Volumetric and transport properties of aqueous sulphuric acid

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Molecular conductance λ_m, viscosity η and density ρ of sulphuric acid at different concentrations in dilute aqueous solution were measured at 293 K. The conductance data were used to calculate the value of the ionic association constant. The experimental values of viscosity and density were used to calculate the A and B coefficients of the Jone–Dole equation and the apparent molar volume Φ_v. The behaviour of these parameters suggests that the ion–solvent interactions in the dilute aqueous sulphuric acid and SO_4^{2-} ion acts as 'structure maker'. The results were utilized for the applicability of modified Jone–Dole and Staurding equations.

Keywords: Conductance; Viscosity; Binary system; Jone–Dole equation; Staurdinger equation

1. Introduction

Volumetric and viscometric studies are used to obtain information regarding interactions among the components of a solution, such as solute–solute, solvent–solvent and solute–solvent [1]. There is an increasing number of reports on volumetric/viscometric studies of solutions involving one or more solute or mixed solvent systems. The co-solutes such as carbohydrate [2], urea [3], and amino acid [4] have been used most frequently in aqueous solutions. A survey of the available literature showed that many studies have been carried out in aqueous solution with methanol [5], dimethyl sulphoxide [6], acetonitrile [7], and acetone [8] as cosolvent. The transport properties of sulphuric acid have been used to investigate the influence of an ionic interaction of electrolyte volumetrically [9]. It is interesting to note that the sulphuric acid is itself an electrolyte and expected to influence the volumetric and viscosimetric properties due to the formation of ionic hydrogen H^+, bisulphate HSO_4^- and sulphate SO_4^{2-} in water.

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The present study was undertaken to research the intermolecular/ionic interactions behaviour of aqueous dilute sulphuric acid.

2. Viscosity equations

The concentration dependence of the viscosity of an electrolyte solution is often interpreted in terms of the semi-empirical equations (10–14) including *Jone–Dole equation*,

$$\eta/\eta_0 = 1 + Ac^{0.5} + Bc^{0.5} \tag{1}$$

where, A and B are the long-range inter-particle (inter-ionic) interaction coefficient and the solute–solvent interaction coefficient respectively and c is the molar concentration of the solute.

In the above viscosity equation, the influence of the solvent on the viscosity of the solution is still not considered. On addition of solute, the viscosity of pure solvent changes with increasing concentration of the solute, and the concentration (mole fraction) of solvent decreases simultaneously. Hence, we have introduced [10] the mole fraction of solvent in the denominator and a *modified Jone–Dole model* can be used as

$$\frac{(\eta/\eta_0) - 1}{(x_s/x_w)^{0.5}} = A_x + B_x(x_s/x_w)^{0.5} \tag{2}$$

3. Experimental

Deionized water was distilled twice with a small quantity of alkaline potassium permanganate. Finally, water was distilled in corning glass apparatus with sulphuric acid. The specific conductance of prepared distilled water for the study was in the order $2 \times 10^{-6}\,\Omega\,cm^{-1}$. The sulphuric acid of AnalaR grade BDH was used as such and solutions were prepared by dissolving the calculated volume of acid for the desired strength in distilled water. The strength of solutions were checked by titrating with standard alkali. Density measurements of solution were made using a pyknometer having a capacity $15\,cm^3$. The pyknometer was calibrated with distilled water having density 0.9972 and $0.9942\,g\,cm^{-3}$ at 298 and 308 K, respectively. A thermostatically controlled water bath capable of maintaining the temperature constant $\pm 0.01°C$ was used during the studies. All weighing was made on a single pan digital balance (citizen make) with an accuracy of 0.0001 g. The density values were reproducible $\pm 0.00002\,g\,cm^{-3}$. *Viscosities* were measured using an Ubbelohde-type capillary viscometer (Agarwal Scientific, Agra, India) which was calibrated with doubly distilled water by measuring efflux time using a stop watch with a resolution of 0.01 s. The average of at least four readings, reproducible within an accuracy of 0.01 s was taken as the final efflux time. The conductometric measurements of sulphuric acid solution at different concentrations were made with a digital conductivity meter (Systronic 306). The conductivity meter was calibrated with standard KCl solution. The accuracy of the conductivity meter was $0.01\,mS\,cm^{-1}$ during the study. The results were checked for constant reading.

4. Results and discussion

The observed densities of the sulphuric acid solution are used to calculate the apparent molar volume of solute using the equation

$$\Phi_v = \frac{M}{d_0} + \frac{1000\,(d - d_0)}{cd_0} \tag{3}$$

where d_0 is the density of solvent, d is the density of solution, M is the molecular weight of solute and c is the molar concentration of solute. The values of density are given in table 1 and calculated values of Φ_v at different concentrations of sulphuric acid are given in table 2. The value of the intercept and slope were computed by using the *Masson's* relation given by the equation

$$\Phi_v = \Phi_v^0 + S_v c^{0.5}. \tag{4}$$

The values obtained for Φ_v^0 and S_v for the sulphuric acid at 293 K are $30.63 \pm 0.45\,\mathrm{cm^3\,mol^{-1}}$ and $5.11 \pm 0.07\,\mathrm{cm^3\,L^{1/2}\,mol^{-3/2}}$ respectively. The Φ_v^0 value is positive indicating thereby a positive interaction between solute and solvent molecules. The S_v is positive, indicating that ions have a good complex ion-forming capacity and strong ion–ion interactions are present in aqueous solutions. There is a slight deviation in the linearity of the plot Φ_v *versus* $c^{0.5}$ in the higher concentration range (above 0.75 M) of sulphuric acid indicating a decrease in S_v value. Such a decrease in slope in the higher concentration range may be due to the existence of mutual forces between

Table 1. Variation in density ρ, apparent molar volume Φ_v and relative viscosities (η/η_0) and specific conductance for different mole concentrations of sulphuric acid at 293 K.

Concentration (mol dm^{-3})	Density ρ (g cm^{-3})	η/η_0	Specific conductance K (mS cm^{-1})
0.05	1.00153	1.0078	24
0.10	1.00477	1.0168	47
0.15	1.00804	1.0243	70
0.20	1.01121	1.0330	91
0.25	1.01441	1.0425	112
0.30	1.01758	1.0552	132
0.35	1.02102	1.0676	152
0.40	1.02383	1.0801	171
0.45	1.02697	1.0963	190
0.50	1.03011	1.1059	210
0.55	1.03325	1.1173	
0.60	1.03625	1.1285	
0.65	1.03924	1.1395	
0.70	1.04232	1.1498	
0.75	1.04543	1.1609	
0.80	1.04867	1.1710	
0.85	1.05168	1.1823	
0.90	1.05462	1.1927	
0.95	1.05767	1.2037	
1.00	1.06072	1.2143	

Table 2.   Concentration of H^+, HSO_4^-, SO_4^{2-} ions Φ_v, and $(x_s/x_w)^{0.5}$ of aqueous sulphuric acid at 293 K.

Concentration of H_2SO_4 (mol dm^{-3})	$(H^+)^{0.5}$ (mol$^{-1/2}$ dm$^{-3/2}$)	$(HSO_4^-)^{0.5}$ (mol$^{-1/2}$ dm$^{-3/2}$)	$(SO_4^{2-})^{0.5}$ (mol$^{-1/2}$ dm$^{-3/2}$)	Φ_v (mL mol^{-1})	$(x_s/x_w)^{0.5}$
0.05	0.2419	0.2037	0.0922	31.5370	0.0306
0.10	0.3314	0.3002	0.0989	32.4385	0.0425
0.15	0.4005	0.3735	0.1019	32.5317	0.0521
0.20	0.4590	0.4349	0.1039	33.0897	0.0602
0.25	0.5108	0.4889	0.1048	33.3001	0.0674
0.30	0.5578	0.5374	0.1053	33.5405	0.0739
0.35	0.6009	0.5819	0.1058	32.9394	0.0799
0.40	0.6413	0.6234	0.1063	34.0664	0.0855
0.45	0.6718	0.6623	0.1068	34.2084	0.0908
0.50	0.7151	0.6989	0.1070	34.3219	0.0957
0.55	0.7493	0.7338	0.1072	34.4080	0.1005
0.60	0.7819	0.7671	0.1074	34.7554	0.1051
0.65	0.8133	0.7989	0.1076	35.0047	0.1095
0.70	0.8435	0.8297	0.1077	35.1080	0.1137
0.75	0.8727	0.8593	0.1078	35.1633	0.1178
0.80	0.9009	0.8879	0.1079	35.0557	0.1218
0.85	0.9282	0.9156	0.1080	35.2191	0.1257
0.90	0.9575	0.9425	0.1081	35.4483	0.1294
0.95	0.9807	0.9686	0.1082	35.5441	0.1331
1.00	1.0058	0.9941	0.1082	35.6243	0.1367
Slope	0.252 dm$^{-3/2}$ mol^{-1}	0.240 dm$^{-3/2}$ mol^{-1}			
Intercept	-0.036 dm$^{-3/2}$ mol$^{-1/2}$	-0.021 dm$^{-3/2}$ mol$^{-1/2}$			

two parts of a completely ionized molecule of sulphuric acid at higher concentration, and to the stable equilibrium concentration of SO_4^{2-} ion formed by the dissociation of HSO_4^-.

The *relative viscosity* of sulphuric acid solution at different concentrations in water was calculated and values are given in table 1. It was concluded that the *modified Jone–Dole equation* is valid in the case of molecular interactions of sugars [15] in dilute aqueous solutions. It has been assumed that the solute molecules behave like monomer units of polymolecular assemblies. We considered it most worthwhile to use the *viscosity* data for the applicability of *modified Jone–Dole equation* (2).

If we consider that molecular assemblies and ions also behave like independent molecules of solute, we can also apply the *Staurdinger equation* to the viscosity data of sulphuric acid:

$$\frac{\eta}{\eta_0} = 1 + knc \tag{5}$$

where k is the characteristic constant and n is the number of monomers present in the molecular assembly. From a plot of concentration *versus* η/η_0, the slope value 0.224 dm^3 mol^{-1} was obtained from the experimental data. The observed values of η/η_0 were also used to examine the linearity relation given by equations (1) and (2). We obtained $B = 0.245$ dm$^{-3/2}$ mol^{-1} and $A = -0.028$ dm$^{3/2}$ mol$^{-1/2}$, whereas the coefficient of *modified Jone–Dole equation* $B_x = 13.035$ and $A_x = -0.181$ were obtained graphically. From the graphs, the linearity has been confirmed for both the equations. It can be concluded from figure 1 that the proposed modified equation for nonionic sugar molecules is also applicable for ions of sulphuric acid as solute. The sulphuric acid
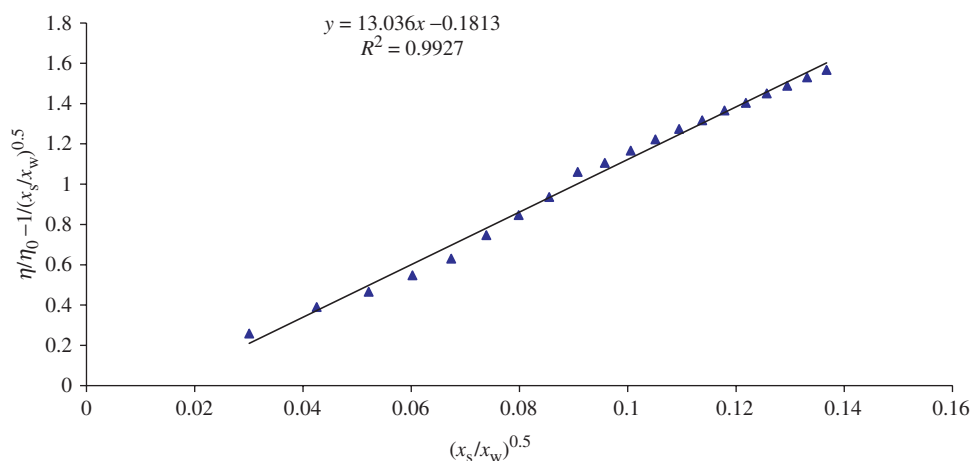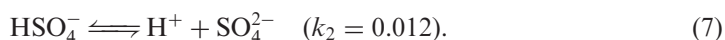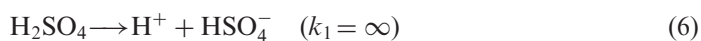
Figure 1. Plot of modified Jone–Dole for aqueous sulphuric acid at 293 K.

is a diprotic acid having two ionization constants. The first ionization constant is very strong in comparison to the second. The first dissociation of uncharged molecules, resulting from the formation of most of the hydronium ion in the first dissociation, suppresses the subsequent second dissociation due to common ion effect. The dissociation of the acid can be represented by the following equilibrium relations ($\rightleftharpoons$ denotes equilibrium):

$$H_2SO_4 \longrightarrow H^+ + HSO_4^- \quad (k_1 = \infty) \tag{6}$$

$$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-} \quad (k_2 = 0.012). \tag{7}$$

In dilute solutions of aqueous sulphuric acid, the concentration of H^+, HSO_4^- and SO_4^{2-} was calculated from the values of the equilibrium constant at fixed temperature. In our study, the concentration of these species has a significant contribution towards interaction present in solution. An attempt has been made to extend the principle of additivity used for weak acids [16] in *viscometric* studies. At each dilution of sulphuric acid, we have calculated the concentration of H^+ ion, of SO_4^{2-} ion, and of HSO_4^- ion separately with the help of the concentration of sulphuric acid in relation to the ionization constant of sulphuric acid. The value 0.012 was used for the ionization constant. The square root of concentration values of each ionic specie is reported in table 2.

It was observed that the concentration of H^+ ion and HSO_4^- ion increased with increasing concentration of sulphuric acid, whereas the concentration of SO_4^{2-} ion is quite smaller and it remains constant (0.0111 mol dm^{-3}) with increasing concentration of sulphuric acid. It is well known that the SO_4^{2-} ion is a powerful structure maker [17]. The designation 'structure maker' is given to a solute that favours the cluster formation of liquid water.

In the present study, we have made an attempt to study the general validity of the viscosity relations equations (1) and (2) with respect to the concentrations of individual ions, namely H^+ ion, HSO_4^- ion and SO_4^{2-} ion, along with the concentration

of sulphuric acid. These observations were, of course, based on the fact that the plot between $c^{0.5}$ *versus* $\eta/\eta_0 - 1$ and $c^{0.5}$ should be linear. The *viscosity* data represented in table 1 were used to estimate the values of slope and intercept. The values obtained for H^+ ion and HSO_4^- ion are recorded in the bottom of the table 2. The value of *viscosity B-coefficient* in case of H^+ ion is nearly the same as that of sulphuric acid. But in the case of SO_4^{2-} ion the plot between $c^{0.5}$ *versus* $\eta/\eta_0 - 1/c^{0.5}$ was not linear according to the *Jone–Dole equation*. From the nature of the curve in figure 2, a logical conclusion is that the SO_4^{2-} ion have a more or less negligible effect towards solution structure or the effect is the same as that of H^+ and HSO_4^- ions up to the concentration $0.15 \, mol \, dm^{-3}$. It is also possible that only the SO_4^{2-} ion has 'structure maker' property, while H^+ ion and HSO_4^- have "structure breaker" character, but in our study the overall value of *viscosity B-coefficient* is positive.

The concentration range used in the study was optimum for the validity of *Jone–Dole equation*, but it failed in the case of SO_4^{2-} ions. The failure of SO_4^{2-} ion is against the well-established fact that the viscosity B-coefficients are additive in the sense that the B-coefficient difference between pairs of salts having common anion remains constant in dilute solution, independent of the nature of the anions [16].

Taking into account of the 'structure maker' nature of SO_4^{2-} ion as well as the principle of additivity of B-coefficient, it can be concluded with a reasonable justification that the value of viscosity B-coefficient was positive in case of H^+ ion, HSO_4^- and H_2SO_4, due to the powerful 'structure maker' nature of SO_4^{2-} ions provided by H_2SO_4. The value $1:4.88:6.88:5.88$ for the ratio $[SO_4^{2-}]:[HSO_4^-]:[H^+]:[H_2SO_4]$ in the dilute solution of sulphuric acid implies that there are seven times H^+ ion available for SO_4^{2-} ion. The SO_4^{2-} ions have four oxygen atoms through which it can constitute a resonating structure like HSO_4^- ion. The SO_4^{2-} ion acts as a resonating centre for other two ions H^+ and HSO_4^- in addition to the possibility of formation of larger aggregates with an increase in the 'structure maker' tendency.
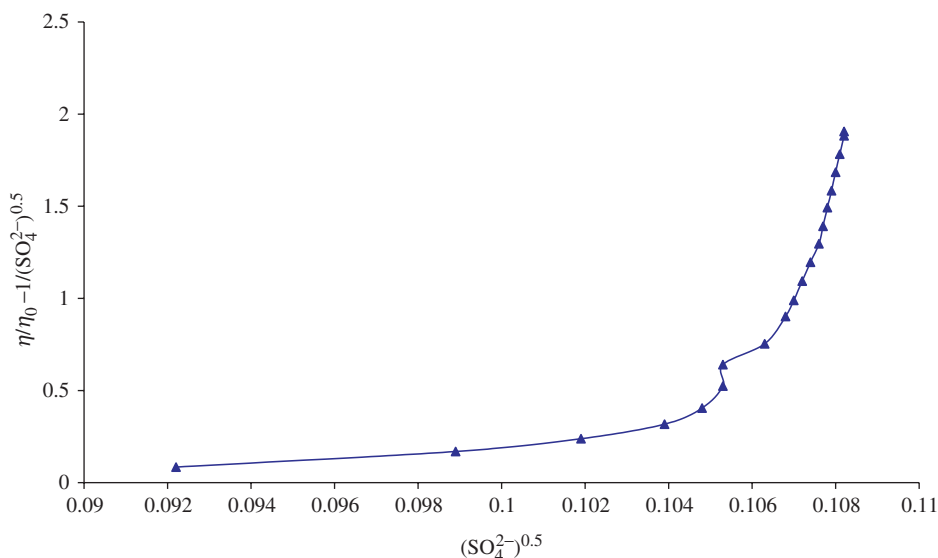

Figure 2. Plot for $(SO_4^{2-})^{0.5}$ *vs.* $\eta/\eta_0 - 1/(SO_4^{2-})^{0.5}$ for aqueous sulphuric acid at 293 K.

Although the sulphuric acid is a strong electrolyte, in the present study it has been concluded that the formation of ion-pairs/ionic aggregates takes place in dilute aqueous sulphuric acid. To prove the existence resonating ion SO_4^{2-} formation, the conductance data were analyzed Arrhenius–Ostwald relation [18] given by the equation

$$\frac{1}{\lambda_m} = \frac{1}{\lambda_m^0} + \frac{c\lambda_m}{\lambda_m^0}\frac{K_A}{2} \qquad (8)$$

where λ_m is the limiting molar conductance, c is molar concentration, and K_A is the association constant.

The *specific conductance* of sulphuric acid in water below the concentration $0.50\,\text{mol}\,\text{dm}^{-3}$ was measured and the data obtained was used to determine the value of molar conductance at different concentrations. The observed values of molar concentrations and *specific conductance* are presented in table 1.

The plot $c\lambda_m$ *versus* $1/\lambda_m$ was linear. The value of K_A calculated from slope and intercept of the plot has significant value $15.00\,\text{cm}^3\,\text{mol}^{-1}$ and the value of λ_m^0 obtained was ($500\,\text{Scm}^{-1}$) at temperature 293 K.

The value of ionic conductance at infinite dilution for HSO_4^- ion ($HSO_4^- = H^+ + SO_4^{2-}$) at same temperature using the literature value of ionic conductance of SO_4^{2-} ion and H^+ ion ($349.5 + 160.0 = 509.8\,\text{S cm}^{-1}$). The calculated value is in good agreement with the experimental results and various ionic equilibria discussed for the formation of ion-pair–ion associations.

5. Conclusion

A perusal of results indicates that the B-coefficient is positive and fairly large for sulphuric acid in the concentration range studied, thereby showing the presence of strong ion-solvent interaction in dilute aqueous solution, which is also evident from the value of Φ_v^0. If we neglect the contribution of H^+ ions formed by dissociation of HSO_4^-, the H^+–HSO_4^- ionic doublet behaves like a solute molecule of sulphuric acid. A similar conclusion has been arrived that the ratio of (B_x/B) is nearly 60 as it was obtained in case of sugars [15].

The solvent water and solute sulphuric acid have protic solvent characteristics, which results in weak ion–ion interaction. The solution contains ionizable proton and can undergo auto dissociation. The auto dissociation is significant in this case due to the encounter of solute molecules with solvent molecules and with charged assemblies formed in the solution, which were confirmed by the conductance data.

The relationship between *viscosity* data and concentration of solute proposed by *Staurdinger* for poly molecular assemblies has been observed in the case of dilute sulphuric acid due to hydrogen bond forming capability and resonating structure of sulphate ion, which can form various ionic equilibria of ion-pairs–ion association.

It can be said that the proposed *modified Jone–Dole equation* in this study can be a model for gaining more information in the field of molecular interaction studies.

References

[1] J.M. McDowali, C.A. Vincent. *J. Chem. Soc., Faraday Trans. I*, **70**, 1862 (1974).
[2] (i) B. Behra, B. Sahu, S. Pradhan, K. Behra. *Indian J. Chem.*, **22A**, 20 (1983); (ii) R.L. Blokhra, S. Kumar. *Indian J. Chem.*, **28A**, 1087 (1989).
[3] M.L. Parmar, D.K. Dhiman. *Indian J. Chem.*, **40A**, 1161 (2001).
[4] A.P. Mishra, P. Kaur, V. Kashyap. *Indian J. Chem.*, **40A**, 100 (2001).
[5] (i) J.S. Sandhu, P. Kaur, V. Kashyap. *J. Indian Chem. Soc.*, **63**, 729 (1986); (ii) J.R. Mohanty, P.C. Mohanty, B.R. Das, P.K. Mishra. *Res. J. Chem. Environ.*, **7**, 33 (2003).
[6] S.D. Das, K. Hazara, S.C. Lahiri. *Z. Phys. Chem. (Frankfurt)*, **138**, 185 (1983).
[7] V.K. Syal, R. Gautam, Shashi, S. Chauhan, S. Agrwal. *Proc. Nat. Acad. Sci. India*, **67A**, 29 (1997).
[8] (i) P.S. Nikam, M. Hasan, N. Nikam, R.R. Ahire. *Asian J. Chem.*, **6**, 789 (1994); (ii) J. Podra. *J. Chem. Phys.*, **39**, 2599 (1963); (iii) F. Kawaizumi, F. Nakao, H. Nomura, *J. Chem. Eng. Data*, **33**, 204 (1988).
[9] M.L. Parmar, A. Kundra. *Electro Chem. Acta*, **28**, 1655 (1983); (ii) O. Redlik, J. Begeleisen. *Chem. Rev.*, **30**, 171 (1942); (iii) J.M. Kolt, C.F. Eckert. *J. Amer. Chem. Soc.*, **64**, 1878 (1942); (iv) H.S. Harned, B. Bowen. *Physical Chemistry of Electrolyte Solutions*, Renihold Publication, New York (1958).
[10] G. Jone, M. Dole. *J. Amer. Chem. Soc.*, **51**, 2950 (1929).
[11] V. Vand. *J. Phys. Colloid. Chem.*, **52**, 277 (1948).
[12] A. Einstein. *Ann. Physik*, **19**, 289 (1906); **34**, 591 (1911).
[13] D.C. Thomas. *J. Colloid. Sci.*, **20**, 267 (1965).
[14] S.P. Moulik. *J. Phys. Chem.*, **72**, 4682 (1968).
[15] N.D. Kandpal, K.N. Mathpal. *National Conference on Recent Advances in Chemical Sciences (RACS)*, p. 16, Dehradune, India (2004).
[16] S.K. Mandal, S.K. Sanyal. *Indian J. Chem. Soc.*, **58**, 1051 (1981).
[17] Y. Marcus. *Ion Solvation*, p. 113, Wiley Inter Sciences, New York (1985).
[18] O. Popvych, R.T.P. Tomkins. *Non Aqueous Solution Chemistry*, p. 255, John Wiley & Sons, New York (1981).