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EFFECT OF TEMPERATURE ON THE INTERACTION PARAMETERS OF AQUEOUS CONCENTRATED SULPHURIC ACID

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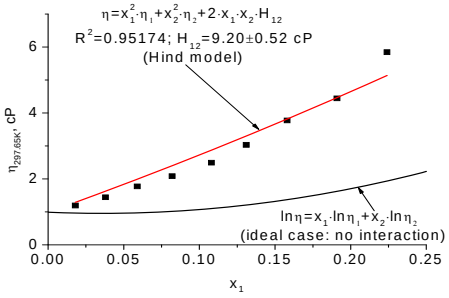
The present study deals with the effect of temperature on the interaction parameters of aqueous sulphuric acid in the concentration range 1.0 to 9.0 moldm^{-3}. The experiments were performed at 297.65K and 308.15K. For determination of interaction parameters d_{12} and H_{12}, Grunberg- Nissan and Hind viscosity models were used respectively. The decrease in d_{12} and H_{12} with increase in temperature shows the structural modification in sulphuric acid- water system.



INTRODUCTION

The essential role of water in chemical processes is closely connected to the aqueous solvation shell of the reacting molecules or ions. The intermolecular interactions are sensitive to the solution structures, solvent polarity, viscosity and presence of foreign molecules or ions in the media. The physical, catalytic, photo-physical and electro-chemical properties of liquids are affected by the intermolecular interactions among molecules.[1-3] The interaction of water with solute represents a central topic in chemistry and biology.[4] Water itself is highly associated and it has a tendency to associate with molecules/ ions (hydration) of high degree.[5] A survey of the available literature showed that aqueous sulphuric acid systems have been studied conductometrically[6-8] and viscometrically.[9-11] Several studies are available on sulphuric acid-water system in aqueous solution.[12-14] In order to obtain important information about the hydration of sulphuric acid, the concept of viscosity has been undertaken. In this work, Grunberg- Nissan and Hind viscosity models were used in order to determine the interaction parameters d_{12} and H_{12} of sulphuric acid-water system. The dependence of d_{12} and H_{12} on temperature was used to study the nature of interaction between sulphuric acid and water.

RESULTS AND DISCUSSION

To determine the interaction parameters in sulphuric acid-water system, Grunberg-Nissan viscosity model was employed.[15] According to this model, the viscosities of various components present in different compositions are related to each other by the logarithmic relationship. The model can be represented as:

$$\ln \eta = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 d_{12} \qquad (1.0)$$

where x_1 and x_2 are the mole fractions of the components having viscosities η_1 and η_2 in pure state whereas η is the viscosity of the mixed solution of two components, d_{12} is a constant which indicates the nature of interactions between two components known as Grunberg-Nissan interaction parameters.

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The value of d_{12} depends upon the nature of the solute and solvent in a binary system. The positive value of d_{12} may be attributed due to the presence of a strong interaction between two components.[16] The negative values of d_{12} are a measure of the presence of dispersion forces in the solution.[17] In Table 1, d_{12} values are collected at two temperatures.

Hind proposed a relation between molecular interaction parameter and the concentration of the solute in solution[18] as given below.

$$\eta = x_1^2 \eta_1 + x_2^2 \eta_2 + 2x_1x_2H_{12} \qquad (2.0)$$

where x_1 and x_2 are the mole fractions of the components having viscosities η_1 and η_2 in pure state whereas η is the viscosity of the mixed solution of two components. H_{12} is a constant known as Hind's interaction parameter. The values of H_{12} at two temperatures are given in Table 1.

Table 1

d_{12} and H_{12} parameters for sulphuric acid (1) + water (2) system for different concentrations at 297.65K and 308.15K

(c)	x_1	x_2	η		d_{12}		H_{12} (cP)	
mol dm^{-3}			297.65K	308.15K	297.65K	308.15K	297.65K	308.15K
1.0	0.018	0.981	1.19	0.84	6.71	5.81	6.27	4.15
2.0	0.038	0.961	1.44	0.98	6.71	5.28	6.59	4.04
3.0	0.059	0.940	1.77	1.15	6.85	5.19	7.14	4.14
4.0	0.082	0.917	2.08	1.30	6.28	4.66	7.11	3.97
5.0	0.108	0.891	2.49	1.45	5.89	3.98	7.25	3.63
6.0	0.131	0.868	3.03	1.70	6.03	4.01	8.02	3.79
7.0	0.158	0.841	3.77	2.24	6.13	4.95	9.02	4.95
8.0	0.191	0.808	4.44	2.66	5.63	4.75	9.12	5.12
9.0	0.224	0.775	5.84	3.16	5.96	4.78	11.22	5.59

At 297.65K: $\eta_1 = 26.7$cP, $\eta_2 = 0.99$ cP; At 308.15K: $\eta_1 = 20.1$cP, $\eta_2 = 0.72$ cP

It is clear from Table 1 that the values of d_{12} and H_{12} are positive which indicates a strong association between sulphuric acid and water. The increase in the viscosity of water with concentration can be explained from the rigid nature of solvation structure formed by the ion and its first hydration shell. It is clear that viscosity of the solution decreases with increase in temperature. The variation in the viscosity at different temperatures was utilized to verify the nature of d_{12} and H_{12}. In order to confirm the nature of the solute in concentrated solution, the temperature effects on these parameters have been investigated at two temperatures. The values of d_{12} and H_{12} decrease with the rise in temperature for sulphuric acid-water system in the concentration region 1.0 to 9.0 moldm^{-3}. It has

been observed that for all the concentrations at 308.15K, the values are less than that at 297.65K, which may be due to the partial dissociation of the associative aggregate formed between ionic species of sulphuric acid including sulphuric acid with water. The study is supported by available literature which shows the variation of interaction parameters with temperature.[19-21]

EXPERIMENTAL

The sulfuric acid used was of GR grade (E. Merck). Doubly distilled water was used to prepare solutions of required concentration. In order to maintain a constant temperature, Tanco made thermostat was used. The solution of sulphuric acid of known concentration was taken in the viscometer (Infusil India Pvt. Ltd.) and the flow time of the solution was measured with the help of a stop watch (Racer). Each measurement was repeated thrice and an average time of flow was used to calculate the viscosity. The densities of solutions were measured using a 15 mL double arm pyknometer having accuracy ±0.00001g/mL and a single pan electronic balance (Citizen).

CONCLUSIONS

It is concluded that sulphuric acid interacts with water and with increase in temperature there may be the partial dissociation of the associative aggregate formed between ionic species of sulfuric acid including sulfuric acid with water due to which the values of d_{12} and H_{12} decrease. The study can be used as a model also for other solvent systems in order to find the nature of intermolecular interaction.

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