Volumetric and Viscometric Behavior of Ferrous Sulfate in Aqueous Lactose Solutions at Different Temperatures

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ABSTRACT

Apparent molar volumes and viscosity B-coefficients for Ferrous sulfate in aqueous lactose solutions were determined from solution density and viscosity measurements at (298.15, 303.15, 308.15, 313.15) K as a function of FeSO$_4$ concentration. The standard partial molar volume and slopes obtained from the Masson equation have been interpreted in terms of solute-solvent and solute-solute interactions, respectively. The viscosity data were analyzed using the Jones-Dole equation and the derived parameters A and B were interpreted in terms of solute-solute and solute-solvent interactions respectively. The standard volume of transfer and viscosity B-coefficients of transfer of ferrous sulfate from water to aqueous lactose solutions were derived to study various interactions in the ternary solutions. The activation parameters of viscous flow for the ternary solutions were also calculated and explained in terms of transition state theory.

Key words: *Partial molar volumes, Viscosity B-coefficients, Ferrous sulfate, Aqueous lactose solutions.*

1. INTRODUCTION

Volumetric studies provide useful information in understanding the behavior of liquid systems, because intramolecular and intermolecular association, complex formation, and related structural changes affect the apparent molar volume, which in turn produce corresponding changes in the density and viscosity.

The investigation of volumetric and thermodynamic properties of carbohydrates or disaccharides has become a subject of increasing interest because of the various physical, biochemical, biomedical and industrially useful properties of these compounds. In addition to their importance in the food industry, chemical industry, and pharmaceuticals they are also able to protect biological macromolecules. In particular carbohydrates located at cell surfaces, are very important as receptors with regard to the structures of hormones, enzymes, viruses, antibodies [1]. Carbohydrates molecules have several hydroxyl groups interact with metal ions to produce a number of metal carbohydrate complexes. These complexes are weak, but interactions are specific. In recent years, the study of volumetric properties of aqueous mixed electrolytic solutions has been found to be useful in understanding specific ion-ion and ion-solvent interactions [2,3]. Volumetric and thermodynamic properties of aqueous carbohydrates solutions with metal ions thus provide

a lot of valuable information regarding solute-solute and solute-solvent interactions. It also provides factors important for the preservation of the biological materials (sugars). For this reason, there has been a number of works revealing the effect of electrolyte in aqueous carbohydrates solutions [4-7]. However, to the best of our knowledge such studies with aqueous lactose solutions and ferrous sulfate are rare in the literature. Hence, in this paper an attempt has been made to unravel the various interactions in the ternary systems of ferrous sulfate + lactose + water at 298.15, 303.15, 308.15, and 313.15 K.

2. EXPERIMENTAL

2.1. Materials

Lactose (purity>99.5%, Thomas Baker) and Ferrous sulfate (purity>99%, standard deviation fine chem.) were used for the present study. Deionized doubly distilled degassed water with a specific conductance <10^{-6} S/cm was used for the preparation of different aqueous solutions of lactose. The physical properties of different aqueous solutions of lactose are reported in Supplementary Table 1. We found no comparable literature data on densities (ρ_0) and viscosities for aqueous solutions of lactose (used as solvents) in this work. Stock solutions of ferrous sulfate in different aqueous solutions of lactose were prepared by mass and then they are further diluted to obtain the different

working solutions. Molalities (*m*) were converted into molarities (*c*) by using the experimental densities [8,9]. All solutions are prepared afresh before use and adequate precautions were taken to avoid evaporation losses during the measurements. The uncertainty in molarity of the ferrous sulfate solutions was evaluated to be within ± 0.0001 mol dm^{-3}.

2.2. Methods
The mass measurements were done on a digital electronic analytical balance (Mettler, AG 285, Switzerland) with a precision of ± 0.01 mg. The densities were measured with a vibrating-tube density meter (Anton Paar DMA 4500 M) and it was maintained at ± 0.01 K of the desired temperatures and calibrated with doubly distilled water and dry air. The uncertainty in density was estimated to be ± 0.00001 g cm^{-3}. The viscosities were measured by means of a suspended Ubbelohde type viscometer. It was calibrated at the experimental temperatures with doubly distilled water and purified methanol [10]. A thoroughly cleaned and perfectly dried viscometer (filled with the experimental solutions) was placed vertically in a glass-walled thermostat maintained to ± 0.01 K of the desired temperatures. After attainment of thermal equilibrium, efflux times of flow were recorded with a digital stopwatch that measures time correct to ± 0.01 s. At least three repetitions of each data (reproducible to ± 0.02 s) were taken to average the flow times. Based on our work on several pure liquids the precision of the viscosity measurements was evaluated to be within ± 0.0003 mPa s and the total uncertainty of the viscosity measurements was 1.5%. Details of the methods and techniques of the density and viscosity measurements were described elsewhere [11-13].

3. RESULTS AND DISCUSSION
The apparent molar volumes (φ_v) of ferrous sulfate in different aqueous solutions of lactose were determined from the solution densities by using the following equation [14-16]:

$$\varphi_v = \frac{M}{\rho_0} + \frac{1000(\rho_0 - \rho)}{m\rho_0\rho} \qquad (1)$$

Where *M* and m are the molar mass and molality of ferrous sulfate in the aqueous solutions of lactose; ρ_0 and ρ are the densities of the solvent and the solution, respectively. Experimental densities (ρ), viscosities (η), and derived parameters at 298.15, 303.15, 308.15, and 318.15 K are reported in Supplementary Table 2. Because of the fact that the φ_v values are independent of the concentrations of lactose for extremely dilute solutions, it can be assumed that φ_v values are equal to the partial molar volume (φ_V^0) at infinite dilution. The plots of φ_v values against square root of molal concentrations ($\sqrt{m}$) of ferrous sulfate were found to be linear. Hence, the partial molar volumes (φ_V^0) at infinite dilution and the experimental slopes (S_V^*) were

determined by using least squares fitting of φ_v values to the Masson equation [14]:

$$\varphi_v = \varphi_V^0 + S_V^* \sqrt{m} \qquad (2)$$

The φ_V^0 and S_V^* values are reported in Table 1. It shows that φ_V^0 values are positive and increase when the molarities of lactose in the mixtures increase and decrease as the temperatures of the respective mixtures increase. This trend in φ_V^0 values indicates the presence of strong solute-solvent interaction and such interactions further strengthen at higher concentrations of lactose in the ternary solutions and decrease when the temperature increases-probably due to more thermal agitations leading to the disruption of developing specific interactions between the solute and solvent molecules at higher temperatures. These trends in φ_V^0 values are clear manifestations of the trends in φ_v values (Supplementary Table 2).

The parameter S_V^* is the volumetric viral coefficient characterizing the pairwise interaction between the solvated species [11,13,16,17]. In the present study, S_V^* is found to be positive for all the ferrous sulfate solutions. For ionic species like ferrous sulfate the positive value of S_V^* suggest that the pairwise interaction is dominated by the charged functional groups. A perusal in Table 1 shows that S_V^* is positive and increases with the increase in temperature and with the increase in lactose concentration in the aqueous solutions.

Apparent molar volumes (ϕ_V) and densities (ρ_0) were used to derive the apparent molar expansibilities (ϕ_E) of lactose solutions by using the relation [3]:

$$\phi_E = \alpha\phi_V + 1000(\alpha - \alpha_0)/(m\rho_0) \qquad (3)$$

where α and α_0 are the coefficients of isobaric thermal expansion of the solvent and solution, respectively and other symbols have their usual significances [18,19].

α and α_0 are defined as: $\alpha = -\rho_0^{-1}(d\rho_0/dT)_P$ and $\alpha = -\rho^{-1}(d\rho/dT)_P$, respectively. The uncertainty of α and α_0 values was $\pm 5\times 10^{-6}$ K^{-1}. The uncertainty of apparent molar expansibilities (ϕ_E) was within $\pm 0.001\times 10^{-6}$ m^3 mol^{-1} K^{-1}. The partial molar expansibilities (ϕ_E^0) were derived from the relation [20]:

$$\phi_E = \phi_E^0 + S_E \sqrt{m} \qquad (4)$$

The φ_E^0 values for the experimental solutions at different temperatures are reported in Table 2. It shows that φ_E^0 values are negative and further decrease

when the temperatures and the lactose concentrations in studied solutions increase. Such a trend in φ_E^0 values may be attributed to structural perturbations caused by the addition of lactose or to the appearance of caging or packing effects [3,20]. However, such effects gradually decrease and lead to the release of solvated H_2O molecules in favor of the bulk water structure and thus decrease volumes and increases densities of the solutions as shown in Table 2. According to Hepler [12], the long-range structure making or breaking ability of the solutes in the solutions can be better characterized by the sign of $(d\varphi_E^0/dT)_P$ terms. If the sign of $(d\varphi_E^0/dT)_P$ is small negative or positive the solute is a structure maker, otherwise it is a structure breaker. $(d\varphi_E^0/dT)_P$ values were obtained from the slopes of linear fits of φ_E^0 values against experimental temperatures (T) with the coefficient of regression (R^2) values lying within the range of 0.99998-0.99999. From the values of $(d\varphi_E^0/dT)_P$, reported in Table 2, it is evident that $FeSO_4$ acts as a structure maker and its structure making ability decreases to some extent when the lactose concentrations increase in the studied solutions.

Partial molar volumes of transfer ($\Delta\varphi_V^0$) (Table 3) from water to different aqueous lactose solutions were determined using the relation [3]:

$$\Delta\phi_V^0 = \phi_V^0 [\text{Aqueous lactose solution}] - \phi_V^0 [\text{Water}] \qquad (6)$$

The ($\Delta\phi_V^0$) value, by definition is free from solute-solute interactions and therefore provides information regarding solute-co solute interactions [20]. As can be seen from Table 3, the value of ($\Delta\phi_V^0$) is positive at all the experimental temperatures and increased monotonically with the increase in concentration of aqueous lactose solutions in the ternary mixtures (Figure 1). The concentration dependence of the thermodynamic properties of the solutes in aqueous solutions can be explained in terms of overlap of hydration co-spheres. According to the co sphere model, as developed by Friedman and Krishnan the effect of overlap of hydration co sphere is destructive [22]. The overlap of hydration co spheres of two ionic species results in an increase in volume, but that of hydration co spheres of hydrophobic-hydrophobic groups results in a net volume decrease. The positive ($\Delta\phi_V^0$) values indicate that ion-hydrophilic and hydrophilic-hydrophilic group interactions are predominant over ion-hydrophobic, hydrophobic-hydrophobic and hydrophilic-hydrophobic interactions and the overall effect of the overlap of the hydration co spheres of ferrous sulfate and lactose reduces the electrostriction of water by ferrous sulfate. Such reduced electrostriction results in a concomitant increase in volume and this effect

further increase as the molarities of lactose in the ternary solutions increase.
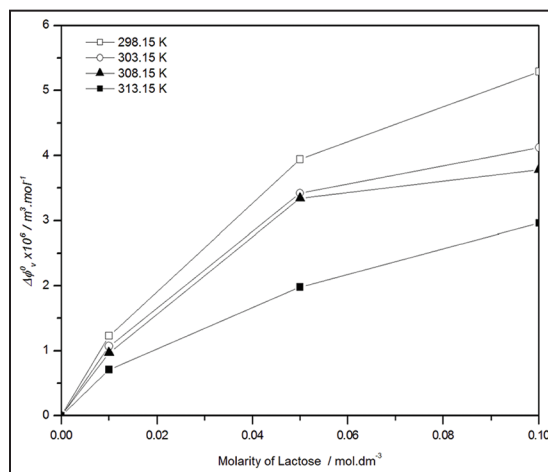
Figure 1: Plots of partial molar volumes ($\Delta\varphi_v^0$) against molality for transfer from water to different aqueous lactose solutions for ferrous sulfate at different temperatures, T=298.15 K (γ); T=303.15 K (⊄); T=308.15 K (▲); and T=313.15 K (■).

Table 1: Partial molar volumes (φ_V^0) and the experimental slopes (S_V^*) of equation (2) for $FeSO_4$ in aqueous solutions of lactose with corresponding standard deviations (σ) at different temperatures.

T/K	$\varphi_V^0 \times 10^6$/m³ mol⁻¹	$S_V^* \times 10^6$/m⁹ᐟ² mol⁻³ᐟ²	σ×10⁶/m³ mol⁻¹
0.00ᵃ			
298.15	121.29	31.00	0.01
303.15	118.74	40.04	0.01
308.15	115.85	47.47	0.02
313.15	114.98	51.33	0.01
0.01ᵃ			
298.15	122.52	32.57	0.02
303.15	119.81	39.32	0.01
308.15	116.82	47.70	0.03
313.15	115.69	50.33	0.02
0.05ᵃ			
298.15	125.30	38.53	0.01
303.15	122.16	43.92	0.03
308.15	119.19	49.79	0.02
313.15	117.94	54.00	0.02
0.10ᵃ			
298.15	126.58	45.94	0.02
303.15	122.86	48.39	0.03
308.15	119.63	51.27	0.04
313.15	117.94	60.26	0.02

ᵃMolarity of lactose in water in mol.dm⁻³

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Table 2: Limiting partial molar expansibilities (φ_E^0) for FeSO$_4$ in aqueous solutions of lactose at different temperatures.

Morality of lactose in aqueous solution/mol dm^{-3}	$\varphi_E^0 \times 10^4$/m^3 mol^{-1} K^{-1}				$S_E \times 10^4$/m^3 mol^{-1} K^{-1}				$(\mathrm{d}\varphi_E^0/\mathrm{d}T)_P$x 10^6/m^3 mol^{-1} K^{-2}
	298.15 K	303.15 K	308.15 K	313.15 K	298.15 K	303.15 K	308.15 K	313.15K	
0.00	−4.693 (±0.062)	−4.715 (±0.062)	−4.745 (±0.063)	−4.750 (±0.062)	16.088 (±0.120)	16.162 (±0.120)	16.301 (±0.140)	16.303 (±0.140)	−4.565
0.01	−5.043 (±0.054)	−5.056 (±0.054)	−5.080 (±0.054)	−5.100 (±0.054)	12.918 (±0.110)	12.944 (±0.100)	13.013 (±0.100)	13.061 (±0.100)	−3.893
0.05	−5.919 (±0.020)	−5.948 (±0.020)	−5.979 (±0.020)	−6.008 (±0.020)	10.024 (±0.090)	10.074 (±0.090)	10.128 (±0.090)	10.177 (±0.090)	−0.591
0.10	−6.922 (±0.040)	−6.957 (±0.040)	−6.985 (±0.040)	−7.017 (±0.040)	18.700 (±0.130)	18.771 (±0.140)	18.834 (±0.140)	18.972 (±0.150)	−0.623

Standard errors are given in parenthesis

Table 3: Partial molar volumes of transfer from water to different aqueous lactose solutions for FeSO$_4$ at different temperatures.

Morality of lactose in aqueous solution/mol dm^{-3}	$\varphi_V^0 \times 10^6$/m^3 mol^{-1}	$\Delta\varphi_V^0 \times 10^6$/m^3 mol^{-1}
T=298.15 K		
0	121.29	0
0.01	122.52	1.23
0.05	125.30	4.01
0.1	126.58	5.29
T=303.15 K		
0	118.74	0
0.01	119.81	1.07
0.05	122.16	3.42
0.1	122.86	4.12
T=308.15 K		
0	115.85	0
0.01	116.82	0.97
0.05	119.19	3.34
0.1	119.63	3.78
T=313.15 K		
0	114.98	0
0.01	115.69	0.71
0.05	116.96	1.98
0.1	117.94	2.96

In addition, partial molar volumes of the solute have been also explained by a simple model [5,6,13].

$$\Delta\phi_V^0 = \phi_{vw} + \phi_{void} - \phi_S$$

where φ_{vw} is the van der Waals volumes, φ_{void} is the volume associated with voids or empty space, and φ_S the shrinkage volumes due to electrostriction.

Assuming the φ_{vw} and have same magnitudes in water and in aqueous lactose solutions for the same solute, the increase in φ_V^0 values and the concomitant positive $\Delta\varphi_V^0$ values can be attributed to the decrease in the shrinkage volume of water by ferrous sulfate in presence of lactose. This fact suggests that lactose has a dehydration effect on the hydrated ferrous sulfate.

Thus, the interactions between ferrous sulfate and lactose can roughly be summarized as follows:

(1) Interaction of Fe^{++} ion with the O atoms in the heterocyclic ring lactose, (2) interaction of the Fe^{++} ion with the linkage O atom of the two rings. (3) Interaction of Fe^{++} ion with the O atom of the OH group of lactose. (4) Interaction of SO$_4$= with the H atom of the OH group of lactose. (5) Ionic- hydrophobic interactions between ions of ferrous sulfate and nonpolar part of lactose (Figure 2). While interactions of 1-4 types impart positive contributions, interaction of 5 types imparts negative contribution to ϕ_V^0 values. Therefore, the overall positive ϕ_V^0 values indicate that ionic group interactions predominate over ionic-hydrophobic interactions. This predominance of ionic group interactions reduces the electrostriction of water by ferrous sulfate and imparts positive contributions to $\Delta\phi_V^0$ values.

The viscosity data of the aqueous and aqueous lactose solutions of ferrous sulfate were analyzed using the Jones-Dole [23] equation:

$$(\eta/\eta_0 - 1)/\sqrt{c} = (\eta_r - 1)/\sqrt{c} = A + B\sqrt{c} \qquad (7)$$

where $\eta_r = \eta/\eta_0$ is the relative viscosity; η_0 and η are the viscosities of solvent and solution, respectively. *A* and *B* are two adjustable parameters that are obtained by a least squares analysis and are reported in Table 4.

The viscosity B-coefficient [24,25] reflects the effects of solute-solvent interactions on the solution viscosity

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Table 4: Values of viscosity A- and B- coefficients for $FeSO_4$ in aqueous solutions of lactose at different temperatures.

Viscosity coefficients	T=298.15 K	T=303.15 K	T=308.15 K	T=313.15 K
c=0.00[a]				
$A \times 10^{-6}/m^{3/2}\ mol^{-1/2}$	−0.004 (±0.0002)	−0.007 (±0.0004)	−0.008 (±0.0006)	−0.012 (±0.0005)
$B \times 10^{-6}/m^3\ mol^{-1}$	0.568 (±0.0030)	0.680 (±0.0020)	0.760 (±0.0030)	0.840 (±0.0060)
c=0.01[a]				
$A \times 10^{-6}/m^{3/2}\ mol^{-1/2}$	−0.006 (±0.0005)	−0.011 (±0.0004)	−0.018 (±0.0007)	−0.017 (±0.0005)
$B \times 10^{-6}/m^3\ mol^{-1}$	0.590 (±0.0080)	0.709 (±0.0060)	0.797 (±0.0050)	0.877 (±0.0070)
c=0.05[a]				
$A \times 10^{-6}/m^{3/2}\ mol^{-1/2}$	−0.011 (±0.0008)	−0.018 (±0.0011)	−0.026 (±0.0013)	−0.025 (±0.0011)
$B \times 10^{-6}/m^3\ mol^{-1}$	0.608 (±0.0090)	0.732 (±0.0110)	0.826 (±0.0140)	0.906 (±0.0170)
c=0.10[a]				
$A \times 10^{-6}/m^{3/2}\ mol^{-1/2}$	−0.016 (±0.0009)	−0.023 (±0.0011)	−0.032 (±0.0017)	−0.029 (±0.0013)
$B \times 10^{-6}/m^3\ mol^{-1}$	0.622 (±0.0080)	0.754 (±0.0050)	0.850 (±0.0090)	0.927 (±0.0130)

[a]Molarity of lactose in water in $mol.dm^{-3}$

Table 5: Viscosity B-coefficients of transfer from water to different aqueous lactose solutions for $FeSO_4$ at different temperatures.

Molarity of lactose in aqueous solution/mol dm^{-3}	$B \times 10^{-6}/m^3$ mol^{-1}	$\Delta B \times 10^{-6}/m^3$ mol^{-1}
T=298.15 K		
0	0.568	0
0.01	0.590	0.022
0.05	0.608	0.040
0.10	0.622	0.054
T=303.15 K		
0	0.681	0
0.01	0.709	0.028
0.05	0.732	0.051
0.10	0.754	0.073
T=308.15 K		
0	0.760	0
0.01	0.797	0.037
0.05	0.826	0.066
0.10	0.850	0.090
T=313.15 K		
0	0.840	0
0.01	0.877	0.037
0.05	0.906	0.066
0.10	0.927	0.087

and provides information about the solvation of a solute and the structure of the solvent in the local vicinity of the solute molecules [26-28]. Table 5 shows that the viscosity B- coefficients for ferrous sulfate in the studied solvent systems are positive and thus suggest

the presence of strong solute-solvent interactions in the studies solutions. These interactions further increase when both the molality of $FeSO_4$ in the ternary solutions and temperatures increase. The A-coefficients values are indicative of solute-solute or ion-ion interactions and in the present study their values support the results obtained from viscosity B-coefficients discussed earlier. Viscosity B-coefficients of transfer (ΔB) from water to aqueous solutions of lactose were determined by using the relation [15]:

$$\Delta B = B[\text{Aqueous lactose solution}] - B[\text{Water}] \quad (8)$$

The ΔB values are depicted in Table 5 as a function of molality of lactose in aqueous solutions and support the results obtained from $\Delta\varphi_V^0$ values discussed earlier (Figure 3).The viscosity data were analyzed on the basis of transition state theory of relative viscosity as suggested by Feakings et al. using the following relation [29-31]:

$$\Delta\mu_2^{\theta*} = \Delta\mu_1^{\theta*} + RT(1000B + \varphi_{v,2}^0 - \varphi_{v,1}^0)/\varphi_{v,1}^0 \quad (9)$$

Where $\varphi_{v,1}^0$ and $\varphi_{v,2}^0$ are the partial molar volumes of the solvent and solute, respectively. The contribution per mole of the solute to the free energy of activation of viscous flow, $\Delta\mu_2^{\theta*}$ of the solutions was determined from the above relation. The free energy of activation of viscous flow for the pure solvent/solvent mixture, $\Delta\mu_1^{\theta*}$, is given by the relation:

$$\Delta\mu_1^{\theta*} = \Delta G_1^{\theta*} = RT\ln(\eta_0\varphi_{v,1}^0)/hN_A \quad (10)$$

Where N_A is the Avogadro's number and the other symbols have their usual significance. The values of the parameters $\Delta\mu_1^{\theta*}$ and $\Delta\mu_2^{\theta*}$ are

Table 6: Values of ($\Delta\varphi_{v,2}^0 - \varphi_{v,1}^0$), $\Delta\mu_1^{\theta*}$, $\Delta\mu_2^{\theta*}$, $\Delta H_2^{\theta*}$ and $T\Delta S_2^{\theta*}$ for FeSO$_4$ in different aqueous solutions of lactose at different temperatures.

Parameters	298.15 K	303.15 K	308.15 K	313.15 K
c=0.00[a]				
($\Delta\varphi_{v,2}^0 - \varphi_{v,1}^0$)$\times10^6$/m^3 mol^{-1}	−103.17	−100.57	−97.62	−96.70
$\Delta\mu_1^{\theta*}$ /kJ mol^{-1}	9.18	9.06	8.96	8.86
$\Delta\mu_2^{\theta*}$ /kJ mol^{-1}	101.04	117.40	129.55	142.05
$T\Delta S_2^{\theta*}$ /kJ mol^{-1}	−850.23	−864.49	−878.75	−893.01
$\Delta H^{\theta*}$ /kJ mol^{-1}	−819.30	−831.99	−844.53	−857.27
c=0.01[a]				
($\Delta\varphi_{v,2}^0 - \varphi_{v,1}^0$)$\times10^6$/m^3 mol^{-1})	−104.40	−101.67	−98.55	−97.39
$\Delta\mu_1^{\theta*}$ /kJ mol^{-1}	9.22	8.89	8.80	8.58
$\Delta\mu_2^{\theta*}$ /kJ mol^{-1}	104.13	121.56	134.37	147.19
$T\Delta S_2^{\theta*}$ /kJ mol^{-1})	−901.55	−916.67	−931.78	−946.90
$\Delta H^{\theta*}$ /kJ mol^{-1}	−797.42	−795.10	−797.42	−799.71
c=0.05[a]				
($\Delta\varphi_{v,2}^0 - \varphi_{v,1}^0$)$\times10^6$/m^3 mol^{-1}	−107.20	−103.91	−100.91	−98.65
$\Delta\mu_1^{\theta*}$ /kJ mol^{-1}	9.26	8.94	8.84	8.63
$\Delta\mu_2^{\theta*}$ /kJ mol^{-1}	107.03	124.42	138.78	151.46
$T\Delta S_2^{\theta*}$ /kJ mol^{-1}	−946.66	−962.53	−978.41	−994.28
$\Delta H^{\theta*}$ /kJ mol^{-1}	−839.63	−838.11	−839.63	−842.82
c=0.10[a]				
($\Delta\varphi_{v,2}^0 - \varphi_{v,1}^0$)$\times10^6$/m^3 mol^{-1}	−108.40	−104.63	−101.38	−99.56
$\Delta\mu_1^{\theta*}$ /kJ mol^{-1}	9.42	8.97	8.88	8.69
$\Delta\mu_2^{\theta*}$ /kJ mol^{-1}	108.86	127.67	142.37	155.62
$T\Delta S_2^{\theta*}$ /kJ mol^{-1}	−999.13	−1015.89	−1032.64	−1049.40
$\Delta H^{\theta*}$ /kJ mol^{-1}	−890.27	−888.22	−890.27	−893.78

[a]Molarity of lactose in water in mol.dm^{-3}

reported in Table 6. The entropy of activation for electrolytic solutions has also been calculated by the relation [21]:

$$\Delta S_2^{\theta*} = -d(\Delta\mu_2^{\theta*}) / dT \qquad (11)$$

where $\Delta S_2^{\theta*}$ has been obtained from the negative slope of the plots of $\Delta\mu_2^{\theta*}$ against T by using a least squares treatment.
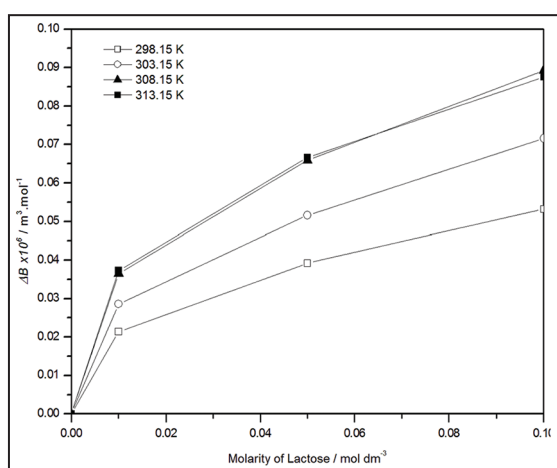
The activation enthalpy (ΔH_2^{θ}) has been calculated using the relation [21]:

$$\Delta H_2^{\theta} = \Delta\mu_2^{\theta*} + T\Delta S_2^{\theta*} \qquad (12)$$

The parameters ($\varphi_{v,2}^0 - \varphi_{v,1}^0$), $\Delta\mu_1^{\theta*}$, $\Delta\mu_2^{\theta*}$, $\Delta H_2^{\theta*}$ and $T\Delta S_2^{\theta*}$ are reported in Table 6. Table 6 shows that $\Delta\mu_1^{\theta*}$ values are almost invariant of the solvent compositions and temperatures and also imply that,
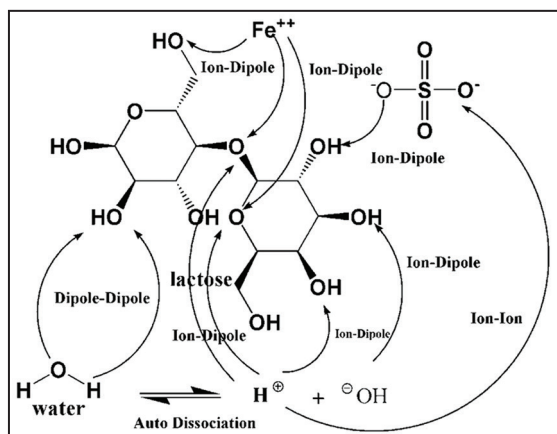
Figure 2: Different possible interactions in aqueous lactose solution in the presence of ferrous sulfate.

Figure 3: Plots of viscosity B coefficients (ΔB) against molality for transfer from water to different aqueous lactose solutions for ferrous sulfate at different temperatures, T=298.15 K (γ); T=303.15 K (γ); T=308.15 K (▲); and T=313.15 K (■).

$\Delta\mu_2^{\theta *}$ values are dependent mainly on the viscosity B-coefficients and $(\varphi_{v,2}^0 - \varphi_{v,1}^0)$ deviations. The $\Delta\mu_2^{\theta *}$ values contain the change in the free energy of activation of the solute in the presence of solvent as well as the contributions from the movement of solute molecules. $\Delta\mu_2^{\theta *}$ Values were found to be positive at all the experimental temperatures and increases when the temperature increases and increase when the lactose concentration in the ternary solutions increases. Such a trend suggests that the process of viscous flow becomes difficult when the lactose concentration in the ternary solutions and temperature increases. Hence, the formation of transition state becomes less favorable in the presence of lactose but becomes somewhat favorable at lower temperatures. The $(\Delta\mu_2^{\theta *} - \Delta\mu_1^{\theta *})$ deviations reflect the change in the activation energy per mole of a solute when one mole of the solvent is replaced by one mole of the solute at infinite dilution. According

to Feakins et al. [29] $\Delta\mu_2^{\theta *} > \Delta\mu_1^{\theta *}$, for solutes with positive viscosity B-coefficients, indicates stronger solute-solvent interactions; thereby suggesting the formation of transition state to be accompanied by the rapture and distortion of the intermolecular forces in solvent structure. The greater the value of $\Delta\mu_2^{\theta *}$ the greater is the structure making tendency of a solute. The comparatively higher positive values of $\Delta\mu_2^{\theta *}$ for FeSO$_4$ in different aqueous lactose solutions than those in aqueous solutions suggest it to be a structure maker in the studied ternaries. The negative $\Delta S_2^{\theta *}$ and $\Delta H_2^{\theta *}$ values in Table 6 for all the experimental temperatures suggest that the transition state is associated with bond formation and increase in order. Although a detailed mechanism for such transition state cannot be easily advanced, it may be suggested that the slip plane is in the disordered state [32-34].

4. CONCLUSION

In summary, partial molar volumes (φ_v^0) and viscosity B-coefficients of FeSO$_4$ in aqueous solutions of lactose indicate the presence of strong solute-solvent interactions and such interactions further strengthen at higher lactose concentrations in ternaries. Furthermore, the trends in $(d\varphi_E^0 / dT)_P$ and $\Delta\mu_2^{\theta *}$ for FeSO$_4$ in the aqueous solutions of lactose suggest that FeSO$_4$ is a net structure promoter in the studied aqueous solutions and it has a dehydration effect on the hydrated lactose.

5. ACKNOWLEDGMENT

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Bibliographical Sketch

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Supplementary Table 1: Density (ρ) and viscosity (η) for different aqueous solutions of lactose at different temperatures.

Aqueous lactose solution/mol.dm^{-3}	T/K	$\rho \times 10^{-3}$/kgm^{-3}	η/mPas
0.01	298.15	0.99833	0.9165
	303.15	0.99779	0.7979
	308.15	0.99619	0.7234
	313.15	0.99458	0.6297
0.05	298.15	1.00427	0.9651
	303.15	1.00273	0.8568
	308.15	1.00101	0.7661
	313.15	0.99932	0.6840
0.10	298.15	1.01119	1.0173
	303.15	1.00942	0.9129
	308.15	1.00817	0.8154
	313.15	1.00655	0.7262

Supplementary Table 2: Molalities (m), densities (ρ), viscosity (η), viscosities and apparent molar volumes (φ_v) for FsSO$_4$ in different aqueous solutions of lactose at different temperatures.

m/mol kg^{-1}	$\rho \times 10^{-3}$/kgm^{-3}	η/mPas	$\varphi_V^0 \times 10^6$/m^{3}mol^{-1}
0.00^a			
T=298.15 K			
0.02	1.00013	0.9113	125.15
0.036	1.00249	0.9203	127.78
0.052	1.00484	0.9270	128.79
0.068	1.00836	0.9394	129.71
0.084	1.00952	0.9439	130.05
0.1	1.01177	0.9519	131.19
T=303.15 K			
0.02	0.99875	0.7483	124.13
0.036	1.00112	0.7569	126.92
0.052	1.00348	0.7645	127.99
0.068	1.00697	0.7752	129.55
0.084	1.00812	0.7808	130.03
0.1	1.01030	0.7877	131.87
T=308.15 K			
0.02	0.99717	0.6779	122.54
0.036	0.99956	0.6865	125.48
0.052	1.00195	0.6939	126.42
0.068	1.00430	0.7049	127.36
0.084	1.00650	0.7099	130.12
0.1	1.00875	0.7163	131.25
T=313.15 K			
0.02	0.99535	0.5880	122.48

Supplementary Table 2: Continued.

m/mol kg^{-1}	$\rho \times 10^{-3}$/kgm^{-3}	η/mPas	$\varphi_V^0 \times 10^6$/m^{3}mol^{-1}
0.036	0.99775	0.5953	125.15
0.052	1.0001	0.6026	126.95
0.068	1.00358	0.6130	128.96
0.084	1.00472	0.6172	129.61
0.1	1.00689	0.6267	131.62
0.01^a			
T=298.15 K			
0.02	1.00135	0.9170	127.18
0.036	1.00371	0.9260	128.50
0.052	1.00602	0.9349	130.06
0.068	1.00946	0.9450	131.63
0.084	1.01057	0.9506	132.38
0.1	1.01288	0.9597	132.55
T=303.15 K			
0.02	1.00085	0.7576	125.17
0.036	1.00323	0.7655	126.83
0.052	1.00557	0.7742	128.33
0.068	1.00905	0.7815	129.92
0.084	1.01018	0.7916	130.60
0.1	1.01241	0.7986	131.85
T=308.15 K			
0.02	0.99926	0.6863	124.12
0.036	1.00167	0.6949	125.67
0.052	1.00399	0.7012	127.72
0.068	1.00746	0.7153	129.63
0.084	1.00859	0.7184	130.34
0.1	1.01070	0.7277	132.82
T=313.15 K			
0.02	0.99768	0.5965	123.06
0.036	1.00008	0.6050	125.08
0.052	1.00242	0.6111	127.11
0.068	1.00588	0.6227	129.34
0.084	1.00697	0.6257	130.55
0.1	1.00919	0.6387	131.91
0.05^a			
T=298.15 K			
0.02	1.00721	0.9315	131.03
0.036	1.00949	0.9404	132.49
0.052	1.01173	0.9494	133.89
0.068	1.01504	0.9594	135.75
0.084	1.01613	0.9650	136.18
0.1	1.01820	0.9765	138.10
T=303.15 K			
0.02	1.00571	0.7673	128.52
0.036	1.00802	0.7761	130.26

Supplementary Table 2: Continued.

m/mol kg^{-1}	$\rho \times 10^{-3}$/kgm^{-3}	η/mPas	$\varphi_V^0 \times 10^6$/m^{3}mol^{-1}
0.052	1.01026	0.7847	132.35
0.068	1.01361	0.7920	134.19
0.084	1.01471	0.8021	134.65
0.1	1.01682	0.8114	136.43
T=308.15 K			
0.02	1.00403	0.6965	126.49
0.036	1.00636	0.7052	128.57
0.052	1.00865	0.7114	130.23
0.068	1.01199	0.7255	132.87
0.084	1.01309	0.7286	133.46
0.1	1.0152	0.7403	135.44
T=313.15 K			
0.02	1.00237	0.6942	124.95
0.036	1.00473	0.6994	126.87
0.052	1.00702	0.7056	129.05
0.068	1.01038	0.7150	131.81
0.084	1.01145	0.7204	132.85
0.1	1.01363	0.7251	134.24
0.10[a]			
T=298.15			
0.02	1.01405	0.9493	133.13
0.036	1.01627	0.9582	135.32
0.052	1.01844	0.9672	136.91
0.068	1.02162	0.9771	139.12
0.084	1.02267	0.9827	139.69
0.1	1.02467	0.9966	141.45
T=303.15			
0.02	1.01236	0.7794	129.65
0.036	1.01462	0.7881	132.29
0.052	1.01685	0.7969	133.69
0.068	1.02011	0.8041	135.90
0.084	1.02116	0.8143	136.78
0.1	1.02321	0.8259	138.53
T=308.15			
0.02	1.01115	0.7085	126.65
0.036	1.01345	0.7172	129.54
0.052	1.01569	0.7234	131.59
0.068	1.01902	0.7376	133.57
0.084	1.02011	0.7407	134.21
0.1	1.02219	0.7549	136.11
T=313.15 K			
0.02	1.00967	0.7378	124.62
0.036	1.01187	0.7453	131.17
0.052	1.01412	0.7528	132.53

Supplementary Table 2: Continued.

m/mol kg^{-1}	$\rho \times 10^{-3}$/kgm^{-3}	η/mPas	$\varphi_V^0 \times 10^6$/m^{3}mol^{-1}
0.068	1.01632	0.7614	133.83
0.084	1.01851	0.7677	135.14
0.1	1.02066	0.7748	136.18

[a]molarity of lactose in water in mol.dm^{-3}

Contd...