.15K, 308.15K and 313.15K temperature.

| C mol.kg$^{-1}$ | $-\phi_K \times 10^{10}$ N$^{-1}$dm$^3$.mol$^{-1}$ | $\phi_v \times 10^3$ dm$^3$.mol$^{-1}$ | Sn |
|----------------|-----------------------------------------------|----------------------------------------|-----|
|                | ZnSO$_4$ in 2.5% Galactose – Water             | ZnSO$_4$ in 5.0% Galactose – Water      | ZnSO$_4$ in 7.5% Galactose – Water      | ZnSO$_4$ in 10.0% Galactose – Water      |
|                | 303.15 K                                      | 308.15 K                                | 313.15 K                                | 303.15 K                                |
| 0.00           | 1.948                                         | 1.948                                   | 1.948                                   | 1.948                                   |
| 0.01           | 1.506                                         | 1.506                                   | 1.506                                   | 1.506                                   |
| 0.02           | 1.066                                         | 1.066                                   | 1.066                                   | 1.066                                   |
| 0.04           | 0.984                                         | 0.984                                   | 0.984                                   | 0.984                                   |
| 0.08           | 0.953                                         | 0.953                                   | 0.953                                   | 0.953                                   |
| 0.10           | 0.918                                         | 0.918                                   | 0.918                                   | 0.918                                   |

Gibb’s free energy

The Gibb’s free energy, $\Delta G$ of the studied systems was calculated by using the relaxation time parameter and other constants.
\[ \Delta G = kT \ln \left[ \frac{kT \tau h}{h} \right] \]  

(9)

where \( k \) is Boltzmann’s constant \((1.23 \times 10^{-23} \text{JK}^{-1})\), \( T \) is the absolute temperature and \( h \) is Planck’s constant \((6.6 \times 10^{-34} \text{Js})\). It has been observed that the values of \( \Delta G \) increase with \( \text{ZnSO}_4 \) as well as with galactose and lactose concentrations. This type of variation suggests closer approach of unlike molecules due to H-bonding. Again \( \Delta G \) decreases with temperature and it is indicative of the rearrangement of molecules in the mixtures. [Representative 3-D plots for \( \text{ZnSO}_4 \) in aqueous galactose mixed solvent at different temperatures (Fig. 16)]. Similar observation was reported earlier [54] and this reveals the decrease in energy leading to dissociation [44].

**Conclusion**

The results of the present study indicate the existence of ion-solvent or solute-solvent interaction. \( \text{ZnSO}_4 \) being an important transition metallic salt for both biologically as well as pharmaceutically situations, interacts well with these two saccharides in aqueous media. However, from speed of sound, density and internal pressure, it is shown that there is strong cohesive force acting during structure making of the solvents in presence of the solute. Relative association and isentropic compressibility data reveal the structure-breaking and making of mixed solvents in terms of ion-solvation. This compressibility also indicates that the ion-solvent interactions are through ion-dipole type between zinc ion and surrounding solvent molecules. However, the apparent molar compressibility shows the ion-solvent interactions of zinc ions to be larger in galactose systems than that in lactose. \( S_n \) shows greater solvation of \( \text{ZnSO}_4 \) in galactose than lactose systems, which supports the above findings. Moreover, the variation of partial molal volume is an added supplement. It suggests galactose molecules interact more constructively with water strengthening the H-bonded network in the mixed solvent systems than that of lactose. The free volume further supports this reduction in solute–solvent association in case of lactose system.
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