A study of β-coefficients of some organic Acids in aqueous solutions of thiourea at room temperature

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Abstract: Relative viscosities of three organic acids viz. ascorbic acid, citric acid and tartaric acid, at different concentration have been determined in aqueous solutions of thiourea (0.2, 0.5, 1.0, 1.2 and 1.5 mol/kg of thiourea) at 298 K. The data has been evaluated using Jones-Dole equation and the obtained parameters interpreted in terms of solute-solute and solute-solvent interaction. The activation parameters of viscous flow have been obtained which depicts the mechanism of viscous flow. All the three organic acids behave as structure breakers in aqueous solutions of thiourea.

Key words: Ascorbic acid; β-coefficients; citric acid; tartaric acid; aqueous solution of thiourea; structure-breaker; viscosity.

1. Introduction

The viscosity data provide important information about various types of interaction occurring in solutions. These studies are of great help in characterizing the structure and properties of solutions. The solution structure is of great importance in understanding the nature of bioactive molecules in the body system. Survey of literature [1-11] shows that although many studies have been carried out for varies electrolytic solutions, little attention has been paid to the behavior of organic acids in aqueous solutions of thiourea.

Such data are expected to highlight the role of organic acids in influencing the β-coefficient in aqueous solutions of thiourea. This consideration prompted us to undertake the present study.

2. Materials and Method

Ascorbic acid, citric acid, tartaric acid and thiourea (all of AR grade) were used after drying over P_2O_5 in desiccators for more than 48 hours. The reagents were always placed in the desiccators over P_2O_5 to keep them in dry atmosphere. Freshly distilled conductivity water (sp. cond. ~10^{-6} /Ohm cm) was used as standard solvent and for making aqueous solutions of thiourea.

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All aqueous solutions of thiourea as well as the solutions of organic acids were made by weight and molarities m, were converted into molarities, c, using standard expressions[12].

$$C = 1000dm/(1000+mM_2) \qquad \text{...... (1)}$$

Where d is the solution density of an organic acid in aqueous solution of thiourea and M_2 the molecular weight of an organic acid.

The density was measured with a hydrostatic balance similar to that reported by Ward and Millero[13] and described elsewhere[14-16] (accuracy in density measurements, $\pm 1*10^{-4} gdm^{-3}$). The relative viscosities (accuracy in density measurements, $\pm 1*10^{-4}$ cp) were measured at the desired temperature using an Oswald's suspended level type viscometer with a flow time 381.43s for water at 298 K. Runs were repeated until three successive determinations were obtained within ±0.1s. Since all flow times were greater than 100s, the kinetic energy correction was not necessary. The relative viscosities of the solutions (ηrel) were calculated by the usual procedure [17, 18]. The density measurements were carried out in a well stirred water-bath whose temperature was controlled to ±0.01 K.

3. Results and Discussion

The relative viscosities and densities of the solutions of ascorbic acid, citric acid and tartaric acid in aqueous solution of thiourea (0.2, 0.5, 1, 1.2, and 1.5 mol kg^{-1}) were measured at 298K. The experimental results of relative viscosities of organic acids in aqueous solution of thiourea have been analyzed by Jones-Dole equation[19]

$$\eta_{rel} = \eta/\eta_0 = 1 + Ac^{1/2} + Bc \qquad \text{...... (2)}$$

Where η and η_0 are the viscosities of the solution of organic acid and solvent (thiourea + water) respectively, c is the molar concentration, A and B are the constant characteristic of solute-solute and solute-solvent interaction respectively. The plots of (η_{rel} -1)/ c½ verses c½ for all the organic acids were found to

be linear, with least scatter. The values of A and B parameters have been calculated using the least square method by fitting the experimental results in Jones-Dole equation and these values, obtained in different compositions of thiourea + water at 298K, are recorded in Table 1.

Table 1. Values of A and B parameters of Jones-Dole equation for ascorbic acid, citric acid and tartaric acid in different compositions of thiourea+water at 298K.

Composition of thiourea in water	A $(dm^{3/2} mol^{-1/2})$	B $(dm^3 mol^{-1})$
Ascorbic acid		
0.0 (water)	-0.25	0.62
0.2	-0.35	0.90
0.5	-0.41	0.99
1.0	-0.45	1.36
1.2	-0.69	1.35
1.5	-0.75	2.03
Citric acid		
0.0 (water)	-0.20	0.82
0.2	-0.25	0.94
0.5	-0.31	1.12
1.0	-0.39	1.28
1.2	-0.44	1.50
1.5	-0.58	1.67
Tartaric acid		
0.0 (water)	-0.50	0.88
0.2	- 0.30	0.93
0.5	-0.70	1.08
1.0	-0.79	1.24
1.2	-0.85	1.56
1.5	-0.92	1.20

A perusal of table 1 shows that the values of coefficient 'A' decrease continuously with increase in composition of thiourea in water at 298K, thereby suggesting that the solute-solute interactions, though weak, go on decreasing with increase with the increase of thiourea content in water. These results indicate that all the three organic acids, mix more ideally with thiourea+water as compared to water and there is perfect salvation of all three organic acids in thiourea+water solutions thereby resulting in weak solute-solute interactions.

It is also clear from Table1 that the values of B-coefficients, for all three organic acids in water and in aqueous solutions of thiourea at 298K, are positive and fairly large suggesting the presence of strong solute-solvent interactions. The value of B-coefficients also increase with increase in thiourea composition in water suggesting that the solute-solvent interaction increase with the increase of thiourea in water at 298K, for all three organic acids, which results in the improvement of solute salvation.

It has been emphasized by many workers that dB/dT is a better criterion for determining the structure making/breaking nature of any solute rather than simply the B- coefficient. So it means that in order to follow this criterion, the temperature effect must be studied.

Since the behaviour of the individual organic acid was found to be linear and identical in different compositions of thiourea + water at 298 K, only 1.0 mol Kg^{-1} thiourea + water composition was selected for studying the effect of temperature. The plots of $(\eta_r- 1)/c^{\frac{1}{2}}$have have been to be linear at 298, 303, 308, and 313 K in accordance with Jones-Dole equation (equation 2) for individual organic acid.

The values of B-coefficients are positive and large, as compared to that of A for all the three organic acids in thiourea + water (1 mol kg^{-1}) solution at all temperatures, showing the presence of strong solute-solvent interaction . The value of dB/dT is positive for all the three organic acids in thiourea + water showing that all three acids act as structure breakers in aqueous solution of thiourea.

The activation enthalpy (ΔH_2^{0*}) can be calculated with the help of following relation[19]:

$$\Delta H_2^{0*} = \Delta \mu_2^{0*} + T\Delta S_2^{0*} \qquad \text{...... (3)}$$

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