5th International Conference on Science, Technology and Management
India International Centre, New Delhi (ICSTM-16)
30th July 2016, www.conferenceworld.in ISBN: 978-93-86171-00-9

AQUEOUS CONCENTRATED SULPHURIC ACID AT 308.15K: VISCOMETRIC STUDY

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ABSTRACT

In the present study, we have investigated the interaction parameters of aqueous concentrated sulphuric acid in the concentration range 1.0 to 9.0 moldm^{-3} at 308.15K by considering Jones-Dole and modified Jones-Dole viscosity equation. The strong ion- solvent interaction has been proposed which indicates the positive value of B-coefficient (solute-solvent interaction). In sulphuric acid-water system, the three concentration regions have been identified: 1.0 to 4.0moldm^{-3}, 4.0 to 7.0moldm^{-3} and 7.0 to 9.0moldm^{-3}. The study is usefulas a model for other solvent systems for the advancement of solution chemistry.

***Keywords**: Interaction parameters, Jones-Dole equation, modified Jones-Dole equation, Sulphuric acid, viscosity.*

1. INTRODUCTION

The transport property like electrical conductance, viscosity and diffusion are useful for the measurement of intermolecular forces present in pure solvent and solutions. The rates at which solute molecule travel or are transported through a solvent or across a membrane are important in many biological processes. When solute is dissolved in a solvent, the molecules of the solvent force the solute particles to separate from each other and release them from the bond that combines these particles in pure state. The molecular interactions of the solvent with non-ionic and ionic solute play an important role in governing the physicochemical behavior of interactions present in solution. The water-ion interaction represents a central topic in chemistry and biology which is used as universal solvent [1]. The concept of viscosity is first meet in fluid flow problems, treated by aerodynamic and hydrodynamic for the measurement of frictional resistance that a fluid in motion offers to an applied shearing force. Viscosity has gained the attention of several workers in characterizing the molecular interactions in aqueous and non-aqueous solution during the past decades [2-9].The measurement of the viscosity of the solution can be carried out with inexpensive apparatus easily and quickly. As a result it is widely used method in the studies of intermolecular interactions present in aqueous and non-aqueous solutions. The viscometric studies provide valuable information regarding interaction parameters in the pure liquids as well as in solutions. The viscosities of various solutions have been correlated with the concentration of solutions and different models have suggested by different workers [10- 18]. In each model, there are specific parameters for interpreting solvent-solvent, solute-solvent and solute-solute interactions in solution phase. The ultimate goal of all the models is to explain the kinds of association, molecular packing, molecular motion and various types of influences on the structure of the solvent. Sulphuric acid is one of the oxy-acid of sulphur and forms ions in water. The literature review showed that sulphuric acid-water systems have been studied conductometrically [19,20], viscometrically. [21, 22] and calorimetrically [23]. These studies shows the dependence of transport properties on concentration of the sulfuric acid.The nature of interaction present in concentrated sulphuric acid-water system still require investigation. Hence the present study deals with the determination of viscosities of aqueous concentrated sulphuric acid 1.0moldm^{-3} to 9.0moldm^{-3} at 308.15K and the analysis of viscosity data in the light of Jones- Dole and modified Jones-Dole equation.

II EXPERIMENTAL

The sulphuric acid used was of GR grade about 98% (E.Merck). Doubly distilled water was used to prepare solutions of the acid. The viscosity measurements were taken in a calibrated suspended-level viscometer (Infusil India Pvt. Ltd.). The viscometer was placed in a thermostated water bath (Tanco) having accuracy ±0.1K for constant temperature. The solution of sulphuric acid of known concentration was taken in the viscometer and the flow time of the solution was measured with the help of a stop watch (Racer). The densities of solutions were measured using a 15 ml double arm pyknomete having accuracy ±0.00001g/ml and a single pan electronic balance (Citizen).

III RESULTS AND DISCUSSION

The viscosity of a solution depends on the sulfuric acid concentration and the temperature of the solution. The viscosity of any solute in aqueous solution is approximately a linear function of concentration. Table 1represent the viscosities of concentrated sulfuric acid obtained in the study at 308.15K. The plot between concentration and viscosity is linear having linearity coefficient 0.93with deviation in the curve in the concentration region 4.0 to 7.0moldm^{-3}as shown in Fig. 1. Such deviations is also observed in reported values of viscosities [22].

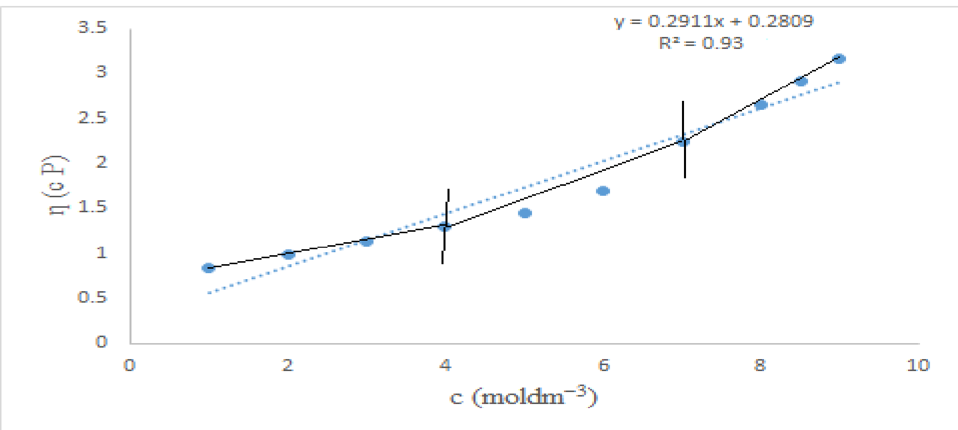
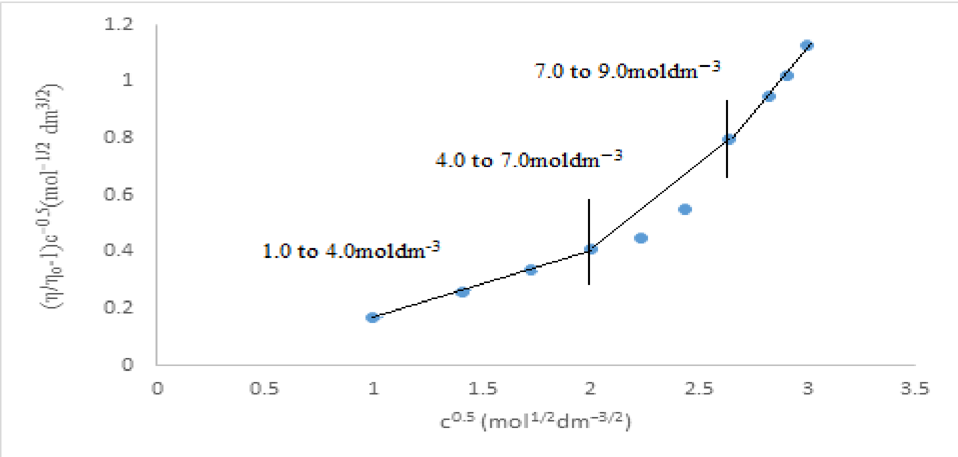


Fig. 1: Variation of viscosity (η) of aqueous sulfuric acid with concentration at 308.15K

The viscosity is a macroscopic property that represents the average behavior of a large number of water molecules in aqueous medium [24]. Hence the increase in the viscosity of water can be explained from the rigid nature of solvation structure formed by the ion and its first hydration shell. The viscosity values observed in the study were used to calculate the value of η/η_o at each concentration (c) which are given inTable 1, where η is the viscosity of the solution and η_o is the viscosity of water. Experimental results obtained at each concentration have been analyzed by Jones- Dole equation (1.0):

$$(\eta/\eta_0 - 1)\, c^{-0.5} = A + B\, c^{0.5} \quad \ldots\ldots (1.0)$$

where A and B are constants which are the measure of solute- solute and solute -solvent interaction respectively. The values of A and B were obtained from the intercept and the slope of linear plot of $(\eta/\eta_0\text{-}1)\, c^{-0.5}$ versus $c^{0.5}$ are shown at the bottom of Figure 2.



1.0 to 4.0 moldm^{-3} (B = 0.24 dm$^{-3/2}$mol^{-1}, A = –0.07); 4.0 to 7.0 moldm^{-3} (B = 0.58 dm$^{-3/2}$mol^{-1}, A = –0.81); 7.0 to 9.0 moldm^{-3} (B =0.89 dm$^{-3/2}$mol^{-1}, A = –1.5)

Fig. 2: Jones-Dole plot for 1.0 to 9.0moldm^{-3} aqueous sulfuric acid at 308.15K

On comparison of the gradients calculated with the help of computer clearly indicates that there exist three sulfuric acid- water systems in the concentration range 1.0moldm^{-3} to 9.0moldm^{-3}. It is clear from Fig. 2 that there exist ion-solvent interactions in all the three concentration region 1.0to 4.0 moldm^{-3}, 4.0 to 7.0 moldm^{-3} and 7.0 to 9.0 moldm^{-3}as indicated by positive value of B-coefficients. The B values increases with increase in concentration which represent the increase in solute -solvent interaction. The value of A decreases with increasing concentration which shows that solute- solute interaction decreases with concentration. In order to verify the presence of three sulfuric acid- water systems in the concentration range 1.0moldm^{-3} to 9.0moldm^{-3}, modified Jones- Dole equation was applied (2.0):

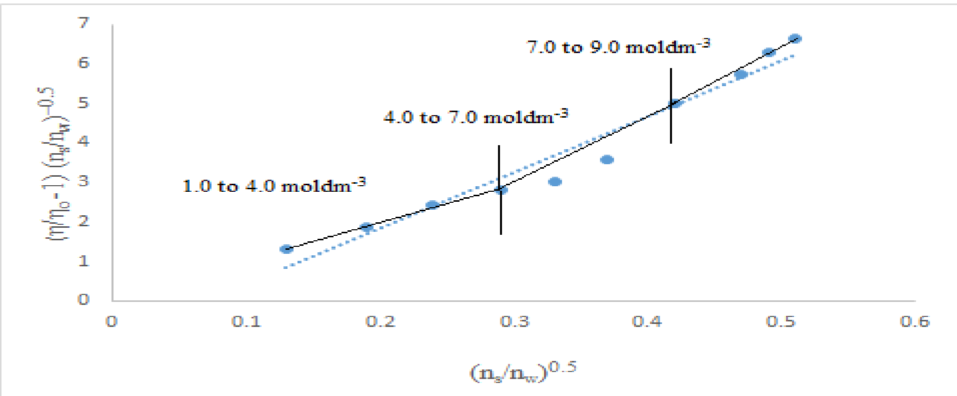
$$(\eta/\eta_0 - 1)\, (n_s/n_w)^{-0.5} = A_x + B_x\, (n_s/n_w)^{0.5} \quad \ldots\ldots\ldots (2.0)$$

where A_x and B_x are the constants which are the measure of interaction parameters, n_s/n_w is the mole fraction of solute and solvent respectively. The values of $(n_s/n_w)^{0.5}$ and $(\eta/\eta_o-1)(n_s/n_w)^{-0.5}$ are collected in Table 1.

Table 1 Variation of viscosity of aqueous sulfuric acid with concentration at 308.15K

c (moldm^{-3})	η (c P)	$c^{0.5}$ (mol$^{1/2}$dm$^{-3/2}$)	ρ (g cm^{-3})	η/η_o	$(\eta/\eta_o-1)c^{-0.5}$ (mol$^{-1/2}$ dm$^{3/2}$)	$(n_s/n_w)^{0.5}$	$(\eta/\eta_o-1)(n_s/n_w)^{-0.5}$
1.0	0.84	1.00	1.06	1.17	0.17	0.13	1.31
2.0	0.98	1.41	1.12	1.36	0.26	0.19	1.88
3.0	1.14	1.73	1.18	1.59	0.34	0.24	2.43
4.0	1.30	2.00	1.23	1.82	0.41	0.29	2.81
5.0	1.45	2.23	1.28	2.01	0.45	0.33	3.02
6.0	1.70	2.44	1.33	2.36	0.55	0.37	3.59
7.0	2.24	2.64	1.39	3.11	0.80	0.42	5.02
8.0	2.66	2.82	1.43	3.70	0.95	0.47	5.74
8.5	2.91	2.91	1.46	3.97	1.02	0.48	6.28
9.0	3.16	3.00	1.49	4.40	1.13	0.51	6.63

The modified Jones-Dole plot for the concentration range 1.0 to 9.0moldm^{-3} is given in Fig. 3 and the values of Ax, Bx are given at the bottom. The plot confirms the presence of three concentration region in sulphuric acid-water system 1.0 to 9.0moldm^{-3} and increase in solute- solvent interaction with increase in concentration as clear from increasing value of B_x coefficient.



1.0 to 4.0 moldm^{-3} (B_x = 9.53 dm$^{-3/2}$mol^{-1}, A_x = 0.08); 4.0 to 7.0 moldm^{-3} (B_x = 17.04 dm$^{-3/2}$mol^{-1}, A_x = –2.3); 7.0 to 9.0 moldm^{-3} (B_x =18.01 dm$^{-3/2}$mol^{-1}, A_x = –2.60.)

Fig. 3: Modified Jones-Dole plot for 1.0 to 9.0moldm^{-3} aqueous sulfuric acid at 308.15K

The presence of three concentration region has also been confirmed from the study of hydrochloric acid- water system in the concentration range 1.0 to 9.0moldm^{-3} [25]. The calculated values of B and B_x which are measure of interaction between solute and solvent have shown that the H_2SO_4 in aqueous medium forms three systems in different concentration range: 1.0 to 4.0moldm^{-3}, 4.0 to 7.0moldm^{-3}and 7.0 to 9.0moldm^{-3}.

IV CONCLUSIONS

It can be concluded that H_2SO_4 interacts with the water molecule and forms the sulfuric acid-water system having different species in three different concentration regions which is justified in view of Jones-Dole and modified Jones- Dole interaction parameters.The results obtained in the study satisfies the validity of Jones-Dole and modified Jones-Dole equation in three different concentration region.The positive value of B-coefficient shows that sulphuric acid acts as structure maker in aqueous solution. The specific solvation behavior of ions furnished by sulfuric acid in water is an important phenomenon which can be used as a model for other solvent systems in the order to find intermolecular interactions present in it.

V ACKNOWLEDGEMENTS

The authors are thankful to Prof. Raj N. Mehrotra, former Professor and Head Chemistry Department, Jodhpur University for useful help with useful suggestions.

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