

Viscometric and Thermodynamic Studies of D-Galactose and D-Maltose in Sodium Sulfide Solution (0.25M) at Different Temperatures

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ABSTRACT:

Densities ρ and Viscosities η of D-Galactose and D-Maltose (0.05-0.4)M in aqueous solution (0.25) M of Na_2S at 298.15, 303.15 and 308.15K have been measured. From these experimental data, apparent molal Volume ϕ_v Limiting Apparent Molal Volume (ϕ_v^o), The slope (S_v^o), Jones-Dole coefficient A and B, The free energy of activation of viscous flow (ΔG^*), The enthalpies (ΔH^*) and Entropies (ΔS^*) were calculated, A values compatible with the (S_v^o) values of weak solute-solute interaction while B came with positive and high, which indicating the strength of the reciprocal interaction type solute-solvent. This serves to strengthen of the structure of solvent. due to hydrophobic hydration and hydrogen bonding between solute and water, sodium sulfide molecules and on the other hand the water molecules rearranges toward formation of a local cage like (clathrates) structure surrounding each solute molecule

Key word: Viscometric and Thermodynamic Studies, D-Galactose, D-Maltose, Sodium sulfide

INTRODUCTION

The study of solutions is of great importance because most of the interesting and useful chemical and biological processes occur in liquid solutions [1]. Studies on interactions of non-ionic solutes with ionic ones in different solvents are significant for investigating their physico-chemical behavior [2-4]. The study of carbohydrates (saccharides) has become a subject of increasing interest because of the multidimensional physical, biochemical and industrially useful properties of these compounds [5-11]. In addition to their importance in the food, pharmaceutical and chemical industries, come to consideration simple saccharides have received

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considerable attention for their ability to protect biological macromolecules. [12, 13]

Polysaccharides are made of carbohydrates (monomers called monosaccharides) joined by glycosidic linkages. Carbohydrates or monosaccharides are normally represented by $(\text{CH}_2\text{O})_n$, where n is at least 3 and greater (for example $n = 3$ yields triose sugars and $n = 6$ yields hexoses like glucose and galactose (Fig.1)), Two monomers joined by glycosidic linkages is called disaccharides The glycosidic bond in maltose is α -1,4glycosidic linkage between two glucose molecules. Most sugars are the hexoses with six carbons and the structural formula $\text{C}_6\text{H}_{12}\text{O}_6$. Sugars can exist in one of two forms: linear or cyclic (ring). Sugars can quickly form ring-shaped structure in water due to the reaction of their keto or aldehyde groups with a hydroxyl group, Carbohydrates can also exist in D- and L-forms. Galactose (Fig).1 is an important hexose found in lactose (milk sugar) along with glucose [14]. Consequently, study of the volumetric properties of carbohydrates in aqueous salt solutions is very useful to obtain information about various types of interactions in solutions [15]. From the survey of literature it appears that there are many studies of partial molal volumes, and viscosities in binary systems of anther biomolecules [16-23].

EXPERIMENTAL SECTION

Materials: Sodium Sulfide $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ (M.wt [24]=240,19g.mol⁻¹)BDH chemicals London, D-Maltose (M.wt= 360.32 g.mol⁻¹)BDH chemicals London, D-Galactose (M.wt180.16 g.mol⁻¹)BDH chemicals London and distilled water. We measured the densities ρ and viscosities η of D-Maltose and D-Galactose (0.05-0.4) Molar concentrations in 0.25 Molar of Na_2S at 298.15, 303.15 and 308.15K.

Densities ρ of all solutions were measured using Density Bottle by James and Prichard [24] procedure in a thermostatic bath controlled to $\pm 0.01\text{K}$, The viscosities η were determined Using a suspended-level ubbelohde Viscometer(Viscometer constant =0.0047 cm² s⁻²) described by lee and shahjahan [26] procedure in a bath controlled to $\pm 0.01\text{K}$ for all measurements.

RESULTS AND DISCUSSION

The density data measured for the solutions of D-Galactose and D-Maltose (0.05-0.4) M in aqueous solution of 0.25 M of Na_2S at 298.15, 303.15 and 308.15K are listed in Table 1. These results shows an increase of density values with increase of the increasing of concentration of D-Galactose and D-Maltose solution at each specified temperature and a decrease of density with increasing temperature at constant molar

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concentration These results are agree with general behavior of liquid solution as soon as viscosity obey the same normal behavior of normal liquid solution.[14-23]

The density data was used to compute apparent molal volumes ϕ_v , using the relation 1. [26,27]

$$\phi_v = \frac{1}{m} \left[\frac{(1000 + mM)}{\rho} - \frac{(1000)}{\rho_0} \right] \dots\dots\dots 1$$

where m are the Molality (mol/Kg) of D-Galactose and D-Maltose solution, M are molecular weight of solute (g/mol), and ρ and ρ_0 are the respective densities of solution and solvent (g/cm³). The values of ϕ_v are tabulated in Table 2. ϕ_v are found to be a linear function of square root for molar concentration C of D-Galactose and D-Maltose in the concentration range studied. A decrease in ϕ_v with square root for molar concentration (C) of D-Galactose and D-Maltose suggests that solute-solvent interaction decreases with the increase amount D-Galactose and D-Maltose in the solution, also a decrease of ϕ_v values with the increasing temperature refers that solute-solvent interaction decreases. The limiting value of partial molal volume at infinite dilution ϕ_v^o is obtained by the computerized least-squares fitting to the equation- 2 [28,29].

$$\phi_v = \phi_v^o + S_v^o \sqrt{C} \dots\dots\dots 2$$

Where ϕ_v^o is the apparent molal volume of D-Galactose and D-Maltose at infinite limited dilution and S_v^o is the experimental slope which is also considered as the volumetric pair wise interaction coefficient [26,27]. The ϕ_v^o reflects the presence of solute-solvent interaction, whereas, S_v^o is indicative of solute-solute interaction. The values of ϕ_v^o and S_v^o are reported in Table 3. Table 3 reveals that ϕ_v^o are positive and large for the all D-Galactose and D-Maltose solution indicating the presence of strong solute- solvent interaction, ϕ_v^o values decrease with that indicate increase in temperature, indicating decreased solute-solvent interaction in solution with rise in temperature, The negative values S_v^o are for all D-Galactose and D-Maltose solution indicating the presence of weak solute- solute interaction[15,16,18]. In fact negative S_v^o values are often obtained in solvents of high dielectric constant [30]. S_v^o Values (become less negative) with increase in temperature, indicating an increased solute-solute interaction in solution with rise in temperature[15,16,18]. The ϕ_v^o more increase where S_v^o more decrease in D-Maltose than D-Galagtose that is

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reveal increase solute-solute interaction and decreased solute-solute interaction.

The viscosity data were analyzed by using the Jones-Dole equation [16, 21, 23].

$$\eta_{rel} = 1 + A\sqrt{C} + BC.....3$$

$$-1/\sqrt{C} = A + B\sqrt{C} 4$$

Where η_r is the relative viscosity of the solution, A and B are the Falkenhagen and Jones-Dole coefficients respectively. Coefficient A accounts for the solute-solute interactions and B is a measure of structural modifications induced by the solute-solvent interactions. The values of A and B have been obtained from the intercepts and slopes of the plots of $\frac{\eta_{rel} - 1}{\sqrt{C}}$ vs. \sqrt{C} (equation 4). The values of A and B are included in table- 5.

Table -5 shows that the values of A-coefficients are negative or very small, whereas those of B-coefficients are largely positive due to hydrophobic hydration and hydrogen bonding between solute and water , sodium sulfide molecules and on the other hand the water molecules rearranges toward formation of a local cage like (clathrates) structure surrounding each solute molecule , suggesting weak solute-solute and strong solute-solvent interactions the D-Galactose and D-Maltose solutions under study . Thus the values of A and B coefficients support the behaviors of ϕ_v^o and S_v^o , which all suggest strong solute- solvent interactions as compared with solute- solute interactions in these D-Galactose and D-Maltose solutions. Also the decreasing values of B-coefficient and increasing values of A-coefficients with a rise in temperature further support our earlier conclusion (drawn from the variations of ϕ_v^o and S_v^o with temperature) that solute-solvent interactions decrease while solute-solute interactions increase with a rise in temperature. The B values more increase where A values more decrease in D-Maltose than D-Galactose that is reveal increase solute-solute interaction and decreased solute-solute that support the behaviors ϕ_v^o and S_v^o .

From transition state theory the Gibbs free energy of activation for viscous flow of solution, ΔG^* (J mol⁻¹) at given temperature and composition is given by [30,31].

$$\Delta G^* = RTLn\left(\frac{V_{1,2}\eta}{hN_A}\right).....5$$

Where R is the gas constant, T is the absolute temperature, h is planks constant, N_A is Avogadros constant and the volume of mole of solution is V_{1,2} obtained from the relation[22]

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$$V_{1,2} = \frac{1000 + mM_2}{\rho \left(\frac{1000}{M + m} \right)} \dots\dots\dots 6$$

Where M_1 and M_2 are molecular weight (g/mol) for solvent (water + 0.25M $K_2S_2O_8$) and solute (D-Galactose and D-Maltose) respectively , m is the Molality (mol/Kg) of D-Galactose and D-Maltose solution ,and ρ is the densities of D-Galactose and D-Maltose solution (g/cm^3) . The values for ΔG calculated via the equation (5) for D-Galactose and D-Maltose are given in Table 6. Tables 6 show that the values of ΔG increase with increase of concentrations and temperature for D-Galactose and D-Maltose.

Furthermore, the enthalpies (ΔH^*) and entropies (ΔS^*) of activation of viscous flow have been calculated from the free energy of activation of viscous flow (ΔG^*) by using the relations

$$\Delta G^* = \Delta H^* - T\Delta S^* \dots\dots\dots 7$$

The values of ΔH^* (the intercept) and ΔS^* (the slope) were deduced from linear plots of ΔG^* vs. temperature ΔH^* gives the structural information of the solute species, whereas, ΔS^* provides information regarding solute-solvent interactions. The results are shown in Table - 6. Tables -6 show that ΔH^* of all the solutions increase with increase in D-Galactose and D-Maltose concentration, suggesting that the formation of activated species necessary for viscous flow appears difficult as the amount of D-Galactose and D-Maltose increases in the solution. The ΔS^* values for all the D-Galactose and D-Maltose are decrease with concentration, suggesting that during the viscous flow the system is more structured than in the initial state. This reports the presence of significant solute-solvent interactions in the systems under study.

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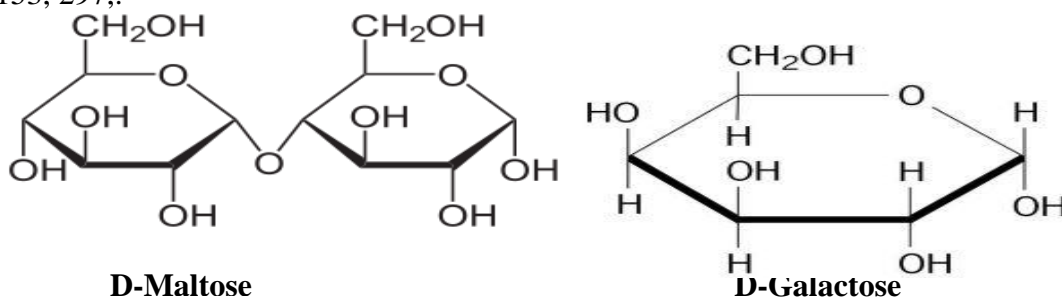
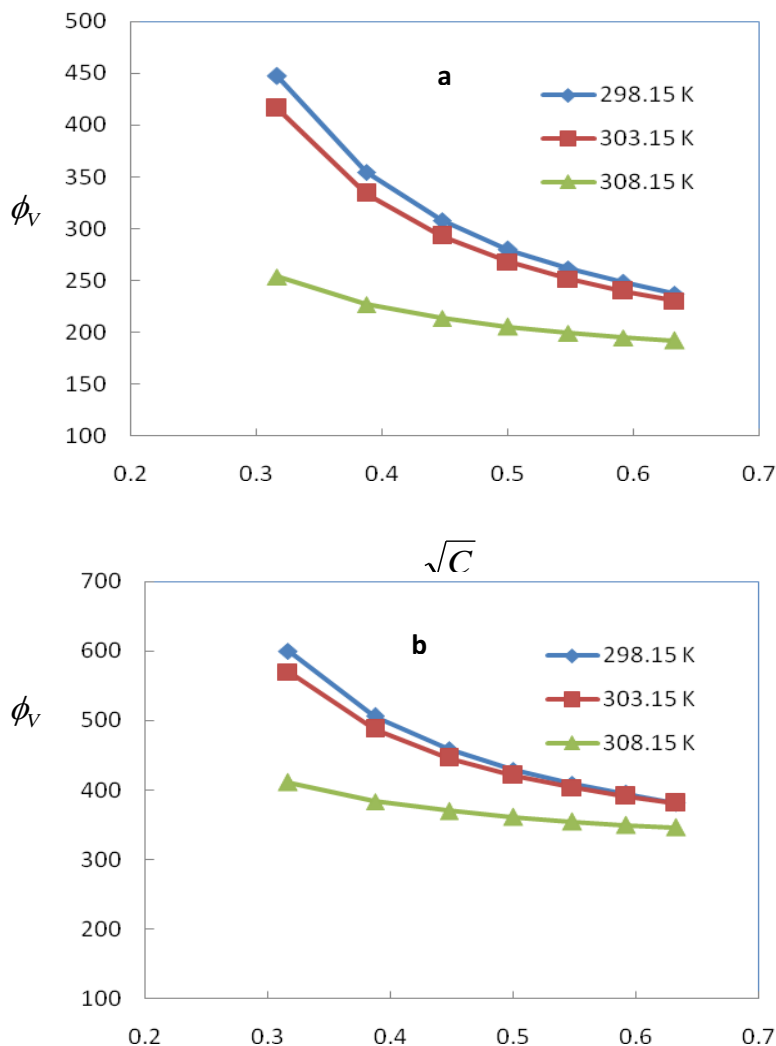


Fig.1



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Fig.2. Plot of ϕ_v vs \sqrt{C} for (a)D-Galactose and (b)D-Maltose (0.05-0.4) M in aqueous Solution of 0.25 M of $K_2S_2O_8$ at 298.15, 303.15 and 308.15K.

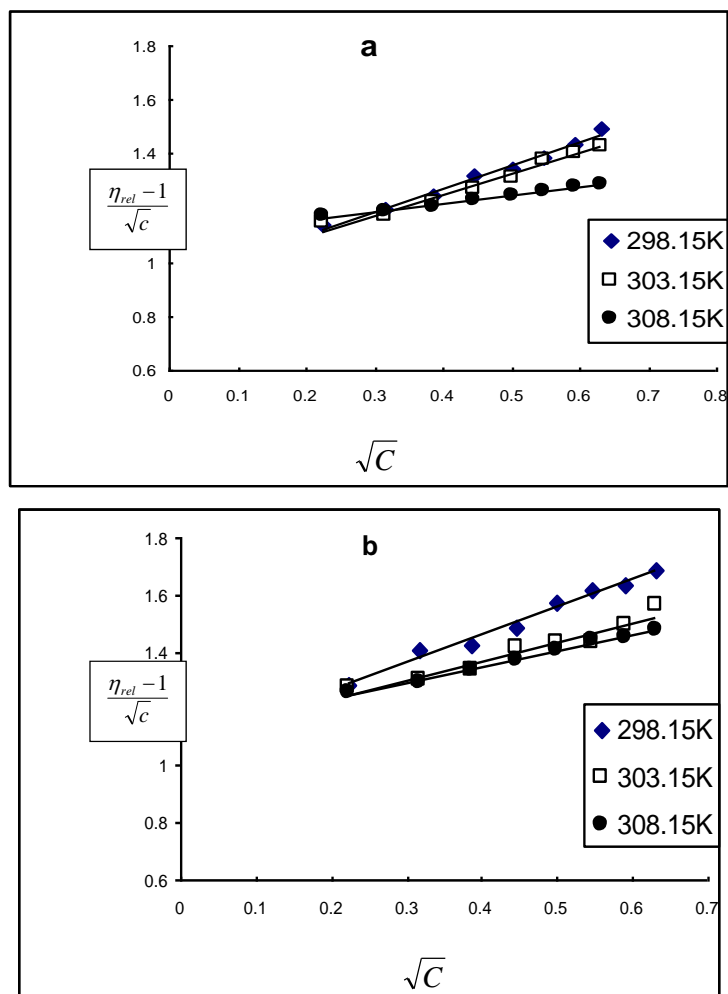


Fig.3. Plot of \sqrt{C} vs $\frac{\eta_{rel} - 1}{\sqrt{c}}$ for (a) D-Galactose and (b)D-Maltose (0.05-0.4) M in aqueous Solution of 0.25 M of Na_2S at 298.15, 303.15 and 308.15K.

Table 1. Experimental molal concentration C, densities ρ and Viscosities η of D-Galactose and D-Maltose (0.05-0.4) M in aqueous Solution of 0.25 M of Na_2S at 298.15, 303.15 and 308.15K.

Conc.(mol/L)	ρ (gm/cm ³)					
	D-Galactose			D-Maltose		
	298.15K	303.15 K	308.15 K	298.15 K	303.15 K	308.15 K
0 solvent	1.0276	1.0244	1.0078	1.0276	1.0244	1.0078
0.05	1.0281	1.0259	1.0139	1.0319	1.0238	1.0162
0.1	1.0305	1.0307	1.0183	1.0361	1.0258	1.0196
0.15	1.0332	1.0326	1.0225	1.0420	1.0293	1.0242
0.2	1.0364	1.0348	1.0264	1.0476	1.0348	1.0275
0.25	1.0396	1.0379	1.0300	1.0536	1.0370	1.0312
0.3	1.0429	1.0405	1.0335	1.0586	1.0393	1.0342
0.35	1.0444	1.0417	1.0376	1.0641	1.0437	1.0391
0.4	1.0506	1.0426	1.0397	1.0751	1.0467	1.0419

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Conc.(mol/L)	D-Galactose			η (cp)	D-Maltose		
	298.15K	303.15 K	308.15 K	298.15 K	303.15 K	308.15 K	
0 solvent	1.0328	0.9834	0.9372	1.0328	0.9834	0.9372	
0.05	1.0641	1.0156	0.9734	1.0990	1.0442	0.9908	
0.1	1.0974	1.0358	0.9929	1.1657	1.0771	1.0247	
0.15	1.1313	1.0688	1.0122	1.2035	1.1117	1.0600	
0.2	1.1801	1.1021	1.0316	1.2571	1.1642	1.0943	
0.25	1.2119	1.1365	1.0506	1.3275	1.1978	1.1292	
0.3	1.2515	1.1862	1.0697	1.3815	1.2159	1.1634	
0.35	1.3003	1.2188	1.0895	1.4206	1.2682	1.1846	
0.4	1.3552	1.2511	1.1073	1.4836	1.3345	1.2190	

Table 2 Experimental square root for molar concentration \sqrt{C} and apparent molal volumes, ϕ_v of D-Galactose and D-Maltose (0.05-0.4)M in aqueous Solution of Na₂S (0.25 M) at 298.15, 303.15 and 308.15K.

\sqrt{C} (mol ^{1/2} /L ^{1/2})	ϕ_v (cm ³ /mol)					
	D-Galactose			D-Maltose		
	298.15K	303.15K	308.15K	298.15K	303.15K	308.15K
0.2236	723.23	660.42	332.25	877.41	814.28	490.50
0.3162	447.05	416.19	253.84	599.74	570.06	411.48
0.3872	354.72	334.27	227.23	506.08	487.96	384.10
0.4472	307.92	293.14	213.60	458.38	445.95	370.01
0.5000	279.70	268.25	205.20	428.99	420.80	361.03
0.5477	261.37	251.53	199.43	409.02	403.79	354.87
0.5916	247.88	239.60	195.04	394.22	390.88	349.60
0.6324	237.26	230.64	191.88	381.45	381.25	345.93

Table3. Experimental limiting value of partial molal volume at infinite dilution ϕ_v^o and the experimental slope S_v^o of D-Galactose and D-Maltose(0.05-0.4)M in aqueous Solution of Na₂S of (0.25 M) at 298.15, 303.15 and 308.15K.

Temperature/K	D-Galactose		D-Maltose	
	ϕ_v^o (cm ³ /mol)	S_v^o (cm ³ /mol)	ϕ_v^o (cm ³ /mol)	S_v^o (cm ³ /mol)
298.15	612.3	-628.2	773.7	-654.0
303.15	562.4	-556.2	719.8	-566.4
308.15	303.4	-186.4	464.7	-197.5

Table 4 Experimental square root for molar concentration and $\frac{\eta_{rel} - 1}{\sqrt{C}}$ for D-Galactose and D-Maltose (0.05-0.4)M in aqueous Solution of 0.25 M of Na₂S at 298.15, 303.15 and 308.15K.

\sqrt{C} (mol ^{1/2} /L ^{1/2})	$\frac{\eta_{rel} - 1}{\sqrt{C}}$ (L ^{1/2} .mol ^{-1/2})					
	D-Galactose			D-Maltose		
	298.15K	303.15 K	308.15 K	298.15 K	303.15 K	308.15 K
0.2236	1.1355	1.1465	1.1725	1.2867	1.2765	1.2559
0.3162	1.1980	1.1685	1.1878	1.4070	1.3011	1.2954
0.3872	1.2464	1.2241	1.2068	1.4268	1.3368	1.3384
0.4472	1.3189	1.2698	1.2252	1.4857	1.4110	1.3748
0.5000	1.3469	1.3113	1.2420	1.5708	1.4358	1.4096
0.5477	1.3868	1.3764	1.2580	1.6165	1.4316	1.4407
0.5916	1.4379	1.4045	1.2747	1.6347	1.4894	1.4462
0.6324	1.4937	1.4303	1.2869	1.6903	1.5644	1.4755

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Table 5 The values of jones-Dole coefficients a and B for D-Galactose and D-Maltose (0.05-0.4)M in aqueous Solution of 0.25 M of Na₂S at 298.15, 303.15 and 308.15K.

Temperature/K	D-Galactose			D-Maltose		
	A (L ^{1/2} .mol ^{1/2})	B (L.mol ⁻¹)	R	A (L ^{1/2} .mol ^{1/2})	B (L.mol ⁻¹)	R
298.15	0.928	0.8606	0.92	0.0749	0.9852	0.98
303.15	0.947	0.7539	0.94	0.1012	0.6685	0.93
308.15	1.099	0.2903	0.98	0.1281	0.5519	0.99

Table 6 The values of ΔG^* (J mol⁻¹), ΔH , ΔS for D-Galactose and D-Maltose (0.05-0.4)M in aqueous Solution of 0.25 M of Na₂S at 298.15, 303.15 and 308.15K.

Conc. (mol/L)	ΔG^* (KJ mol ⁻¹)			ΔH^* (KJ mol ⁻¹)	ΔS^* (J.mol.K ⁻¹)
	298.15K	303.15 K	308.15 K		
D-Galactose					
0.05	66724	67731	68747	61667	202.2
0.1	66794	67775	68791	61795	199.7
0.15	66862	67845	68831	61937	197.0
0.2	66957	67913	68870	62174	191.3
0.25	67014	67983	68910	62282	189.6
0.3	67085	68083	68947	62452	186.2
0.35	67175	68144	68987	62666	181.2
0.4	67262	68196	69015	62898	175.3
D-Maltose					
0.05	66817	67815	68806	61844	199.0
0.1	66973	67902	68903	62137	193.0
0.15	67058	67989	68997	62200	193.8
0.2	67173	68125	69084	62395	191.1
0.25	67314	68189	69172	62651	185.8
0.3	67422	68237	69258	62796	183.6
0.35	67498	68350	69312	62946	181.4
0.4	67599	68475	69167	63710	156.8

دراسة لزوجية وحرارية للكالتوز والمالتوز في محلول كبريتيد الصوديوم (0.25)مولاري بدرجات حرارية مختلفة.

الخلاصة

قيست كثافة ρ ولزوجة محاليل مختلفة التركيز لكل من (D-Galactose and D-Maltose) في محلول كبريتيد الصوديوم بتركيز مولاري (0.25mol/L) أجريت القياسات في درجات حرارة مختلفة تراوحت بين (298.15, 303.15 and 308.15K). استخدمت النتائج في حساب الحجم المولالي الظاهري ϕ_v و الحجم المولالي الظاهري المحدد () والميل () ومعاملتي جونس و دول (A و B) والدوال الحرارية و الطاقة الحرة للانسياب اللزج (ΔG^*) و الانتالبي (ΔH^*) و الانتروبي (ΔS^*). قيم A جاءت متوافقة مع قيم () في ضعف التأثيرات بين ايون -ايون بينما بقيت قيم B موجبه وعاليه مما يؤكد على قوة التأثيرات المتبادله من نوع ايون-مذيب وهذا يعمل على تقوية تركيب المذيب وذلك تبعاً للتأثير الهيدروجيني والاماهة الكاره للماء بين المذاب والماء وكبريتيد الصوديوم من جهة ومن جهة اخرى قيام جزيئات الماء باعادة ترتيب نفسها بشكل قفص تحيط بجزيئات المذاب .