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Volumetric and Viscometric Studies of Electrolyte in Aqueous solution of Glucose at different Temperature

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ABSTRACT: - *Volumetric and viscometric studies of electrolyte in aqueous glucose solution were done at temperature range of 293.15, 303.15 and 313.15 from the determined value of density, partial molar volume (Φ_v) and viscosity (η) were evaluated. Density data were analysed and discussed using Masson empirical relationship and viscosity data were analysed using Jones- Dole equation to evaluate partial molar volume, viscosity A and B coefficient .All parameter were discussed as a function of concentration and temperature. Obtained data was analysed to discuss the solute-solute and solute–solvent interactions. Structure making and breaking aspects of electrolyte in aqueous glucose were discussed.*

KEYWORDS*: Partial molar volume; Masson equation; Jones -Dole equation; Viscosity.*

INTRODUCTION

Studies on thermodynamic properties have been made on aqueous ternary system containing carbohydrates and amino acids has been reported in earlier study. In recent years, the hydration characteristics of carbohydrates and their interactions with electrolytes and non-electrolytes [1-4] in aqueous media have developed a great deal of interests, due to their significant importance in various fields such as biology, biochemistry, catalysis, and pharmaceutical industry [5].

In this paper we reported density, viscosity, apparent molar volume of electrolyte(0.05-0.15m) (sodium sulphate, potassium sulphate and magnesium sulphate in 0.20m Glucose solution at 293.15, 303.15and 313.15K .we also reported partial molar volume at infinite dilution, transfer partial molar volume, partial molar expansibilities, Falkenhagen coefficient and Jones Dole Coefficient which are calculated by experimentally measured density and viscosity.

Methodology

The Glucose and metal sulphate were used are of analytical grade. Freshly distilled water with specific conductance of 10^{-6} **Ω cm^{-1}**was used to prepare solution throughout the experiment. The best way of studying the volumetric properties of solvents was done with pre-calibrated specific gravity bottles(made up of Pyrex glass) under thermostatic conditions at temperature range of 293.15, 303.15, and 313.15K.The mass measurement were done on digital electronic balance(Sartorius GC103).For Viscosity determination we have used Ostwald's viscometer. Temperature was controlled by thermostatic water bath with ±0.1 ^{0}c accuracy.Volumetric and viscometric studies plays an important role in disclosing the various types of interactions occurring in solution.

RESULTS AND DISCUSSION

Parameter Used and Their Respective Equations-

Volumetric Properties The apparent molar volume of electrolyte in aqueous Glucose was calculated by following equation [6].

$$\Phi v = M/d0 - 1000(d-do)/d0c$$

Where d_0 and d are the densities of solvent and solution respectively; c is the molar concentration in gram/litre and M is molecular weight of solute. In order to have insight of solute-solvent interactions the obtained data was analysed by using Masson equation.[7]

$$\mathbf{\Phi v = \Phi v_0 + Sv\sqrt{c}}$$

The value of partial molar volume at infinite dilution(Φ_{v0}) and experimental slope ($_{SV}$) for electrolyte in aqueous Glucose solution at different temperature are given in Table. 1.

The value of apparent molar volume were found to be positive and increased in linear manner with temperature indicating presence of strong solute-solvent interactions.

The transfer partial molar volume of electrolyte from water to aqueous Glucose solution was calculated and summarised in Table2.

$$\mathbf{\Delta\Phi v_{0tr} = \Phi v_0}\text{ (mixed solution)} - \mathbf{\Phi v_0}\text{ (in water.)}$$

The standard transfer partial molar volume provides the information about solute-co-solvent interactions. Friedman and Krishnan[8] co-sphere overlap model observes that the overlap of co-sphere of two ionic species shows an increase in

volume whereas the overlap of hydrophobic-hydrophobic and ion-hydrophobic species resulted net decrease in the volume.
In the studied system, the pair interaction between electrolyte (sodium/ potassium/ and magnesium sulphate) and glucoseis of four types:

1) Cation-hydrophobic interaction: interactions between the hydrophobic parts of the glucose molecules and the cations of the co- solute.
2) Anion-hydrophobic: interaction between the hydrophobic non-polar group of glucose and the anion of electrolyte.
3) Cation-hydrophilic interaction: interaction between the hydrophilic polar group of glucose and the Cation of the electrolyte.
4) Anion - hydrophilic interaction: interaction between the hydrophilic polar group of glucose and the anion of the electrolyte

.

Types (1), (2), and (4) contribute negative values to volume, whereas type (3) contributes a positive value to volume. It has been concluded that type (3) is predominant in case of potassium –fructose system. While in sodium and magnesium sulphate negative partial volume of transfer obtained at lower temperature.

It is found that the value of $\mathbf{\Delta\Phi v_{0tr}}$ **(Table. 2)** is negative for sodium and magnesium sulphateand positive for potassium sulphate. In case of sodium sulphate value of $\Delta\Phi v_{0tr}$ turns positive and in magnesium sulphate less negative value which turns positive at 313.15K was found. In potassium sulphate these become more positive at higher temperatures.

Negative **A** and positive **B** values **(Table. 2)** were found for all studied salt –glucose system. The values of Δ**G(Table:3/4/5)** were found to be positive at all studied temperatures and concentration.

Positive values of Sv indicate presence of weak solute–solute interaction. This solute-solute interaction decreases with rise of temperature which may be attributed to increase in solvation of ions. In case of potassium sulphate these indicates decrease in solvation of ions. Thus for this all systems the positive values of Φv_0 in compare to the Sv values, indicates the solute-solvent interaction lead over solute-solute interaction. Similar result has been reported for amino acids in presence of magnesium chlorides [9] and nitrate. [10]

The $\mathbf{\Delta\Phi v_{0tr}}$ are found to be positive for potassium sulphate **(Table 2)** at all studied temperatures. $\Delta\Phi v_{0tr}$ increases with increase in temperature indicate the dominance of hydrophilic–hydrophobic interactions.The positive $\Delta\Phi v_{0tr}$ for electrolyte at different temperature may also be attributed to decrease in electrostriction effect in presence of glucose.
Singly charged K^+ prefer a lower density aqueous environment when it an introduced in aqueous glucose solution. Water molecules collapse into the spaces around their neighbours. Partial collapse of such clathrates structures formed through gathering .These ions allow rotations of the water molecule dipole towards the oppositely charged ions, through weak interactions, so as to increase the free movement of water molecules [11]. Due to cavity creation solvent–solvent interaction become stronger and as a result of that ability of K_2SO_4 is minimized and resulting positive transfer volume. On increasing temperature this result is ascribed to breakage of the solvent structure. This result is due to ionic dissociation or decreasing solute–solute interaction.

The $\mathbf{\Delta\Phi v_{0tr}}$ are found to be negative for magnesium sulphateand sodium sulphate **(Table-2)** at lower temperatures. Negative $\Delta\Phi v_{0tr}$ decreases and turn positive at 313.15K. This can be explained as increase in volume of shrinkage in solution in presence of electrolyte molecule. This may be due to strong interaction occurring between ion dipole of electrolytes and glucose. On increasing temperature the overlap of coordination hydrosphere electrostriction of neighbouring water molecules will be reduced. This is conscientious for the lowering structure making tendency of these ions at higher temperature.

Magnesium sulphate has small size, radius[12] and high charge density when it is dissolved in glucose solution .It interacts with solvent dipole to the form of solvation sheath and cause the alteration in the structures and orientation of the molecules surrounding the ion .When the concentration increases the water cluster surrounding the ion tends to join their neighbour and forms flickering cage, forcing the ions to get inside these cages. On increasing temperature cluster break down. That result in the breakage of the solvent structure on increasing temperature. This is also a cause in an increase in structural volume.

The variations of Φv_0 with the temperature[13]can be given by expression.

$$\mathbf{\Phi_{v0} = a_0 + a_1 T + a_2 T^2}$$

Where T is temperature in Kelvin .The value of coefficient a_0, a_1 and a_2 are calculated by least square method.
The temperature dependencevalue of $\mathbf{\Phi v_0}$ for electrolyte in aqueous glucose solution has been calculated. The result obtained as-

For Sodium sulphate in aqueous glucose solution

$$\Phi v_0 = 4.151 - 0.03307T + 0.00025T^2$$

For Potassium sulphate in aqueous glucose solution

$$\Phi v_0 = -194.601 + 1.396T - 0.00213T^2$$

For Magnesium sulphate in aqueous glucose solution

$$\Phi_{v0} = 217.568 - 1.393T + 0.00246T^2$$

The increase in the value of $\mathbf{\Phi_{E0}}$ with increase in temperature for sodium sulphate and magnesium sulphates(**Table 2)** in 0.2m aqueous glucose solution indicates presence of caging effect and its behaviour just like symmetrical tetra alkyl ammonium salt[14] and like nickel sulphatein aqueous manitol[15]. The value of $\mathbf{\Phi_{E0}}$decreases with increase in temperature for potassium sulphate (**Table 2)** in 0.2m aqueous glucose solution indicates absence of caging effect and its behaviour just like that common electrolytes.In other words the solute occupies the interstitial space in the solvent i.e. water resulting in hydrophobic structure making character.

According to Hepler [16]negative sign of $\mathbf{(\partial^2\Phi_{v0}/\partial T^2)_p}$ value found for potassium sulphate **(Table -2)** in 0.2m aqueous glucose solution ascribed structure breaking tendency of potassium sulphate in both water and in glucose solution.opposite behaviour in found in case of sodium sulphate and magnesium sulphate(**Table -2)** in 0.2m aqueous glucose solution has been illustrate as structure making ability of this solute in ternary system[17].

$$\mathbf{\Phi_{E0}=(\partial\Phi_{v0}/\partial T)_{p=} a_1+2a_2T}$$

The structure making and breaking capacity of solute might be interpreted with the help of **Helper's**reasoning i.e. on the basis of sign of following expression, it has been assumed that structure making solute have positive and structure breaking solute have negative value.

$$\mathbf{(\partial\Phi_{E0}/\partial T)\, p = (\partial^2\Phi_{v0}/\partial T^2)\, p = -a_2}$$

VISCOMETRIC STUDIES

Time of flow was determined for each system at selected concentration and temperature. The viscosity was determined from the formula $\mathbf{\eta/\eta_{0=} td/t_0d_0}$where n, t & d are the absolute viscosity, time of flow and density of solution, while η_0, t_0 andd_0 are same quantities for the solvent water.

Viscosity data of each system were analysed by **Jones-Dole equation**[18]

$$\mathbf{\eta/\eta_0 = \eta r = 1+A\, c^{1/2}+BC}$$

Where ηr is relative viscosity, c is molar concentration, the constant A is the Falkenhagen coefficient and B[19]is the Jones- Dole coefficient related to solute- solute and solute -solvent interaction respectively .The values of A and B parameter have been obtained by least square method. The temperature derivative of B coefficienthad also been calculated.

The small A value indicates that they contribute very little to absolute viscosity .The values of coefficient A shows that these are negative both in purely aqueous solution of electrolytes well as in aqueous glucose solution at different temperatures indicate the presence of weak ion –ion interaction. . Viscosity B parameter was found to be large and positive which indicating strong ion-solvent interactions

The sign of (dB/dT) value was found to provide information regarding the structure making and breaking ability of solute in solvent media. In general (dB/dT) was negative for structure making and positive for structure breaking. In case of sodium sulphate and magnesium sulphate in 0.2m aqueous glucose solution the positive values of B decrease with increasing temperature indicates that solute solvent interaction weakenedwith the rise of temperature. The negative value of temperature coefficient (dB/dT), showing the structure-making ability of anhydrous sodium sulphate and magnesium sulphate in aqueous glucose solution.

It was depicted that **B** for potassium sulphate in aqueous glucose solution increases with increase in temperature, since positive **dB/dT**value shows that potassium sulphate acts as structure breaker in water and aqueous glucose solution .These are in identical agreement with the conclusion drawn from Hepler equation as discussed earlier. The values of B are larger positive as compared to A values, sustaining the behaviour of Φ_{v0} and Sv. The superior magnitude of B coefficient suggests the pre-eminence of solute- solvent interactions over solute- solute interaction. In purely aqueous solution these electrolyte shows structure breaking tendency.

The viscosity data has been calculated on the basis of Feakins transition state theory. The values of **ΔG** are positive[20] and large indicating the structure-making ability of the solute. It again enhance the earlier findings, which are through the $\partial^2\Phi v/\partial T^2$ and dB/dT studies, that the values of ΔG are positive and increase with increasing concentration of solute (sodium sulphate and potassium sulphate) signifying that the interactions between solute and solvent molecules in the ground state are less strong than in the transition state.

The value of activation enthalpy **ΔH** were found to be positive while entropy of activation **ΔS** were found to be negative at all the experimental solutions at all experimental temperaturessuggesting that the transition state is associated with

bond making with increased order. The structure making tendency of salts are in the order of Mg salt > Na salt. Similar trend reported by [21]in the studies of alkali metal propionates in propionic acid and ethanol mixtures

Conclusion

It has been concluded that in salt–glucose system sodium and magnesium sulphates behaves as a structure maker at lower temperature. Potassium sulphate behaves as a structure breaker and sodium and magnesium sulphates also behave as a structure breaker at high temperature.

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Table: 1 apparent molar volume ($ø_v$) cm3mol^{-1}of electrolyte in 0.2m aqueous solution of Glucose at different temperatures

Conc.	**Sodium sulphate**			Potassium Sulphate			Magnesium Sulphate		
	293.15 **K**	303.15K	313.15K	293.15 **K**	303.15 K	313.15K	293.15 **K**	303.15K	313.15K
0.05M	16.141	17.311	18.5041	32.025	33.500	34.359	**20.550**	**21.276**	**22.483**
0.10M	16.272	17.390	18.6077	32.182	33.710	34.647	**20.664**	**21.354**	**22.587**
0.15M	16.289	17.461	18.6471	32.320	33.945	34.836	**20.706**	**21.426**	**22.626**

Table: 2 Partial molar volume at infinite dilution Φv_0, Experimental slope Sv, $\Delta\Phi v_{0tr}$, ΦE_0, A, B, coefficient, Hepler and (dB/dT) of electrolyte in 0.2m aqueous solution of Glucose at different temperatures.

		Sodium sulphate			Potassium Sulphate			Magnesium Sulphate		
		293.15K	303.15 K	313.15 K	293.15 K	303.15 K	313.15 K	293.15 K	303.15 K	313.15 K
Φv_0	cm^3mol^{-1}	15.94	17.1	18.31	31.61	32.87	33.70	20.33	21.06	22.28
Sv	cm^3 lit $^{1/2}mol^{-3/2}$	0.933	0.92	0.893	1.81	2.72	2.94	0.974	0.922	0.893
$\Delta\Phi v_{0\ tr}$	cm^3mol^{-1}	-0.645	0.03	0.78	2.15	2.93	3.58	-0.252	-0.173	0.509
ΦE_0	$cm^3mol^{-1}K^{-1}$	0.113	0.118	0.123	0.147	0.104	0.062	0.048	0.097	0.146
A	m^3mol^{-1}	-0.017	-0.017	-0.012	-0.015	-0.017	-0.018	-0.018	-0.017	-0.116
B	m^3mol^{-1}	0.203	0.202	0.18	0.215	0.227	0.231	0.206	0.203	0.178
Hepler constant		0.0005			-0.00426			0.00492		
dB/dT) constant		-0.00118			0.00091			-0.00145		

Table 3 Values of ΔG, ΔH and ΔS of Na_2SO_4 in 0.2m aqueous solution of Glucose at different temperatures.

Na_2SO_4	ΔG	ΔG	ΔG	ΔS	H
$mol.d^{-3}m$	J mol^{-1}	J mol^{-1}	J mol^{-1}	J $mol^{-1}K^{-1}$	J $mol^{-1}K^{-1}$
	293.15K	303.15K	313.15K		
0.05	30744.72	31397.209	31952.295	60.379	13060.979
0.1	30745.28	31397.913	31950.081	60.240	13102.768
0.15	30748.00	31400.609	31954.321	60.316	13082.847

Table 4values of ΔG, ΔH and ΔS of K_2SO_4 in 0.2m aqueous solution of Glucose at different temperatures

K_2SO_4	ΔG	ΔG	ΔG	ΔS	H
mol.d^{-3}m	J mol^{-1}	J mol^{-1}	J mol^{-1}	J mol^{-1}K^{-1}	J mol^{-1}K^{-1}
	293.15K	303.15k	313.15k		
0.05	30749.19	31401.98	31957.46	60.413	13055.15
0.1	30754.35	31409.28	31965.56	60.560	13017.44
0.15	30759.77	31415.02	31971.73	60.597	13011.94

Table: 5 Values of ΔG, ΔS and Δ H of MgSO4 in 0.2m aqueous solution of Glucose at different temperatures.

$MgSO_4$	ΔG	ΔG	ΔG	ΔS	H
mol.d^{-3}m	J mol^{-1}	J mol^{-1}	J mol^{-1}	J mol^{-1}K^{-1}	J mol^{-1}K^{-1}
	293.15K	303.15K	313.15K		
0.05	32428.48	33098.06	33705.98	63.875	13713.78
0.1	32410.22	33079.02	33686.36	63.807	13715.43
0.15	32397.06	33063.34	33667.86	63.540	13780.57

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