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Studies on Apparent Molal Compressibility and Molal Volume of $ZnSO_4$ 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 ($ZnSO_4$) 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 Zn^{2+} and SO_4^{2-} 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 ($ZnSO_4$) 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 Zn^{2+} como SO_4^{2-} 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.

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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.

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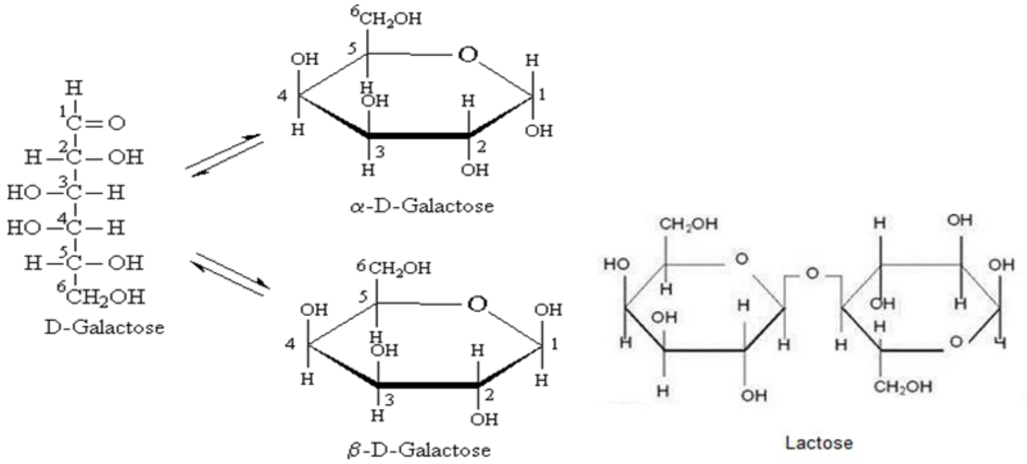

Scheme 1. Structures of galactose and lactose.

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 $\times 10^3$ 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 $\pm 3\times 10^{-3}$ 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 ±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 ±0.01 K around the sample holder. The reproducibility for speeds of sound measurements was $\pm 5 \times 10^{-1} ms^{-1}$.

Results and discussion

The experimentally measured values of density, ρ, viscosity, η 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 $ZnSO_4$ 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].

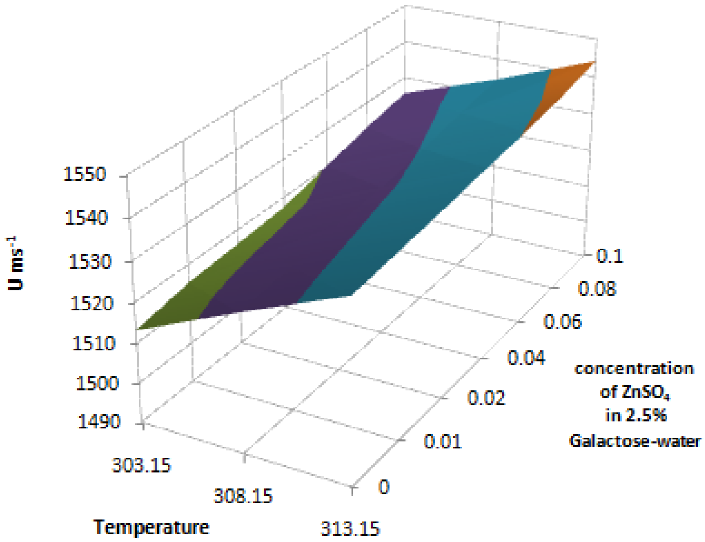

Fig. 1. 3-D Representative plot of ultrasonic velocity, U *vs* Concentration (mole kg^{-1}) of $ZnSO_4$ in 2.5% Galactose-water mixed solvent at T = (303.15K, 308.15K, 313.15K).

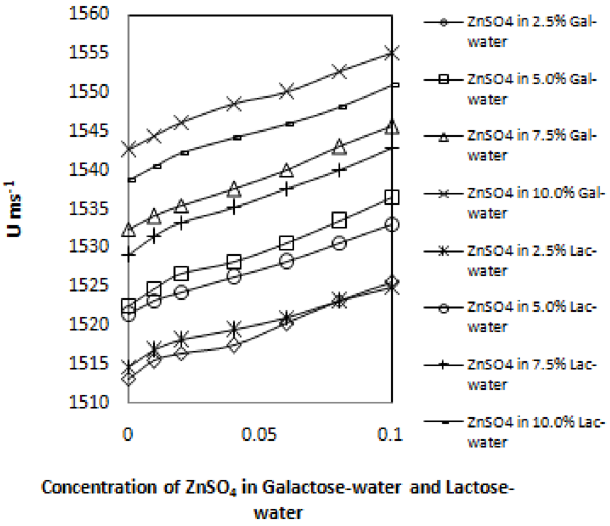

Fig. 2. Variation of speed of sound, U *vs*. Concentration (mole kg^{-1}) of $ZnSO_4$ in Galactose-water and Lactose-water mixed solvent at 303.15K.

Table 1. Experimentally determined density, ρ, viscosity, η 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}	**ρ x 10^{-3} kg.m^{-3}**			**η x 10^{3} kg.m^{-1}.s^{-1}**			**U m.s^{-1}**		
$ZnSO_4$ in 2.5% 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	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	0.7891	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
$ZnSO_4$ in 5.0% 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	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
$ZnSO_4$ 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	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
$ZnSO_4$ 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	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

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Isentropic compressibility and molal compressibility

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

$$\beta s = 1/\rho U^2 \qquad (1)$$

where ρ 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, $\beta s_{(\text{solvent intrinsic})}$ and $\beta s_{(\text{solute intrinsic})}$ [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 βs 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, ϕ_k was also studied, which can be determined by using the formula [36]:

$$\phi_k = \frac{1000(\beta_s\ \rho_0 - \beta_s^0 \rho)}{c\rho\rho_0} + \frac{\beta_s M}{\rho} \qquad (2)$$

where ρ and β_s^0 are the density and isentropic compressibility of the solvent (aqueous-galactose), ρ and β_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 Φ_k from figures 5 and 6, it reveals that ϕ_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 ϕ_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 molar compressibilty 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 slightly more important in the former systems.

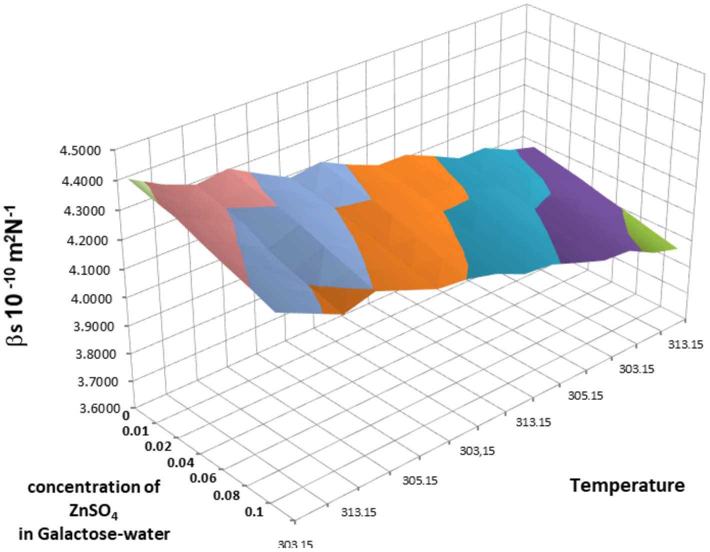

Fig. 3. 3-D Representative plots of β_s *vs* Concentration (mole kg^{-1}) of $ZnSO_4$ in Galactose-water mixed solvent at T = (303.15K, 308.15K, 313.15K).

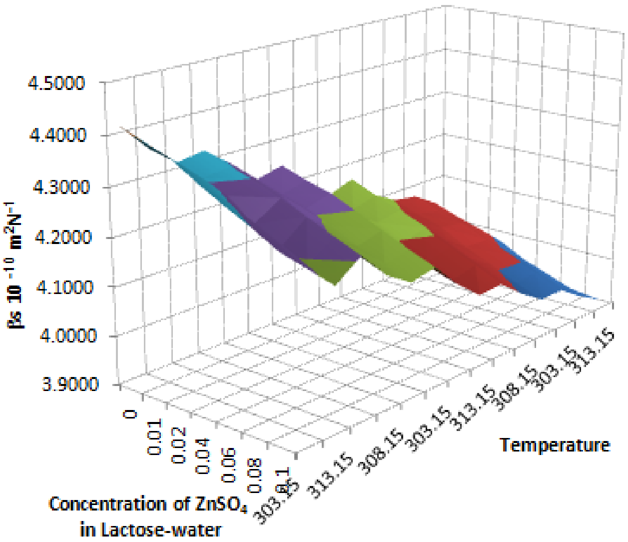

Fig. 4. 3-D Representative plots of β_s *vs* Concentration (mole kg^{-1}) of $ZnSO_4$ in Lactose-water mixed solvent at T = (303.15K, 308.15K, 313.15K).

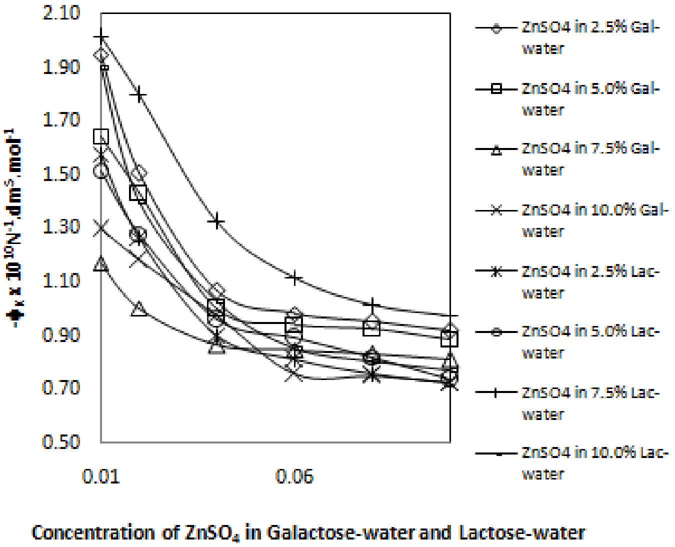

Fig. 5. Variation of apparent molar compressibility, ϕ_k *vs* Concentration (mole kg^{-1}) of $ZnSO_4$ in Galactose-water and Lactose-water mixed solvent at 303.15K.

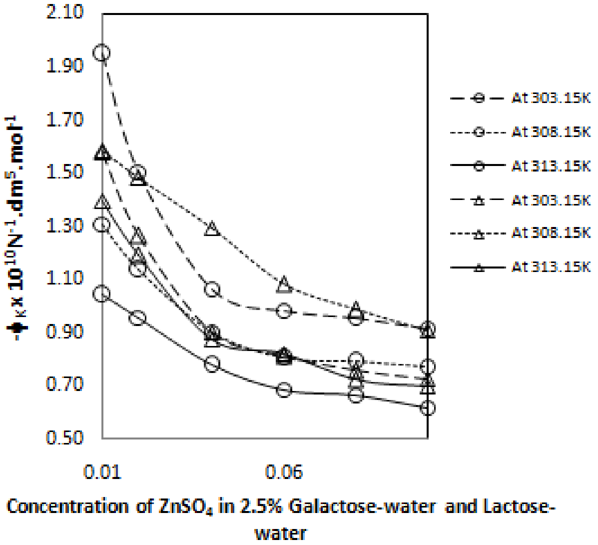

Fig. 6. Variation of apparent molar compressibility, ϕ_k of $ZnSO_4$ in 2.5% Galactose-water and Lactose-water *vs.* Temperature (303.15K, 308.15K, 313.15K).

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Table 2. Calculated values of isentropic compressibility, β_s, Internal pressure, π_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}	**β_sx 10^{10} $N^{-1}.m^2$**			**π_ix 10^9 pa**			**V_fx 10^8 m^3mol^{-1}**		
$ZnSO_4$ in 2.5% 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	4.3386	4.2805	4.2261	2.6285	2.5302	2.4444	2.1042	2.4706	2.8686
0.01	4.3160	4.2636	4.2115	2.6346	2.5353	2.4509	2.0878	2.4524	2.8413
0.02	4.3019	4.2493	4.1978	2.6413	2.5433	2.4580	2.0692	2.4250	2.8110
0.04	4.2806	4.2271	4.1761	2.6436	2.5471	2.4619	2.0568	2.4059	2.7865
0.06	4.2521	4.2036	4.1560	2.6441	2.5479	2.4645	2.0452	2.3919	2.7657
0.08	4.2235	4.1785	4.1340	2.6517	2.5593	2.4682	2.0178	2.3500	2.7415
0.10	4.1976	4.1547	4.1118	2.6617	2.5709	2.4784	1.9866	2.3090	2.6916
$ZnSO_4$ in 5.0% 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	4.2414	4.1909	4.1491	2.6382	2.5458	2.4543	2.0304	2.3662	2.7618
0.01	4.2209	4.1741	4.1318	2.6427	2.5507	2.4603	2.0171	2.3477	2.7376
0.02	4.2033	4.1594	4.1154	2.6468	2.5558	2.4658	2.0036	2.3285	2.7123
0.04	4.1816	4.1388	4.0947	2.6572	2.5573	2.4687	1.9715	2.3139	2.6911
0.06	4.1545	4.1140	4.0724	2.6654	2.5579	2.4706	1.9450	2.3015	2.6727
0.08	4.1267	4.0925	4.0486	2.6746	2.5592	2.4822	1.9168	2.2869	2.6227
0.10	4.0992	4.0715	4.0247	2.6810	2.5697	2.4935	1.8925	2.2481	2.5745
$ZnSO_4$ 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	4.1473	4.1027	4.0546	2.6687	2.5640	2.4672	1.9104	2.2547	2.6463
0.01	4.1311	4.0857	4.0399	2.6732	2.5692	2.4735	1.8978	2.2377	2.6223
0.02	4.1171	4.0693	4.0258	2.6858	2.5737	2.4790	1.8668	2.2209	2.5989
0.04	4.0924	4.0476	4.0044	2.6860	2.5840	2.4818	1.8587	2.1857	2.5798
0.06	4.0656	4.0231	3.9827	2.6868	2.5843	2.4824	1.8489	2.1750	2.5657
0.08	4.0386	3.9992	3.9602	2.6917	2.5845	2.4935	1.8296	2.1640	2.5198
0.10	4.0131	3.9745	3.9373	2.6992	2.5849	2.5046	1.8062	2.1533	2.4751
$ZnSO_4$ 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	4.0544	4.0072	3.9791	2.6939	2.5875	2.5006	1.8081	2.1368	2.4765
0.01	4.0371	3.9909	3.9589	2.6971	2.5921	2.5038	1.7991	2.1229	2.4620
0.02	4.0212	3.9754	3.9396	2.7012	2.5959	2.5085	1.7871	2.1080	2.4425
0.04	3.9956	3.9492	3.9150	2.7069	2.5965	2.5089	1.7684	2.0977	2.4301
0.06	3.9774	3.9207	3.8939	2.7073	2.5969	2.5096	1.7584	2.0863	2.4160
0.08	3.9519	3.8997	3.8695	2.7135	2.6027	2.5182	1.7378	2.0621	2.3798
0.10	3.9284	3.8761	3.8471	2.7212	2.6114	2.5279	1.7149	2.0319	2.3408

Free volume and partial molal volume

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

$$\mathrm{V_f} = (\mathrm{M_{eff}U/K\eta})^{3/2} \tag{3}$$

$$\pi_\mathrm{i} = \mathrm{bRT}\left(\frac{\mathrm{K\eta}}{\mathrm{U}}\right)^{\frac{1}{2}}\frac{\rho^{2/3}}{\mathrm{M_{eff}^{7/6}}} \tag{4}$$

$$\tau = 4\eta/3\rho\mathrm{U}^2 \tag{5}$$

$$\mathrm{R_A} = \left(\rho/\rho_0\right)\left(\frac{\mathrm{U_0}}{\mathrm{U}}\right)^{\frac{1}{3}} \tag{6}$$

where, M_{eff} is the effective molecular mass and K is a constant equal to 4.28 x 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 $ZnSO_4$ 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 $ZnSO_4$ 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, τ, is found to be increasing with the concentrations of $ZnSO_4$ as well as carbohydrates (Table 3) and shows a decreasing trend with temperature [Representative 3-D plots for $ZnSO_4$ 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 $ZnSO_4$ as well as with galactose and lactose concentrations. However, the values are little higher in case of $ZnSO_4$ 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, ϕ_v, of $ZnSO_4$ have been calculated from the measured values of densities of mixed solvents and solutions using the following relation:

$$\phi_\mathrm{v} = \frac{1000(\rho_0 - \rho)}{\mathrm{c}\rho\rho_0} + \frac{\mathrm{M}}{\rho} \tag{7}$$

where, ρ_0 and ρ 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 ($ZnSO_4$). 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 ϕ_v for $ZnSO_4$ 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 ϕ_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 ϕ_v is due to strong solute-solvent interaction [48].

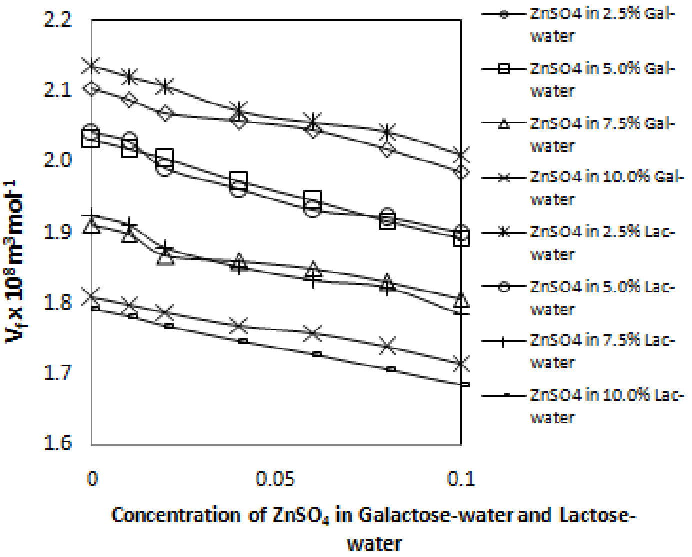

Fig. 7. Variation of free volume, V_f *vs.* Concentration (mole kg^{-1}) of $ZnSO_4$ in Galactose-water and Lactose-water mixed solvent at 303.15K.

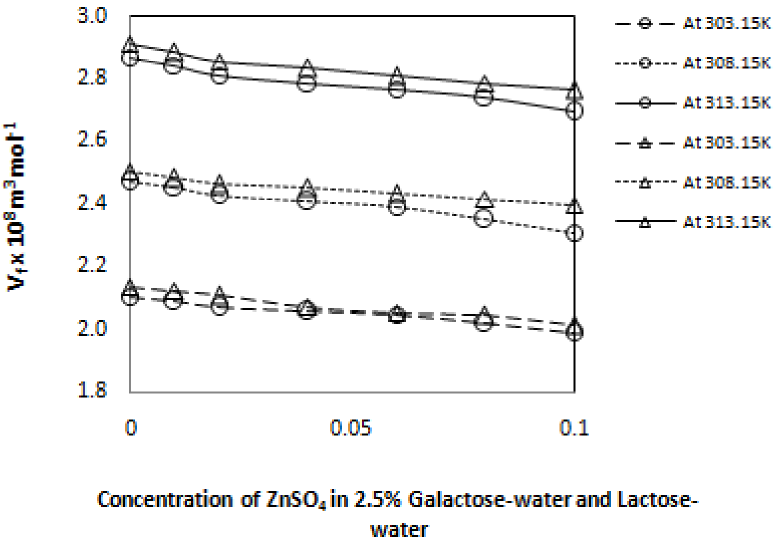

Fig. 8. Variation of free volume, V_f of $ZnSO_4$ in 2.5% Galactose-water and Lactose-water *vs.* Temperature (303.15K, 308.15K, 313.15K).

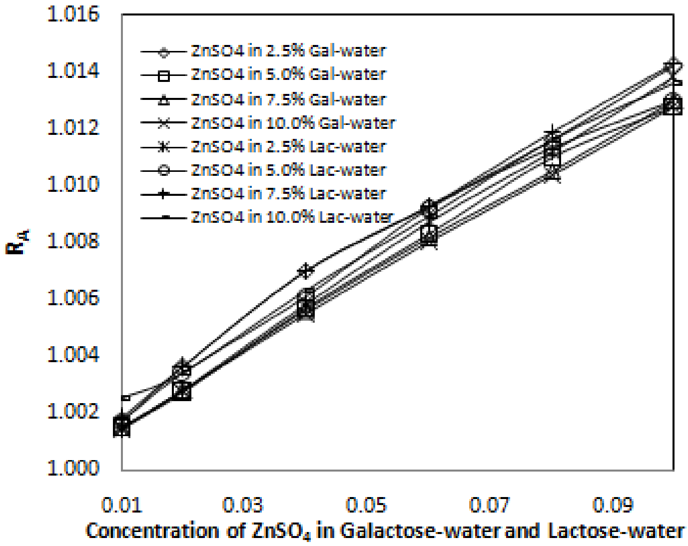

Fig. 9. Variation of Relative association, R_A *vs* Concentration (mole kg^{-1}) of $ZnSO_4$ in Galactose-water and Lactose-water mixed solvent at 303.15K.

Table 3. Calculated values of Relative association, R_A, viscous relaxation time, τ, Gibbs' free energy change, ΔG 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**			**τ x 10^{13} s**			**ΔG x 10^{-21} k.J.mol^{-1}**		
$ZnSO_4$ in 2.5% 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				4.9449	4.4163	3.9748	3.8307	3.5275	3.2409
0.01	1.0017	1.0017	1.0016	4.9657	4.4370	4.0004	3.8464	3.5451	3.2657
0.02	1.0036	1.0032	1.0031	4.9954	4.4708	4.0299	3.8687	3.5740	3.2940
0.04	1.0070	1.0066	1.0061	5.0209	4.4988	4.0581	3.8876	3.5976	3.3208
0.06	1.0093	1.0091	1.0092	5.0430	4.5214	4.0840	3.9040	3.6166	3.3454
0.08	1.0116	1.0120	1.0121	5.0913	4.5786	4.1125	3.9395	3.6642	3.3721
0.10	1.0142	1.0148	1.0139	5.1474	4.6361	4.1694	3.9804	3.7116	3.4251
$ZnSO_4$ in 5.0% 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				5.0953	4.5770	4.1120	3.9425	3.6629	3.3717
0.01	1.0015	1.0013	1.0016	5.1140	4.6004	4.1345	3.9561	3.6822	3.3927
0.02	1.0027	1.0025	1.0026	5.1359	4.6263	4.1604	3.9721	3.7036	3.4168
0.04	1.0057	1.0054	1.0055	5.1974	4.6520	4.1875	4.0165	3.7245	3.4418
0.06	1.0083	1.0079	1.0083	5.2475	4.6729	4.2114	4.0522	3.7415	3.4637
0.08	1.0110	1.0106	1.0108	5.3008	4.6988	4.2688	4.0899	3.7624	3.5159
0.10	1.0128	1.0131	1.0132	5.3497	4.7588	4.3258	4.1241	3.8105	3.5669

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$ZnSO_4$ 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
$ZnSO_4$ 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

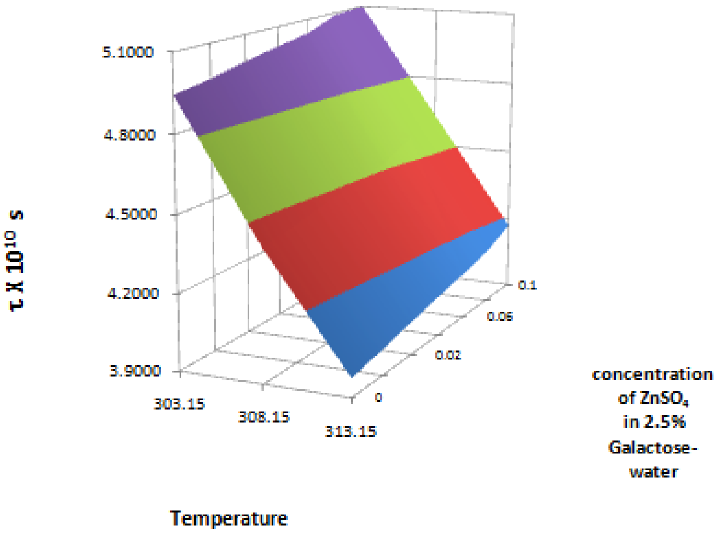

Fig. 10. 3-D Representative plots of Relaxation time, τ *vs* Concentration (mole kg^{-1}) of $ZnSO_4$ in 2.5% Galactose-water mixed solvent at T = (303.15K, 308.15K, 313.15K).

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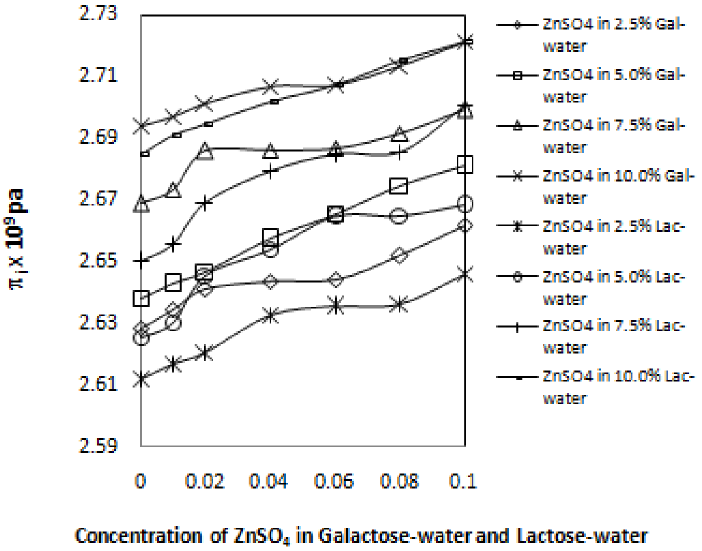

Fig. 11. Variation of internal pressure, π_i *vs* Concentration (mole kg^{-1}) of $ZnSO_4$ in Galactose-water and Lactose-water mixed solvent at 303.15K.

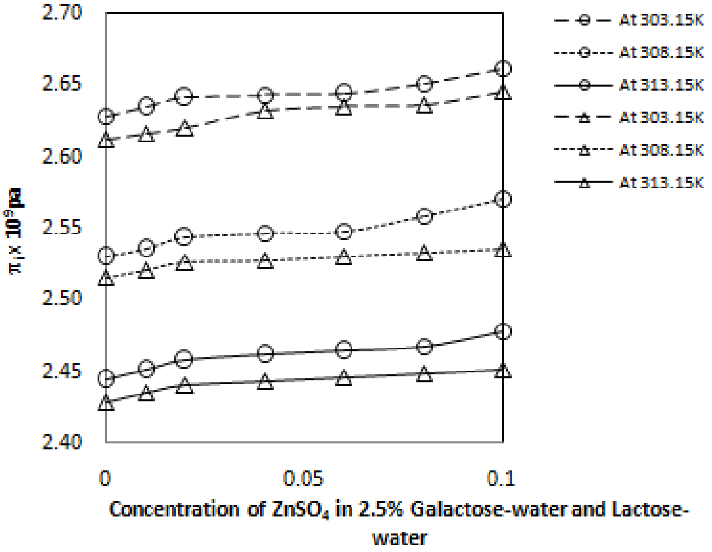

Fig. 12. Variation of internal pressure, π_i *vs* Concentration (mole kg^{-1}) of $ZnSO_4$ in 2.5% Galactose-water and Lactose-water *vs.* Temperature (303.15K, 308.15K, 313.15K).

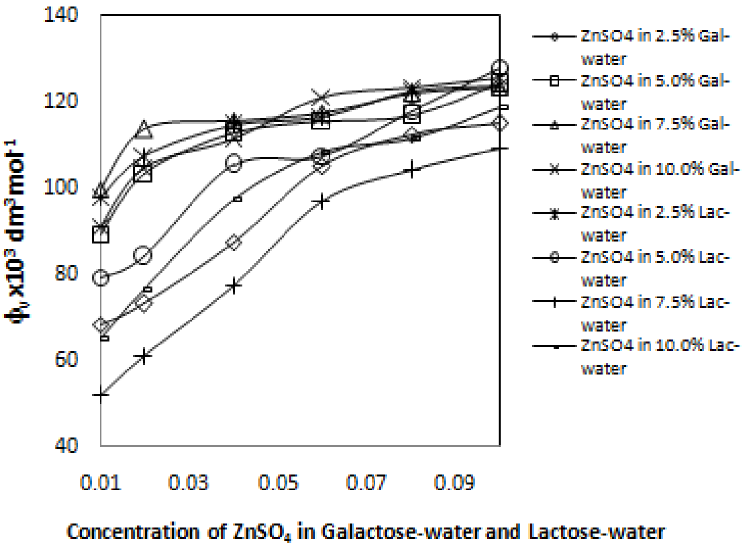

Fig. 13. Variation of apparent molal volume, ϕ_v *vs*. Concentration (mole kg^{-1}) of $ZnSO_4$ in Galactose-water and Lactose-water mixed solvent at 303.15K.

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]

$$S_n = \frac{n_0}{n_i}\left(1 - \frac{\beta_s}{\beta_s^0}\right) \tag{8}$$

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 attaction 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].

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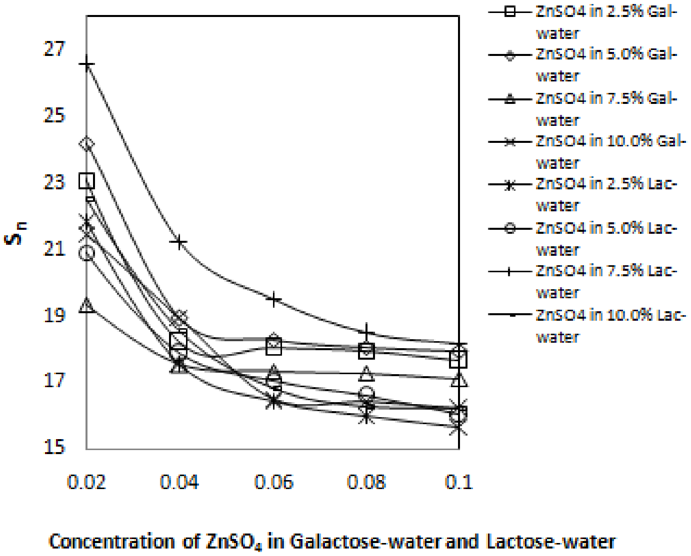

Fig. 14. Variation of Solvation number, S_n *vs*. Concentration (mole kg^{-1}) of $ZnSO_4$ in Galactose-water and Lactose-water mixed solvent at 303.15K.

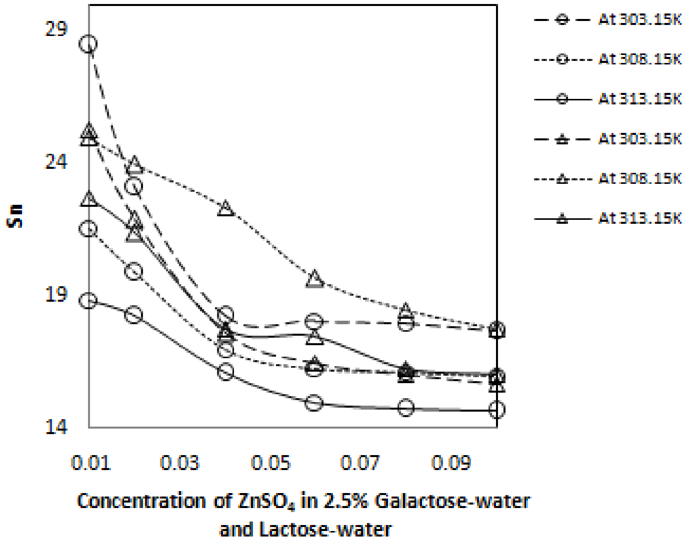

Fig. 15. Variation of Solvation number, S_n *vs* Concentration (mole kg^{-1}) of $ZnSO_4$ in 2.5% Galactose-water and Lactose-water *vs* Temperature (303.15K, 308.15K, 313.15K).

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Table 4. Calculated values of apparent molar compressibility, ϕ_K, apparent molar volume, ϕ_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}	**-ϕ_K x 10^{10} N^{-1}.dm^5.mol^{-1}**			**ϕ_v x 10^3 dm^3.mol^{-1}**			**Sn**		
$ZnSO_4$ in 2.5% 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									
0.01	1.948	1.308	1.043	68.38	87.94	97.72	28.4481	21.5268	18.8116
0.02	1.506	1.137	0.956	73.15	97.64	107.44	23.0721	19.8422	18.2036
0.04	1.066	0.905	0.777	87.57	99.74	112.00	18.1933	16.9449	16.0423
0.06	0.984	0.805	0.685	105.22	111.69	114.91	18.0341	16.2203	14.9548
0.08	0.953	0.792	0.666	112.62	113.77	116.17	17.9491	16.0973	14.7009
0.10	0.918	0.773	0.617	114.93	114.86	126.65	17.6391	15.9283	14.6283
$ZnSO_4$ in 5.0% 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									
0.01	1.644	1.163	1.342	89.18	118.10	88.86	26.0659	21.5809	22.4147
0.02	1.436	1.041	1.177	103.49	122.75	117.83	24.1845	20.1984	21.7908
0.04	0.999	0.765	0.851	112.75	124.77	119.86	18.9315	16.6598	17.5432
0.06	0.943	0.740	0.764	115.58	126.80	121.90	18.2919	16.3464	16.4442
0.08	0.928	0.688	0.737	116.80	127.61	123.93	18.0639	15.6461	16.1175
0.10	0.889	0.646	0.715	124.12	129.88	126.93	17.9537	15.2249	15.9989
$ZnSO_4$ 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									
0.01	1.171	1.295	1.072	99.63	89.99	89.83	20.7882	22.0151	19.2282
0.02	1.002	1.187	0.967	113.66	108.82	108.72	19.3441	21.5902	18.8040
0.04	0.864	0.894	0.781	115.64	110.81	110.72	17.5394	17.7667	16.3496
0.06	0.848	0.827	0.703	117.62	115.97	117.48	17.3543	17.0633	15.5660
0.08	0.830	0.783	0.679	121.96	119.53	119.47	17.2692	16.5955	15.2885
0.10	0.811	0.767	0.667	123.47	121.52	121.46	17.1006	16.4875	15.2372
$ZnSO_4$ 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									
0.01	1.297	1.252	1.486	91.07	81.62	118.87	22.4074	21.3315	26.5685
0.02	1.182	1.102	1.423	104.84	109.41	123.35	21.4666	20.7705	25.9324
0.04	0.971	0.951	1.060	111.43	113.68	125.29	18.9622	18.8944	20.9844
0.06	0.756	0.917	0.878	121.11	121.06	127.24	16.5023	18.7287	18.5399
0.08	0.748	0.817	0.829	123.43	123.39	128.02	16.4310	17.4094	17.8385
0.10	0.721	0.779	0.776	125.60	125.57	130.20	16.1981	17.0267	17.2276

Gibb´s free energy

The Gibb’s free energy, ΔG of the studied systems was calculated by using the relaxation time parameter and other constants.

$$\Delta G = kT\ln\left[\frac{kT\tau}{h}\right] \tag{9}$$

where k is Boltzmaan's constant (1.23×10^{-23} JK^{-1}), T is the absolute temperature and h is Planck's constant (6.6×10^{-34} Js). It has been observed that the values of ΔG increase with $ZnSO_4$ as well as with galactose and lactose concentrations. This type of variation suggests closer approach of unlike molecules due to H-bonding. Again ΔG decreases with temperature and it is indicative of the rearrangement of molecules in the mixtures [Representative 3-D plots for $ZnSO_4$ 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]

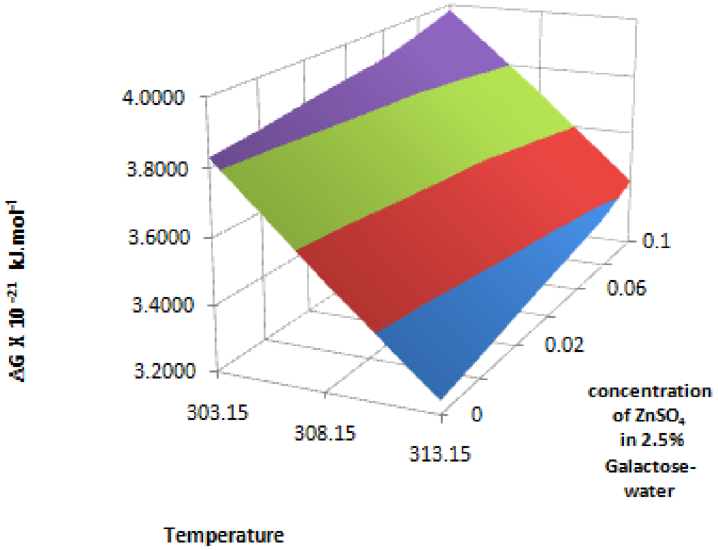

Fig. 16. 3-D Representative plots of Gibb's free energy ΔG *vs* Concentration (mole kg^{-1}) of $ZnSO_4$ in 2.5% Galactose-water mixed solvent at T = (303.15K, 308.15K, 313.15K).

Conclusion

The results of the present study indicate the existence of ion-solvent or solute-solvent interaction. $ZnSO_4$ 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 compressibilty shows the ion-solvent interactions of zinc ions to be larger in galactose systems than that in lactose. S_n shows greater solvation of $ZnSO_4$ 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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