VISCOSITIES AND FLOW ACTIVATION ENERGIES OF CARBOXYLIC ACIDS IN AQUEOUS SOLUTIONS

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Viscosities η for formic, acetic, propionic and butyric acids in aqueous solutions were determined using thermostated Ubbelohde flow viscometer in the temperature range of 25° to 65°. The flow activation energies $E\eta$ were determined using Andrade type equation, where the slope of log η vs 1/T plot gives $E\eta$. Explanation of the results are given in terms of acid-acid, acid-water and water- water interactions with special emphasis on hydrogen bonding in solutions.

Key words: Viscosities of acids, Flow activation.

Introduction

Present investigations were done to study the nature of association of simple bifunctional organic molecules in aqueous solution. We are reporting here the viscosity results for carboxylic acids (i.e. formic, acetic, propionic and butyric acids) in aqueous solution at different temperatures.

It has been shown by several investigators [1-5] that the carboxylic acids dimerize in aqueous solutions. Rossotti *et. al.* [6] have carried out the most extensive series of measurements and have shown that, while higher oligomers form in the solution of the acid after acetic, dimerization is the major process occurring over most of the low concentration range for all the acids investigated. According to Schrier *et. al.* [7] the longer the hydrocarbon chain, the stronger is the association of the acids of course, this gives support to the hypothesis of hydrophobic association. According to Pauling *et. al.* [8] the values of 2.70 A° for hydrogen bonding in formic acid is smaller than that in ice 2.76 A° as expected for this stronger bond. The distance from each hydrogen atom to the nearer of the two adjacent oxygen atoms in the acetic acid has been reported to be 1.075 ± 0.05 A°. This is in considerably greater than the value 1.01 A° as is to be expected in consequence of the increase strength of the hydrogen bond. From the enthalpy of dimerization 14.12 Kcal/mole, the bond energy for formic acid is found to have the values 7.06 Kcal/mole. The value of 7.6 Kcal/mole is similarly found for the hydrogen bond energy in acetic acid [9-10]. These values are 50% greater than those of ice.

Properties of carboxylic acids and their mixtures have been discussed in terms of cyclic dimers and of strong attraction [11,12] between the monomer and cyclic acid dimers.

Experimental

A Townson Mercer thermostate, which was provided with an electrically driven stirrer, a heating coil, a constant thermoregulator and a Beckman thermometer, was used for the temperature measurements. The temperature of the bath was kept constant by means of a heating coil, and a constant circulation of water was maintained for particular reading. The actual temperature of the bath was determined by means of standard thermometer graduated to ±0.1°. The time of flow of distilled water was measured five times on five different days, with five independent fillings of the viscometer.

The densities of the solutions were measured accurately to 0.01% by use of calibrated pycnometer of about 25 cm³ capacity. The viscosity measurements were made by using an Ubbelohde viscometer having fine capillary with flared end in order to minimize kinetic energy corrections. The time of flow was measured at least three times for each solution and agreed to within ± 0.02 second.

All acids were of analytical grade.

Results and Discussion

Viscosities were calculated for the binary systems of formic, acetic, propionic and butyric acids in water at various temperatures by the equation

$$\eta_2 = \frac{t_2}{t_1} \cdot \frac{\rho_2}{\rho_1} \, \eta_1 \quad \text{......................} (1)$$

Where η_2, t_2 and ρ_2 are viscosity, flow time and density of mixture, whereas ρ_1, t_1 and η_1 are the density, flow time and viscosity of water respectively.

Flow activation energy is obtained by the equation.

$$\eta = A \exp (E\eta/RT) \quad \text{............................} (2)$$

taking log of equation no. (2) we get

$$\log \eta = E\eta/2.303RT + \log A \quad \text{..............} (3)$$

From the slope of the plot of log η vs 1/T flow activation energy ($E\eta$) was calculated.

The values of viscosities are shown in Fig. 1-4. The viscosity increases with concentration and may be

explained by stronger hydrogen bonding [14] in acid water system. The hydrogen bond formed by water are not sufficiently strong to lead to an appreciable concentration of the polymerized molecule in the vapour phase.
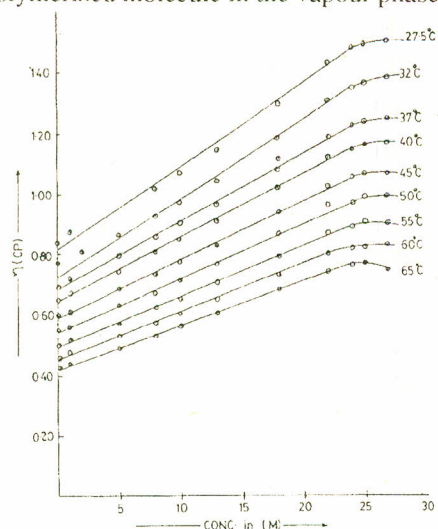

Fig. 1. Relative viscosity (CP)-concentration curves for formic acid in water.
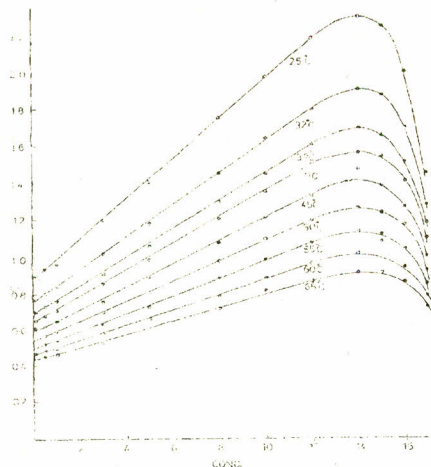

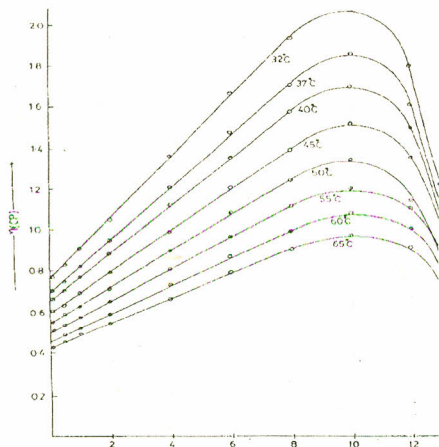Fig. 2. Viscosity-concentration curve for acetic acid in water.

Fig. 3. Viscosity (CP)- concentration curves for propionic acid in water.
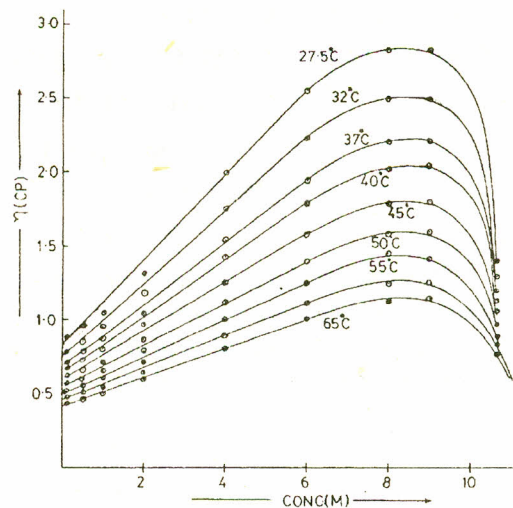

Fig. 4. Viscosity (CP)-concentration curves for butyric acid in water.

The strength of hydrogen bonds in these acids with water seems to increase from formic to butyric acid which increases until it reaches a maximum at 26.95M, 14M, 10M, and 8.5M of formic, acetic, propionic and butyric acids respectively in Fig. 1-4. The presence of viscosity maximum as a function of concentration is in good agreement with other workers [15-18].

The addition of carboxylic acid to water enhances the structure of the system and causes the viscosity to increase rapidly. According to M. Afzal *et. al.* [19] the above process compete with the opposite process in which the degree of structure is reduced as a result of solute- solvent interactions as carboxylic acids concentration in the mixture increases. This gradual breakdown in solution structure is accompanied by gradual increase in monotonic viscosity. The appearance of viscosity maximum is to be expected as a result of these process.

It is noted that all other carboxylic acids studied except formic acid, a maximum viscosity is observed at different molarities. For formic acid in water, viscosity still increases with toward higher molarities and this fact resembles to that of F. Kohler *et. al.* [11]. They measured the viscosities of mixtures of these acids with amines. This observation has been confirmed using NMR techniques by Hertz and Tutch. [20] However all other acids exhibit acid-acid association. The association is most conspicuous, when the acid chain is large. Therefore it may be said that in formic acid, there is uniform random distribution of solvent and solute molecules.

In order to understand the behaviour of change of viscosity with temperature, and to calculate the flow activation energies for these systems, log η vs 1/T has been plotted using equation (3) and from the slope of these plots

TABLE 1. FLOW ACTIVATION ENERGY Eη (J MOLE^{-1}) OF CARBOCYCLIC ACIDS.

| S. No.	Conc. of formic acid (M)	Eη	Conc. of acetic acid (M)	Eη	Conc. of propionic (M)	Eη	Conc. of butyric (M)	Eη
1.	0.1	1436	0.1	1464	0.1	1532	0.1	1596
2.	1.0	1464	0.5	1496	0.5	1595	0.5	1641
3.	5.0	1464	1.0	1542	1.0	1441	1.0	1675
4.	8.0	1464	3.0	1651	2.0	1778	2.0	1741
5.	10.0	1454	5.0	1680	4.0	1886	4.0	1972
6.	13.0	1436	8.0	1804	6.0	1915	6.0	2031
7.	18.0	1436	10.0	1737	8.0	1994	8.0	2083
8.	22.0	1436	12.0	1884	10.0	1915	10.68	1368
9.	24.0	1436	14.0	1915	12.0	1718	-	-
10.	26.95	1457	15.0	1859	13.0	1368	-	-
11.	-	-	16.0	1824	13.23	1149	-	-
12.	-	-	16.95	1436	-	-	-	-
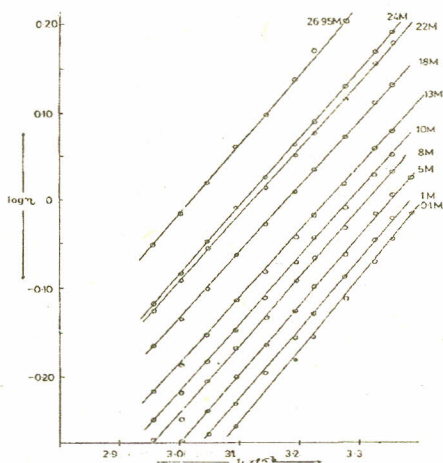
Fig. 5. Plot of the log of viscosity of formic acid in water vs. the reciprocal of the absolute temperature.

flow activation energy is determined. All acids obey straight line equation and the data for formic acid-water as representative of all other systems is shown in Fig. 5. The standard deviation in log η varies from± 0.19 to ±325 cP for all systems. Whereas the standard deviation in flow activation energies (Eη) varies between (±2 to ±3) Jmole^{-1} for all these systems. The flow activation energies for all these systems are shown in Table1.

It is evident from the values of flow activation energies, that for formic acid Eη values do not vary much with concentration. The computed flow activation energies values for formic acid change by 21 ± 2 Jmole^{-1} when concentration changes from 0.1 M to 26.95 M. Flow activation energy for other acids show variation which is more significant. For acetic acid the Eη value rises as function of concentration of 1464 ± 2 Jmole^{-1} at 0.1 M reaching a maximum around 14M with value of 1915± 3 Jmole^{-1} and falling back again to 1436 ±3 Jmole^{-1} at 16.95M. Similar trends are shown by propionic and butyric acids, although the trends are more marked here, the overall behaviour appear very

much the same. For propionic acid starting with the minimum Eη values of 1532 ±2 Jmole^{-1} at 0.1 M and the maximum of 1994 ±3 Jmole^{-1} is found around 8M concentration. Finally for butyric acid, the maximum occurred around 8M as well as with the value of 2083 ±3 Jmole^{-1}. These values are in line with the argument that the side chain in these acids gradually give large flow activation energies. This can be explained in terms of relaxation of the side chain for acetic, propionic and butyric acids as the concentration rises. This argument may be valid only if the flow activation energy is temperature independent, which seems to be true in our case, since straight line plots are more or less uniform.

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