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Viscosity and Conductance Studies on Hydration of Copper Sulphate Pentahydrate at 308K & 313K

Anchal Aneja*[1], Renu Loshali[2], Kailash Tamta[3], Jagdish Prasad[4], N. D. Kandpal[1]
[1]*Physical Chemistry Laboratory, Department of Chemistry, Kumaun University, SSJ Campus, Almora, Uttarakhand, India*
[2]*Department of Chemistry, Shri Ram Singh Dhoni Rajkiya Mahavidhalaya, Jainti (Almora) Soban Singh Jeena University, Uttarakhand, India*
[3]*Department of Chemistry, Government Degree College, Kanda (Bageshwar) Soban Singh Jeena University, Uttarakhand, India*
[4]*Department of Chemistry, Hukum Singh Bora Government Post Graduate College, Someshwar (Almora), Soban Singh Jeena University, Uttarakhand, India*
Corresponding Author: anchalaneja@kunainital.ac.in

Abstract
Viscosities and conductance of solutions of copper sulphate pentahydrate in water have been determined in the concentration range 0.1 to 0.8 moldm^{-3} *at 308K and 313K. The data have been analyzed in the light of Jones-Dole equation* $\eta / \eta_0 = Bc + 1$. *The results of the study revealed that at both the temperatures copper sulphate pentahydrate behave as a structure maker in water. The value of dissociation constant, ΔG, ΔH and ΔS shows that formation of ion-pair and their interactions with water molecules takes place in the process of hydration of copper sulphate pentahydrate. The* λ_m^0 *, conductivity at infinite dilution increases with the concentration which justify the strong association between the components of copper sulphate pentahydrate in water.*

Keywords: *Hydration of copper sulphate, Viscosity, B-coefficient, Solute-solvent interaction, Conductance*

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I. INTRODUCTION

Copper and its compounds have been used as disinfectant agent for many Centuries [1]. It was recognized as the first metallic antimicrobial agent in 2008 by the United State Environmental Protection Agency. This led to many studies on various properties of copper salts, copper complexes and copper nanoparticles [2]. The measurements of viscosity, conductance, density and sound velocity have been used in recent years in understanding the nature of systems and physicochemical behaviour like internal structure, molecular association, complex formation, internal pressure, hydration molecular interactions etc. of solutes in aqueous and non-aqueous solutions [3-7]. The behaviour of any reactant in any solvent is useful and plays an important role in the synthesis of chemical substances including nanomaterials [8]. The conductometric study on cobalt soap has been used to evaluate the critical micelle concentration in the solvent dimethyl formamide [9]. The measurement of viscosity, conductance, ultrasonic velocity and density has been used to determine the physicochemical properties and structure of alkaline earth and transition metal soaps in mixed or single organic solvents [10-13]. The physicochemical properties such as density and viscosity play an important role in the design, evaluation of heat and mass transfer in industrial processes [14-15]. Water is a most common solvent for electrolytes as well as non-electrolyte solutes. In case of ionic substances, when placed in water forms positive and negative ions. These ions are surrounded by water molecules with their opposite charge ends directed towards the ion. The process is known as hydration of solute in water. The ions are known as hydrated ions. The measurement of viscosity and conductance of aqueous solutions of the solute is useful in evaluation of intermolecular and interionic interactions. The information related to the ion-ion, ion-solvent and solvent-solvent interactions is of fundamental importance for understanding the reaction trades and equilibria of dissolved electrolytes [16]. The densities and viscosities of $CuSO_4$-H_2SO_4-H_2O solutions have been reported to describe the hydration behaviour of copper sulphate pentahydrate in order to access its importance in industrial copper electrorefining and also in electroplating both [17]. The specific character of copper sulphate pentahydrate is that it has chemical composition $CuSO_4.5H_2O$ in crystalline state. The hydration behaviour of such electrolytes is still lacking in relation to viscometric and conductometric measurement in order to assert the molecular interactions present in aqueous solution. Though there are reports on viscosities of some hydrated and anhydrous salts of transition metal sulphates including copper sulphate pentahydrate in aqueous solution at different temperature [18]. The measurement of conductance of such electrolyte in aqueous solution is still important for the interpretation of the hydration along with the viscometric measurements under same conditions. It would be interesting to examine the structure modification of water by the hydrated copper sulphate solute which get enhanced or subdued due to their presence. In the present study we reported the experimental viscometric and conductometric data of aqueous copper sulphate pentahydrate solution at temperature 308K and 313K which have been interpreted in terms of molecular interactions and hydration behaviour of the copper sulphate pentahydrate.

1.1 Experimental Methods

Copper sulphate pentahydrate (AR Grade) was used, as received. The stock solutions of the salt were prepared by dissolving the weight quantity in double distilled water. The stock solution was diluted to the required volume with the distilled water.

Deionized water was distilled twice with small quantity of potassium permanganate and few drops of dilute sodium hydroxide. The purity of prepared water was confirmed by measuring the specific conductance in order of $< 2 \times 10^{-6}\ \Omega^{-1}cm^{-1}$ was always taken for the experimental study. Thermostatically controlled thermostat (Tassco Kanpur) capable of maintaining the temperature constant to ±0.1°C was used during the all measurements in the study.

1.1.1 Conductance Measurement

The conductance was measured with the help of calibrated digital conductivity meter CM 180, Elico Limited. A dip type conductivity cell of cell constant 1.0 cm^{-1} having platinized electrode was used. Single phase stabilizer A.C. mains 50Hz was connected with the conductivity meter in order to maintain the supply of current at constant voltage. The calibration of conductivity meter was carried out with the standard potassium chloride solution. The error limit in the measurement was ±0.5%. By using the values of specific conductance, molar conductance can be calculated by the formula.

1.1.2 Viscometric Measurement

The viscosity measurement was carried out with a calibrated suspended level viscometer (Infusil India Pvt. Limited). The solution of copper sulphate pentahydrate of known concentration was taken in the fixed volume of the viscometer and the flow time of the solution was measured with the help of stop watch (Racer). The densities of the solution were measured using 10 mL double armed Pyknometer having accuracy ±0.00001 g/L and single pan electronic balance (Citizen).

II. RESULT AND DISCUSSION

The relative viscosities measured for the solution of copper sulphate pentahydrate have been used to calculate the value of $\frac{\eta}{\eta_0} - 1$ and the specific conductivities of the solution have been used to calculate the molar conductance of the solution at each concertation from the experimental data of Table 1.

Table 1: Densities, Relative Viscosity and Specific Conductance of $CuSO_4$-H_2O System at 308K and 313K.

S. No.	Temperature (K)	Concentration (c) (mol dm^{-3})	Relative Density	Relative Viscosity	Specific Conductance (K_s) ($m\Omega^{-1}cm^{-1}$)
1.	308	0.1	1.0084	1.0744	7.8
2.	308	0.2	1.0177	1.1177	10.9
3.	308	0.3	1.0401	1.1945	13.4
4.	308	0.4	1.0508	1.2574	17.1
5.	308	0.5	1.0719	1.3524	20.8
6.	308	0.6	1.0786	1.3967	21.5
7.	308	0.7	1.101	1.5521	23.8
8.	308	0.8	1.118	1.7314	25.1
9.	313	0.1	1.0099	1.0435	7.8
10.	313	0.2	1.0192	1.1645	11.4
11.	313	0.3	1.0417	1.2152	14.5
12.	313	0.4	1.0529	1.2809	17.9
13.	313	0.5	1.0718	1.3588	21.2
14.	313	0.6	1.0802	1.4408	22.8
15.	313	0.7	1.1018	1.5797	24.7
16.	313	0.8	1.1134	1.6521	25.9

The relative density (d_1/d_2), time of flow for solution and solvent were used to calculate the value of $\frac{\eta}{\eta_0}$, using the following relation:

$$\frac{\eta}{\eta o} = \frac{d_1}{d_2} \times \frac{t}{t_0} \tag{1}$$

Where d_1 and d_2 are the densities of solution and water. t and t_o is the time of flow for the solution and water measured by the viscometer. The specific conductance data have been utilized to calculate the λ_m (molar Conductance) of the solution using the following relation given in equation 2:

$$\lambda_m = \frac{(\mathrm{Ks} - \mathrm{Ksolvent}) \cdot \mathrm{Kcell} \cdot 1000}{c} \tag{2}$$

Where, Ks is the specific conductance of the solution, $K_{solvent}$ is the specific conductance of the solvent, K_{cell} is the cell constant and c is the molar concentration of the solutions.

The values of molar conductance λ_m and $\frac{\eta}{\eta_0} - 1$ are listed in Table 2 at each concentration along with square root of concentration in the concentration range 0.1 mol dm^{-3} to 0.8 mol dm^{-3}.

Table 2: The values of $\frac{\eta}{\eta_0} - 1$ and λ_m of $CuSO_4.5H_2O$ for different concentration at 308K and 313K.

S. No.	Temperature (K)	Concentration(c) (mol dm^{-3})	$\sqrt{c}$ ($mol^{1/2}\,dm^{-3/2}$)	$\frac{\eta}{\eta_0} - 1$	λ_m (S cm^2 mol^{-1})
1	308	0.1	0.3162	0.0744	74.8
2	308	0.2	0.4472	0.1177	54.5
3	308	0.3	0.5477	0.1945	44.6
4	308	0.4	0.6325	0.2574	42.7
5	308	0.5	0.7071	0.3524	41.5
6	308	0.6	0.7746	0.3967	35.8
7	308	0.7	0.8367	0.5521	33.9
8	308	0.8	0.8944	0.7314	31.3
9	313	0.1	0.3162	0.0435	77.8
10	313	0.2	0.4472	0.1645	56.0
11	313	0.3	0.5477	0.2152	48.2
12	313	0.4	0.6325	0.2809	44.7
13	313	0.5	0.7071	0.3588	42.3
14	313	0.6	0.7746	0.4408	37.9
15	313	0.7	0.8367	0.5797	35.2
16	313	0.8	0.8944	0.6521	32.3

The calculated values of viscometric and conductometric measurements collected in Table 2 were used to analyze the hydration behaviour of copper sulphate pentahydrate in aqueous solution at constant temperature.

Interpretation of Viscometric Measurements

Copper sulphate pentahydrate consist five water molecules in solid state. When it dissolved in water, the water molecules also dissolved in water. The hydration of these water molecules is influential in the process of hydration of copper sulphate pentahydrate.

We have used the concentration range towards higher concentration of copper sulphate pentahydrate. The hydration may be represented by the following equations:

$$CuSO_4.5H_2O(s) \longrightarrow \underset{\text{Ion-Pair}}{Cu^{2+}(aq)\,SO_4^{2-}(aq)} + \underset{\text{Ion-Pair}}{5(H^+\,OH^-)}\ (aq) \tag{3}$$

$$\underset{\text{Ion-Pair}}{Cu^{2+}(aq)\,SO_4^{2-}(aq)} \rightleftharpoons Cu^{2+}(aq) + SO_4^{2-}(aq) \tag{4}$$

$$\underset{\text{Ion-Pair}}{H^+\,OH^-(aq)} \rightleftharpoons H^+(aq) + OH^-(aq) \tag{5}$$

It is believed that hydrophilic and hydrophobic interactions take place in water-rich regions of aqueous acid Solution [19]. It is interesting to point out that according to equation 3, it is in principle possible that the ion pairs formed in the aqueous solution can affect the hydration behaviour of copper sulphate. Theoretically, the Structural geometry $CuSO_4.nH_2O$ is also expected the Value of n may be 1,2,3….n. Moreover, there is another important aspect in interpretating the hydration behaviour of hydrated solutes in aqueous solutions in the light of various interactions between solute and solvent constituents. The various types of interactions occurring between the solute-components and water can be considered as follows:

(1) Hydronium ion is formed as a result of water molecule and hydrogen ion having a typical bond between them covalent bond. It's concentration relative to hydroxide ion is direct measure of pH of the solution (Oxonium ion).

(2) The Eigen cation which is tetrahydrate $H^+(H_2O)_3$, the Zundel cation which is symmetrical dihydrate $H^+(H_2O)_2$ and stoyanov cation extended Zundel Cation $H^+(H_2O)_2(H_2O)_4$ hexahydrate. The predominant cation is Stoyanov cation [20].

(3) The water molecule beyond the first solvation shell must orientate in order to their dipole to point ward and away from solvated anion to accommodate water molecule with free O-H stretch.

(4) In water SO_4^{2-} ion can interact with the water molecules and can form the contract structure of species $SO_4^{2-}(H_2O)n$. The value of n may be between 30 to 55.

The relative viscosities of aqueous solution of copper sulphate pentahydrate reported in Table 2 were used to analyze the hydration behaviour using Jones Dole equation [21]:

$$\frac{\frac{\eta}{\eta_0}-1}{\sqrt{c}} = B\sqrt{c} + A \tag{6}$$

The Jone-Dole coefficient B have been calculated for both the experimental temperature by the use of least square method. The plots between $\sqrt{c}$ versus $\frac{\frac{\eta}{\eta_0}-1}{\sqrt{c}}$ are represented in Figure 1 and Figure 2.

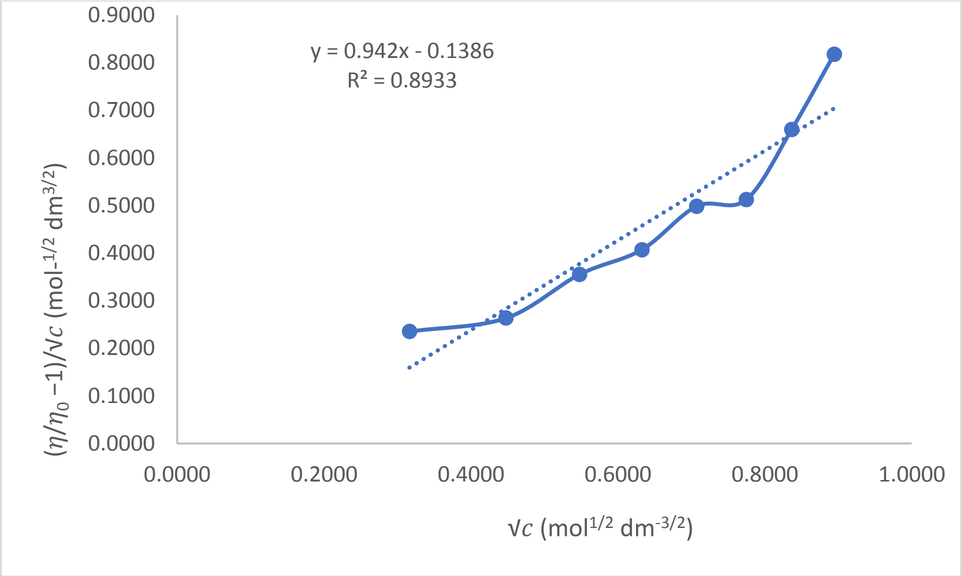

Fig 1. Plot between $\sqrt{c}$ versus $\frac{\frac{\eta}{\eta_0}-1}{\sqrt{c}}$ for copper sulphate pentahydrate at temperature 308K (B= 0.9420)

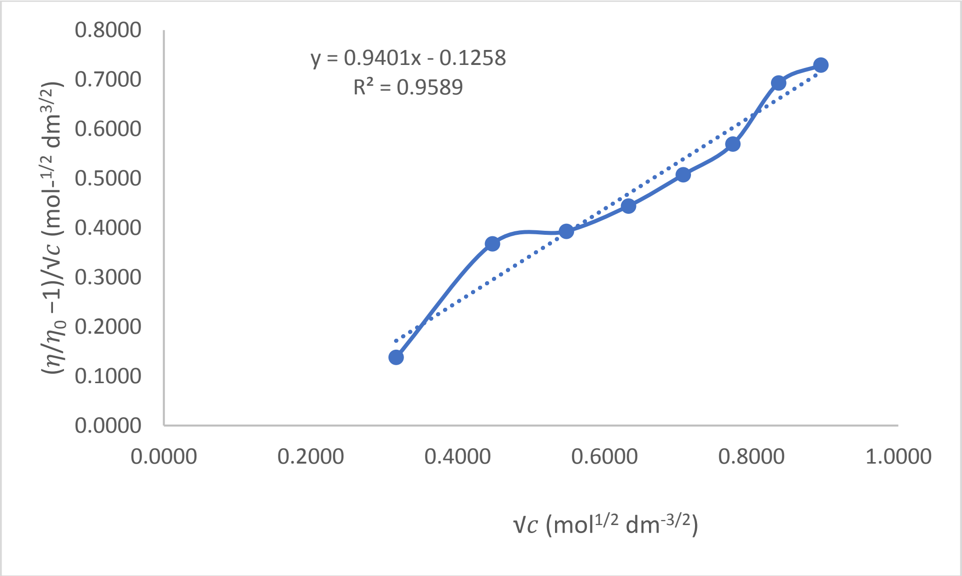

Fig 2. Plot between $\sqrt{c}$ versus $\frac{\frac{\eta}{\eta_0}-1}{\sqrt{c}}$ for copper sulphate pentahydrate at temperature 313K (B = 0.9401)

The value of B coefficient obtained at both temperatures are reported in the bottom of each respective figure. The value of B Coefficient is positive having large magnitude 0.9420 and 0.9401.

It represents the presence of solute-solvent interactions present in aqueous solution of copper sulphate pentahydrate. The value of A is very small with negligible magnitude confirms the absence of ion-ion interaction in the aqueous copper sulphate pentahydrate solutions. Positive value of B indicates strong copper sulphate-water interaction and is the indication of structure-making behaviour [22].

In the solution having higher concentration of copper sulphate pentahydrate, the enveloping of ion pairs of cations and anions by the water molecules is possible. Under this condition, the ion-pair surrounded by water molecule can be considered as non-ionic solute and reduced form of Jones-Dole equation can be used to examine the hydration behaviour of copper sulphate pentahydrate [23] shown in equation 7.

$$\frac{\eta}{\eta_0} - 1 = Bc \tag{7}$$

The plot between c versus $\frac{\eta}{\eta_0} - 1$ at both the temperatures have been shown in figure 3 and figure 4.

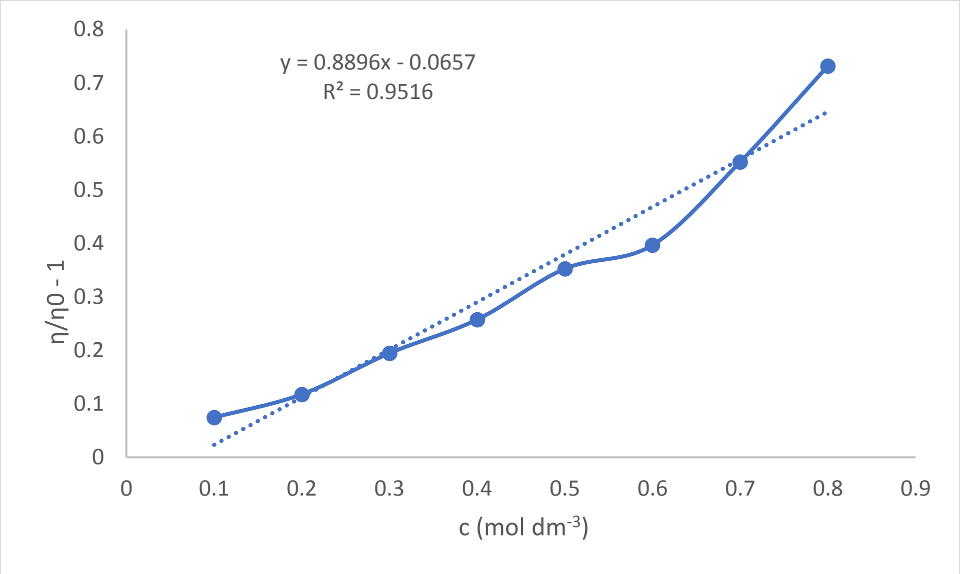

Fig 3. Plot Between c versus $\frac{\eta}{\eta_0} - 1$ for Copper Sulphate pentahydrate at temperature 308K (B = 0.8896)

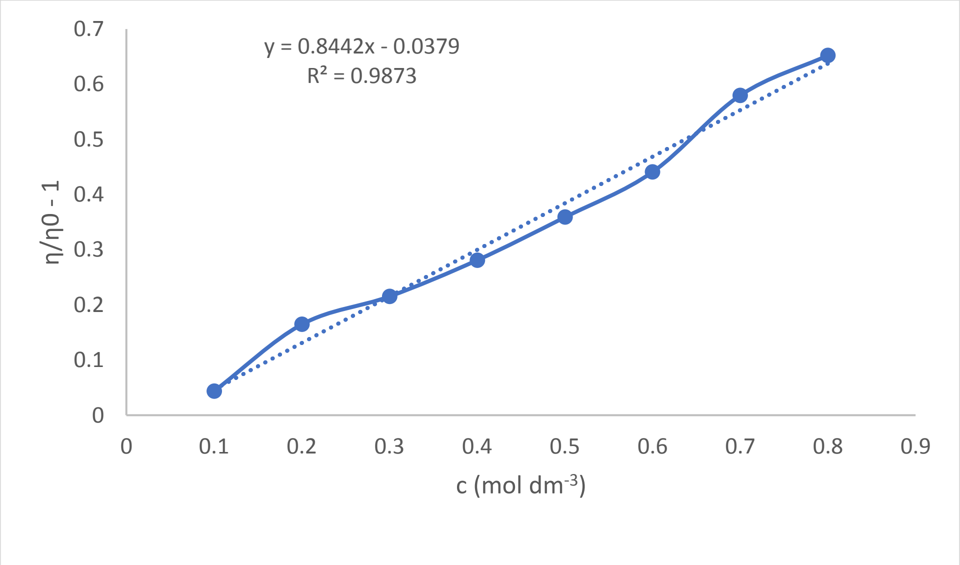

Fig 4. Plot between c versus $\frac{\eta}{\eta_0} - 1$ for copper sulphate pentahydrate at temperature 313K (B = 0.8442)

The value of B obtained from Figure 3 and 4 are given in the bottom of the respective figures. The linear nature of the plots having linearity coefficient > 0.9 show the applicability of the model. It is also suggestive that the hydration process is favoured by the formation of ion-pairs in the aqueous solution of copper sulphate. The B parameter which measures the structure making/ Breaking Capacity of any electrolyte also contains the contribution from structural behaviour of hydrated species and is dependent on solute-solvent interaction in solvents [24]. It is more precious criteria for determining solute-solvent interaction by calculating the dB/dT. The negative value of dB/dT confirm the structure maker behavior of the solute and positive value of dB/dT confirm the structure breaking tendency of solute. The effect of B coefficient for copper sulphate pentahydrate in water shows negative sign of dB/dT shows that copper sulphate pentahydrate behaves as a structure maker in the process of hydration.

Interpretation of Conductometric Measurements

In order to confirm the hydration behaviour of copper sulphate observed from the viscometric results, we have examined the behaviour in this regard with the analysis of conductometric measurement on copper sulphate shown in Table 2. For this purpose, the Kraus-Bray conductivity equation given by equation (8) has been used:

$$\frac{1}{\lambda m} = \frac{1}{\lambda_m^0} + \frac{\lambda_m c}{\lambda_m^{0^2} kc} \tag{8}$$

The limiting molar conductance λ_m^0 and dissociation constant K_c were obtained from the intercept and slope of the plot $\frac{1}{\lambda m}$ versus $\lambda_m c$. The representative plots between $\frac{1}{\lambda m}$ and $\lambda_m c$ are shown in Figure 5 and Figure 6 at temperature 308 K and 313 K respectively

The values of λ_m^0 have been calculated for both the temperatures from these plots (Intercept = $\frac{1}{\lambda_m^0}$)

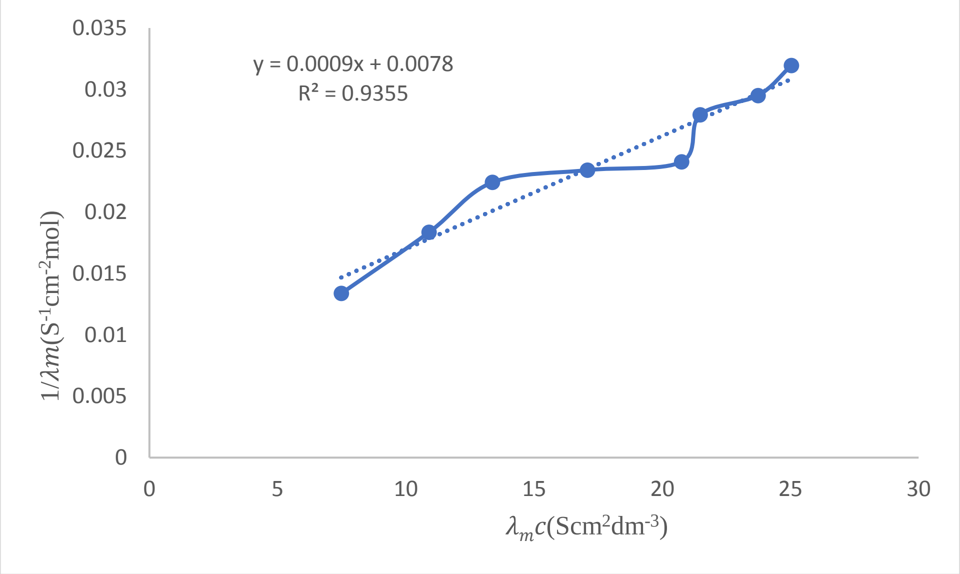

Fig 5. Plot Between $\lambda_m c$ versus $\frac{1}{\lambda m}$ for copper sulphate pentahydrate at 308K

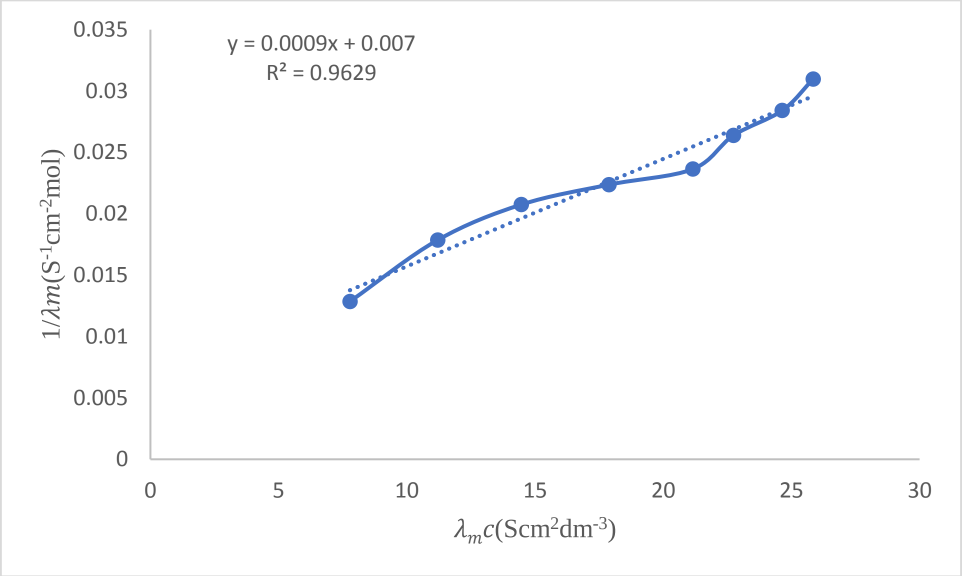

Fig 6. Plot between $\lambda_m c$ versus $\frac{1}{\lambda m}$ for copper sulphate pentahydrate at 313K

Figure 5 and Figure 6 shows that the $1/\lambda_m$ increases linearly with $\lambda_m c$ at constant temperature. The values of molar conductance λ_m at infinite dilution were also obtained from these plots.

Conductance data also analyzed to obtained the value of K_c (Dissociation Constant) along with ΔG, ΔH and ΔS can be calculated by given formula:

$$\Delta G = -2.303RT\log K_c \quad (9)$$

$$\log K_c = \frac{-\Delta H}{2\cdot 303R}\left(\frac{1}{T}\right) \quad (10)$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} \quad (11)$$

These values are given in Table 3

Table 3: The values of λ_m^0 , K_c, ΔG, ΔH and ΔS of $CuSO_4.5H_2O$ at 308K and 313K.

S. No.	Temperature (K)	λ_m^0 (S cm^2 mol^{-1})	K_c	ΔG kJmol^{-1}	ΔH Jmol^{-1}	ΔS JK^{-1}mol^{-1}
1.	308	128.2051	0.0676	6.9001	-18.2293	-22.4633
2.	313	142.8571	0.0544	7.5758	-18.2293	-24.2621

From the study of conductance, the behaviour of copper sulphate pentahydrate in hydration process confirms the structure maker behaviour or strong solute-solvent interactions is in agreement with the conclusion drawn from the viscometric study. The value of λ_m decreases with the concentration which indicates the decrease in the motion of the ion due to the more hydration of the charged species in water. since in the solutions at infinite dilution the motion of the ions depends soley on the interactions between the surrounding solvent molecules.Therefore the value of λ_m^0 equally give the information about the ion solvent interaction [25]. The higher value of λ_m^0 at higher temperature may be interpretated as a measure of higher ion solvent interactions or solute-solvent interactions. The calculated values of λ_m^0 are also given in table 3. The value of dissociation constant obtained at temperature 308K > 313K, which indicates that with the increase of temperature more association between solute and solvent species takes place. The enthalpy of hydration remains constant with negative sign in magnitude (-18.2293 Jmol^{-1}), which supports the formation of ion-pair enveloped by the water molecules in the primary hydration shell.

III. CONCLUSION

In the concentration range 0.1 to 0.8 moldm^{-3} of copper sulphate pentahydrate forms the hydrated ion-pairs in the process of hydration at and above temperature 308K. The behaviour of copper sulphate pentahydrate considered the following characteristics behaviour in the hydration process:

1. The studies suggest that ion-solvent interactions are stronger and ion-ion interactions are absent.
2. The extent of interactions and structure making ability of copper sulphate pentahydrate confirmed by the criterion dB/dT has negative sign and B coefficient are positive.
3. The formation of ion-pair in water-rich region by the copper sulphate pentahydrate and its components formed in water are surrounded by a network of highly ordered water molecules (Strong hydration sphere).

4. The electrostatic, chemical and physical interactions such as dipole-dipole or dipole-induced dipole interactions are present in the process of hydration of copper sulphate pentahydrate in self-association water network with H-bonding. The crystalline water also participitate as a component in the process of hydration.

5. The hydration behaviour of copper sulphate pentahydrate examined in the study can play a significant role as a model in the industrial, medicinal, pharmaceutical and nanochemistry.

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