

THE STUDY OF CORRELATION OF B-COEFFICIENT WITH OTHER ADDITIVE PROPERTIES FOR CROTONIC ACID

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Viscosities of crotonic acid solutions in aqueous and aqueous butanol mixtures (2%, 4%, 6%, v/v) were measured at various concentrations 1.0×10^{-3} to 5.0×10^{-3} mol.dm⁻³ at different temperatures 35° to 50°C. Ion-ion and ion-solvent interactions were studied in terms of A and B-coefficients of Jones-Dole equation. The negative values of B-coefficients increased with rise of temperatures led to the conclusion that crotonic acid in aqueous and aqueous butanol mixtures behaves as structure maker. Thermochemical data in terms of activation parameters such as energy of activation (E_a), change in free energy of activation (ΔG^{*}) and change in entropy of activation (ΔS^{*}) as a function of temperature, salt concentration and solvent composition were also evaluated.

Key words: Viscosities, Jones-Dole equation, Ion-ion interaction, Ion-solvent interaction, Thermodynamic parameters.

Introduction

B-coefficient provides the basis for the study of thermochemical data. The ion additive property of B-coefficient correlates it with other ion additive properties i.e. enthalpies, Gibbs free energies and entropies of hydration, solvation and transfer between solvents (Nightingale and Benck 1959; Kaminsky 1957; Stokes and Mills 1965; Nandi and Hazra 1989). Although a large collection of data on ionic coefficient is available for aqueous and non-aqueous media (Arnett et al 1965; Corraduri et al 1992; Dakar and Khakimov 1994; Fahimuddin et al 1995a&b, 1997c; Kpadi et al 1997) but there exists so far no theory. The solvation of the ions and their effects on the structure of the solvent in the near environment of the solute particles is explained by Jones-Dole (Jones and Dole 1929). The electrostatic forces which tend to maintain a quasilattice of the ions in the solution (an ionic atmosphere of oppositely charged ions) would stiffen the solution i.e. increase its viscosity. Since these forces are proportional to the square root of the concentration in very dilute solutions, it occurred to Jones and Dole (Jones and Dole 1929) to state the expression for the fluidity.

$$\frac{\phi}{\phi_0} = 1 + A'C^{1/2} + B'C \dots \dots \dots (1)$$

where ϕ and ϕ_0 are fluidity of solution and solvent respectively and C is the molar concentration of electrolyte in mol.dm⁻³.

$$\text{As } \frac{\eta}{\eta_0} = 1/\eta/\eta_0 \dots \dots \dots (2)$$

Jones-Dole expression in terms of viscosity is expressed as:

$$\frac{\eta}{\eta_0} = 1 + AC^{1/2} + BC \dots \dots \dots (3)$$

where η and η_0 are the viscosity of solution and solvent respectively, A and B are the coefficients of Jones-Dole equation. A represents ion-ion interaction which depends on the interionic forces and B represent ion-solvent interaction which is related to the volumes of the ions.

The present study is concerned with the measurement of the ion-solvent interaction of crotonic acid in aqueous and aqueous butanol mixtures and correlates it with thermochemical data as a function of solvent effect and temperature and also determines the nature of solute in aqueous and mixed solvent system.

Experimental

Crotonic acid (CH₃CH=CHCOOH) BDH laboratory, butanol of Analar R grade, double distilled water were used to prepare the solutions. All the glassware used were of Pyrex A grade quality. Viscosities were measured by Ostwald viscometer type Techniconomial constant 0.1 Cs/S capillary ASTMAD 445. Densities were measured by relative density bottle having the capacity of 10 ml. Time flow of solvent and solutions was taken by stopwatch (Advanced-85 Quartz) having a least count of 0.2 sec. Temperature was maintained con-

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stant with the help of thermostatic water bath type Haake-13 Karlsruhe, Germany having constant ± 0.01 .

Time flow and densities of crotonic acid solutions were measured in the range of concentrations 1×10^{-3} to 5.0×10^{-3} mol.dm⁻³ in aqueous and aqueous butanol mixtures from 2% to 6% (v/v) at different temperatures between 30° to 50°C with the interval of 5°C.

Results and Discussion

The viscosity data for concentration of crotonic acid 1×10^{-3} to 5×10^{-3} mol.dm⁻³ in aqueous and aqueous butanol mixtures 2%, 4%, 6% (v/v) at 30° to 50°C are tabulated in Table 1. Results show that the viscosities of crotonic acid solutions decrease with increase in concentration of acid and also with the rise of temperature and increase with increase in percent composition of aqueous butanol at a fixed temperature. Viscosity data was found to follow the Jones-Dole equation.

Table 1

Viscosities of crotonic acid in aqueous and aqueous butanol mixtures at different temperatures

[Salt].10 ³ (mol.dm ⁻³)	Viscosities (m.p.)			
	35°C	40°C	45°C	50°C
0% Butanol				
1.0	8.208	7.308	6.552	6.025
2.0	8.042	7.315	6.872	6.178
3.0	8.049	7.001	6.408	5.943
4.0	7.887	6.991	6.408	5.886
5.0	7.536	6.849	6.267	5.611
2% Aqueous butanol				
1.0	9.238	8.272	7.636	7.051
2.0	9.070	8.114	7.485	6.906
3.0	8.919	7.974	7.346	6.626
4.0	8.745	7.647	7.032	6.336
5.0	8.568	7.649	7.036	6.335
4% Aqueous butanol				
1.0	9.728	8.824	8.225	7.588
2.0	9.540	8.557	8.003	7.303
3.0	9.178	8.280	7.738	7.043
4.0	9.017	8.066	7.594	6.992
5.0	8.739	8.001	7.411	6.807
6% Aqueous butanol				
1.0	10.990	9.762	8.991	8.199
2.0	10.450	9.352	8.656	7.950
3.0	10.170	9.232	8.622	7.838
4.0	9.903	8.857	8.322	7.647
5.0	9.693	8.808	8.268	7.572

Values of A and B coefficients of Jones-Dole equation can be obtained from the intercept and slope of the straight line respectively:

$$[\eta/\eta_0 - 1] / C^{1/2} = A + BC^{1/2} \dots \dots \dots (4)$$

Values of A and B coefficients at different temperatures (30° to 50°C) and aqueous and aqueous butanol mixtures (0% to 6%, vv⁻¹) are shown in Table 2.

Representative linear regression plot of η_{sp}/\sqrt{C} versus \sqrt{C} in aqueous butanol at 45°C is shown in Fig 1. Results show that the value of ion-ion interaction represented by A-coefficient of Jones-Dole equation are higher in aqueous media rather than aqueous butanol mixtures. Low values of A-coefficient and higher butanol content of solvent show that hydration is greater than ion-ion interaction. Values of A coefficient decrease as the temperature increases. The decrease is due to increasing kinetic energy of ions and collision between the ions increased with the result of decrease in A values.

Table 2

Values of Jones-Dole parameters for crotonic acid in aqueous and aqueous butanol mixtures at different temperatures

Temperatures (°C)	The values of Jones-Dole coefficients	
	A (dm ³ .mol ⁻¹) ^{1/2}	B (dm ³ .mol ⁻¹)
0% Butanol		
35	5.780	-76.50
40	5.788	-72.02
45	6.232	-81.31
50	7.110	-90.95
2% Aqueous butanol		
35	3.343	-52.59
40	3.621	-58.56
45	3.663	-59.88
50	4.037	-66.75
4% Aqueous butanol		
35	-1.732	-6.207
40	-1.669	-7.240
45	-1.662	-6.914
50	-0.398	-21.56
6% Aqueous butanol		
35	1.867	-50.80
40	0.426	-20.61
45	0.134	-11.23
50	0.069	-22.19

Negative values of B-coefficients decrease with the rise of temperature. The negative values of B-coefficients is due to "depolymerization" of the solvent water. This behaviour is equivalent to a rise in structural temperature (Donald and Jenkins 1995). As temperature rises, there is less structure in the water and similar effect is caused by ion having negative B-coefficients. The greatest proponent of the relation of the B-coefficients of aqueous ions to their effect on the structure of water was given by Gurney (Gurney 1953). He showed a local loosening of the water structure for ions with $B < 0$ at room temperature and also used the concept of the solvent cosphere. Decrease in the values of B-coefficient with the rise of temperature in aqueous and aqueous butanol mixtures suggests that the crotonic acid behaves as structure maker in both solvent systems.

Decrease in B-coefficients may be explained by the consideration of the fact that this effect may be due to the formation

of mixed solvent clusters, which are more strongly bound to each other, become bulkier and are therefore unable to interact with ions for the lack of proper orientation around the ions. Large negative values of B-coefficient increases as the composition of solvent increased due to decrease in ion-ion interaction, and also at high temperatures. The surrounding sheath of the solvent molecule around the ion is broken and ion-solvent interaction weakens. This results in an increase in the chance for ions to interact each other.

Table 3

Thermodynamic parameters for crotonic acid in 6% aqueous butanol at different temperatures

10^3 [Salt] (mol.dm ⁻³)	Energy of activation E_{η} (K.J.mol ⁻¹)	Free energy change ΔG^* (K.J.mol ⁻¹)	Entropy change ΔS^* (J.K ⁻¹ .mol ⁻¹)
308°K			
1.0	15.27	69.45	-175.9
2.0	14.88	69.32	-176.7
3.0	14.04	69.25	-179.2
4.0	13.87	69.18	-179.5
5.0	13.30	69.131	-181.2
313°K			
1.0	15.27	70.26	-175.6
2.0	14.88	70.15	-176.5
3.0	14.04	70.11	-179.1
4.0	13.87	70.01	-179.3
5.0	13.30	69.99	-181.1
318°K			
1.0	15.27	71.17	-175.8
2.0	14.88	71.07	-176.7
3.0	14.04	71.06	-179.3
4.0	13.87	70.97	-179.5
5.0	13.30	70.96	-181.2
323°K			
1.0	15.27	72.05	-175.7
2.0	14.88	71.96	-176.7
3.0	14.04	71.93	-179.2
4.0	13.87	71.86	-179.5
5.0	13.30	71.84	-172.6

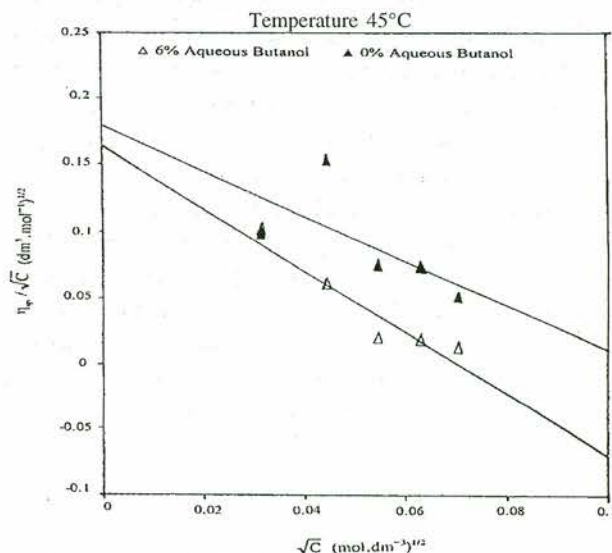


Fig 1. Plot of η_{sp}/\sqrt{C} versus \sqrt{C} for crotonic acid in aqueous and 6% aqueous butanol at 45°C.

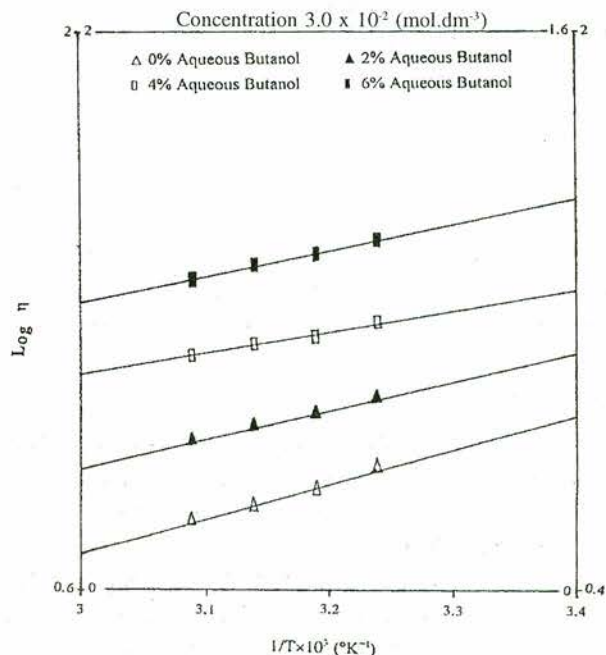


Fig 2. Plot of $\log \eta$ versus $1/T$ for crotonic acid at concentration 3.0×10^{-2} (mol.dm⁻³) in 0 to 6% aqueous butanol.

The temperature coefficient of the viscosity of solutions (Fahimuddin and Saeed 1998d) defining the activation energy for viscous flow is expressed as:

$$\eta = A e^{E_{\eta}/RT} \dots\dots\dots(5)$$

where E_{η} is the energy of activation, R is gas constant and T is absolute temperature. Results for energy of activation (E_{η}), free energy change of activation (ΔG^*) and entropy change of activation (ΔS^*) at different temperatures in 6% (v/v) aqueous butanol mixtures are tabulated in Table 3. The results show that energy of activation (E_{η}) decreased with increase in percent composition of aqueous butanol and with concentration of crotonic acid. Due to their structure forming nature, less ions are produced in the solvent matrix to cause resistance in flow. This results a decrease in activation energy with the increase in concentration of crotonic acid and butanol mixtures. The specimen graph of $\log E_{\eta}$ versus $1/T$ for crotonic acid at concentration $3.0 \times 10^{-2} \text{ mol.dm}^{-3}$ in aqueous and 2 to 6% aqueous butanol mixtures is shown in Fig 2. Free energy change of activation (ΔG^*) for viscous flow (Fahimuddin *et al* 1998e) is given by:

$$G^* = RT \ln \frac{\eta V}{hN} \dots\dots\dots(6)$$

where h is Planck's constant, N is Avogadro number, R is gas constant and V is the volume of one mole of solution particles. Results show that free energy change of activation decreased with the increase in concentration of crotonic acid and also with increase in temperature.

The change of entropy of activation (ΔS^*) is given by:

$$\Delta S^* = \frac{E_{\eta} - \Delta G^*}{T} \dots\dots\dots(7)$$

The values of entropy change of activation as a function of concentration of crotonic acid, percent composition of aqueous butanol and temperature are found to be negative.

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