

INTERACTION OF OXALIC ACID IN AQUEOUS SULPHURIC ACID WATER SYSTEM: VISCOMETRIC STUDIES.

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ABSTRACT

The viscosity η and density ρ have been measured for the oxalic acid in aqueous sulfuric acid of different concentration at 298K. Viscosity has been measured using uplobe Viscometer (Infusil). From the experimental data viscosity parameters, viz viscosity B- coefficient, B and Staudinger coefficient, kn are calculated. B-coefficient decreases with the increase in the concentration of sulfuric acid. The presence of ion-solvent interaction was formed in the system. The results have been discussed on the basis of interaction parameters.

KEYWORDS: Oxalic Acid, Sulphuric Acid, Viscosity, Viscosity B- Coefficient

INTRODUCTION

The nature of oxalic acid has been studied in the solution of mineral acids volumetrically and it has been reported [1] that in aqueous solution of 0.01 Mol dm^{-3} oxalic acid, 87.1 percent of it exist in the form of HC_2O_4^- . But in the presence of molar mineral acid solution the dissociation of oxalic acid is suppressed to a large extent and only 5.5 percent exist in the dissociated $\text{C}_2\text{O}_4^{2-}$ form. Therefore, in 0.01 Mol dm^{-3} oxalic acid, the concentration of oxalic acid and monocarboxylate ion is 94.43 respectively. Hence the contribution of $\text{H}^+\text{C}_2\text{O}_4^-$ towards the rate of oxidation is only 5 percent.

The sulfuric acid has been used as solvent to investigate the interaction forces of electrolytes volumetrically (2). Recently we have reported the interaction parameters and solution behavior of aqueous sulfuric acid in the concentration range $0.05\text{-}1.0 \text{ Mol dm}^{-3}$ obtained from conductance and viscosity measurements (3). The nature of oxalic acid in aqueous solutions, has been determined and structure breaking nature in water has been reported (4,5). Though the Jone Dole equation is applicable in the lower concentration range, but in the present study the sulfuric acid has been used as a solvent upto the concentration range 10.0 Mol dm^{-3} . We have also investigated the transport properties of oxalic acid in relation to the interaction parameters as a function of ions furnished by the oxalic acid in aqueous solution in aqueous solution in place of concentration of acid. The viscometric study also includes the effect of oxalic acid as a co-solute in aqueous sulfuric acid. This study has been undertaken to understand the changes in interactions that occurs with the presence of oxalic acid in aqueous sulfuric acid.

EXPERIMENTAL

The GR grade of hydro-chloric acid (E-Merck) was used for making solutions using doubly distilled water. The viscosity measurement was taken in a calibrated suspended-level Viscometer (Infusil India Pvt. Ltd.). The Viscometer was placed in a thermostated water bath (Tanco) having accuracy $\pm 0.1 \text{ K}$ for constant temperature. The solution of sulfuric

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 15ml double arm pycnometer having accuracy + 0.00001 g/ml and a single pan electronic balance (citizen).

RESULT AND DISCUSSIONS

In the present study the solutions of sulfuric acid were used as a solvent. The solutions were prepared by direct addition of solid oxalic acid as solute in aqueous solution of sulfuric acid. So that its ionization can take place in the presence of a mineral acid. The values of relative viscosities η/η_0 at different concentration of oxalic acid (0.055 to 0.275) in aqueous solution of sulfuric acid at 298 K of different molarity are presented in Table.

Table 1: The Variation of η/η_0 With Concentrations of Oxalic Acid in Aqueous Solutions of Sulphuric Acid At 298 K

	Concentration Of H_2SO_4 Mol Dm^{-3}	Oxalic Acid (η/η_0)				
		0.055 Mol Dm^{-3}	0.110 Mol Dm^{-3}	0.165 Mol Dm^{-3}	0.220 Mol Dm^{-3}	0.275 Mol Dm^{-3}
1	2	0.0178	0.0231	0.0266	0.0306	0.0331
2	3	0.022	0.0281	0.0323	0.0359	0.0418
3	4	0.0284	0.0304	0.0325	0.0353	0.039
4	6	0.0544	0.063	0.0654	0.0682	0.0769
5	8	0.0648	0.071	0.0751	0.079	0.0864
6	9	0.1016	0.113	0.1198	0.1268	0.1422
7	10	0.1577	0.1708	0.1752	0.183	0.1899

The data of η/η_0 of oxalic acid in aqueous sulphuric acid were analyzed with the help of Jones-Dole equation [6] given by $\eta/\eta_0 - 1, c^{0.5} = A + B c^{0.5}$ and Staudinger equation [7] $\eta/\eta_0 - 1 = kn c$. The values of interaction parameters obtained from these equations by the plots between $\eta/\eta_0 - 1, c^{0.5}$ versus $c^{0.5}$ and $\eta/\eta_0 - 1$ versus c are given in Table 2.

Table 2 Variation of Interaction Parameters of Oxalic Acid With Molarity of Aqueous Sulphuric Acid At 298 K

S.No.	Concentration H_2SO_4 (mol dm^{-3})	A $\text{dm}^{3/2}$ Mol $^{-1/2}$	B dm^{-3} mol $^{-1}$	Linearity	Kn	Linearity
1	2	0.0848	-0.0431	0.9356	0.0692	0.9853
2	3	0.1041	-0.054	0.8138	0.086	0.9921
3	4	0.1512	-0.1596	0.8794	0.0475	0.9824
4	6	0.2968	-0.3097	0.9319	0.0910	0.9448
5	8	0.3542	-0.3879	0.9233	0.0929	0.9869
6	9	0.5466	-0.5709	0.9081	0.1726	0.9765
7	10	0.8936	-1.0668	0.9507	0.1393	0.9737

The magnitude of A increases with the concentration of sulphuric acid in water. It shows that the ion-ion or solute-solute interactions are strong in higher concentration region of sulphuric acid. Further it is also clear that increase in A coefficient with concentration of sulphuric acid, the ion-ion/ ion-solute interactions are strengthened by the addition of sulphuric acid to water. It can be concluded that the sulphuric acid acts as structure maker in aqueous solution but the oxalic acid acts as structure breaker in aqueous sulphuric acid.

The B- coefficient for oxalic acid in aqueous solution of sulphuric acid has negative value. If one assume that the contribution of individual solute towards B-coefficient is additive. The resultant value of B-Coefficient of oxalic acid in aqueous sulphuric acid should be positive with large magnitude.

The value of kn was observed for oxalic acid in aqueous sulphuric acid increases with the concentration of sulphuric acid. If we consider the value of K constant, which depends on medium and shape of the solute species in solution, the increase in kn value can be attributed only by the increase in value of n . The n represents the numbers of monomers present in molecular aggregate/polymeric species form by the solute monomer or the size of the solvated ion/solute. In our results the value of kn changes from 0.0692 to 0.1726 with the change of concentration from 2 to 10 mol dm^{-3} of sulphuric acid. The increase in kn value suggest that the information of self associated aggregates increases with the increase in the concentration of the sulphuric acid, which justifies the structure making nature of sulphuric acid in water in presence of oxalic acid.

CONCLUSIONS

It is clear that both the acids form species in water in presence of each other different from species forms separately in water. The value of kn also confirm the conclusion drawn from the interaction parameters A and B . which indicate that both the solutes behave as structure maker in water, but the B Coefficient for oxalic acid in aqueous solution of sulphuric acid as negative value. In the study the sulphuric acid behaved as solvent which is indicated by the linearity of the plots for all the concentration of sulphuric acid $>0.090+ 0.009$.

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