

It was noticed that the rate of propagation of the step was constant and was of the order of  $3.079 \times 10^{-5}$  cm/sec in pure solution at 2 mA/cm<sup>2</sup>. When the concentration of HCl was  $10^{-9}$  M, there was no significant change in the rate of propagation of layers. The rate of propagation of layers changed to  $2.462 \times 10^{-5}$  cm/sec, when the concentration of HCl in electrolytic bath was increased to  $10^{-5}$  M. With  $10^{-4}$  M HCl the rate further decreased to  $2.155 \times 10^{-5}$  cm/sec. The layer type of growth changed over to ridge type of growth with further increase in HCl concentration in the electrolytic bath.

At 5 mA/cm<sup>2</sup> the rate of layer growth formation was  $4.311 \times 10^{-5}$  cm/sec in pure solution and up to  $10^{-9}$  M HCl the growth rate was not affected. With the increase in HCl concentration from  $10^{-8}$  M to  $10^{-6}$  M the growth rate decreased to  $3.703 \times 10^{-5}$  cm/sec. When the concentration of chloride ions was increased from  $10^{-6}$  M to  $10^{-4}$  M layers began to break up and completely changed over to ridge type of growth at the concentration of  $10^{-3}$  M HCl.

In the presence of HBr at 2 mA/cm<sup>2</sup> the rate of propagation of layers remained almost constant up to  $10^{-9}$  M HBr. With the further increase in HBr concentration to  $10^{-7}$  M the growth rate changed from  $3.079 \times 10^{-5}$  to  $2.462 \times 10^{-5}$  cm/sec. When the concentration of HBr was increased to  $10^{-6}$  M the rate further decreased to  $1.468 \times 10^{-5}$  cm/sec. On increasing the concentration to  $10^{-4}$  M HBr the rate reached the minimum value and finally the layers began to break up at higher concentration of HBr.

The growth rate of layers was affected at iodide concentrations of  $10^{-8}$  M and  $10^{-7}$  M.

Layers grow on the (100) plane of copper by bunching mechanism. But in presence of halide ions the rate is decreased due to their specific adsorption<sup>6-8</sup>.

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### Apparent Molal Volumes & Viscosities of Valeric Acid & Sodium Valerate in Water

K. J. PATIL\*, P. V. PATIL & O. B. THAKARE

Department of Chemistry, Institute of Science, Nagpur 1

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Apparent molar volumes and viscosities of aqueous solutions of valeric acid and sodium valerate of different concentrations have been measured at 25°. It has been found that the viscosity *B* coefficient for valerate anion is much greater than that for the valeric acid. The apparent molal volume ( $\phi_v$ ) data

have been used to calculate the critical micelle concentration of sodium valerate in water. The concentration dependence of  $\phi_v$  in the low and the high concentration regions is explained on the basis of hydrophobic hydration and micelle formation due to structural interactions of the solute with water.

RECENT reviews<sup>1-5</sup> on the properties of aqueous solutions have stressed the importance of structural changes introduced by the solute. Small ions attract water molecules (hydrophilic hydration), most large organic ions and molecules strengthen the hydrogen bonds of neighbouring water molecules (hydrophobic hydration), and intermediate ions break the structure of water. Three properties namely apparent molal volume ( $\phi_v$ ), apparent molal heat capacity and viscosity *B* coefficient have proved to be sensitive to hydrophobic hydration<sup>6-9</sup>. The negative volume of mixing of most non-electrolytes and water, the negative concentration dependence of  $\phi_v$  of hydrophobic solutes, the presence of a minimum in  $\phi_v$  and large increase in volume at critical micelle concentration (cmc), have been all explained on the basis of structural reinforcement of solvent water in dilute region and structure breaking effect in concentrated region of solutions<sup>10</sup>.

The aim of the present work is to study the effect of weak acid molecules (carboxylic acid, from acetic to valeric acid, in a hypothetical undissociated state) on solvent water structure and the interaction between solute molecules, as these acids are known to form dimers (self-association) in non-aqueous solvents and even in water<sup>11</sup>. The volumetric and viscosity data for acetic to butyric acids in water at 25° already exist in literature. The study has been extended to valeric acid. There are very few studies<sup>12</sup> which differentiate between the interaction of a large anion and that of a neutral molecule derived from it, with water. Keeping this point in view, the viscosity measurements have been carried out for sodium valerate in water to obtain the individual ionic *B* coefficients. For the determination of critical micelle concentration (cmc) and the apparent molal volume at infinite dilution (which is required for the application of ionization correction for valeric acid), the density measurement were made for sodium valerate-water system at 25° for the concentration range 0-1.0 mole/litre.

Valeric acid (May & Baker) was directly used. Sodium salt of valeric acid was prepared in the laboratory by mixing calculated quantities of the acid and sodium hydroxide. Slightly less than required amount of alkali was added to prevent the excess of sodium ions. The solution was concentrated on a water-bath and then the salt was precipitated out by adding a mixture of acetone and ethanol (2:1). The salt was recrystallized from absolute ethanol and dried in an oven at 60°-80° for 4-5 hr. The dried salt was kept *in vacuo* for several days.

All the solutions were prepared fresh in doubly distilled water. The viscosity measurements were made using a Tuan and Fuoss<sup>13</sup> type viscometer (time of flow for water at 25° was  $465.00 \pm 0.2$  sec) in a specially made thermostatic bath (accuracy  $\pm 0.005^\circ$ )

TABLE 1 — APPARENT MOLAR VOLUME AND VISCOSITY DATA

Solute	$\bar{V}_2^0$ (ml/mole)	$\bar{V}_2^{0E}$ (ml/mole)	$\frac{d\phi_V}{dc}$	Viscosity A coefficient	Viscosity B coefficient
Formic acid	34.69	-2.3	+0.220	—	—
Acetic acid	51.53	-5.5	+0.107	+0.002	0.110
Propionic acid	—	—	—	-0.006	0.250
Butyric acid	84.60	-7.9	Negative	-0.013	0.270
Valeric acid	102.55	-6.6	-1.200	+0.040	0.260
Sodium valerate	86.90	—	-8.0	-0.110	0.800

in which water from U-10 ultra-thermostatic bath (accuracy  $\pm 0.02^\circ$ ) was circulated. Prior to the measurements, the viscometer was calibrated with a 20% sucrose solution. The accuracy in the viscometer measurements was better than 0.1%. Evaluation of the results was done by the well-known Jones-Dole viscosity equation. The variation of the parameter  $\eta_r - 1/\sqrt{c}$  (where  $\eta_r - 1$  is specific viscosity) was plotted as a function of  $\sqrt{c}$  ( $c$  = moles/litre) for valeric acid, sodium valerate, and acetic, propionic and butyric acids (data obtained from literature<sup>14</sup>). From the slopes and intercepts of the curves the viscosity  $B$  and  $A$  coefficients† were calculated (Table 1).

From the density data (accuracy  $\pm 0.00005$ ), the apparent molal volumes ( $\phi_V$ ) were calculated using Eq. 1

$$\phi_V = \frac{1000(d_0 - \bar{d})}{c \cdot d_0} + \frac{M_2}{d_0} \quad \dots(1)$$

where  $M_2$  is the molecular weight of solute and  $d_0$  and  $\bar{d}$  are the densities of solvent and solution respectively. The necessary ionization correction was applied for the  $\phi_V$  data of valeric acid by the method of King<sup>11</sup>. The extrapolation of  $\phi_V$  curve to infinite dilution yields  $\phi_V^0$  ( $= \bar{V}_2^0$ , partial molal volume of solute at infinite dilution), which enables one to calculate the excess partial molal volume ( $\bar{V}_2^{0E} = \bar{V}_2^0 - V_2^0$ , where  $V_2^0$  is the molal volume of solute). The values of  $\bar{V}_2^0$ ,  $\bar{V}_2^{0E}$  and  $d\phi_V/dc$  (the slope of the plot of  $\phi_V$  versus  $c$ ) for valeric acid along with the similar data for other acids obtained from literature are shown in Table 1.

In the concentration range investigated for sodium valerate, the  $\phi_V$  values, following the method of Redlich and Mayer<sup>15</sup>, were described by Eq. 2

$$\phi_V = \phi_V^0 + hc \quad \dots(2)$$

where  $\phi_V = \phi_V^0 - 1.868 \sqrt{c}$ . Values of limiting partial molal volume  $\bar{V}_2^0 = \phi_V^0$  and the slope  $h$  were obtained from the plot of  $\phi_V - 1.868 \sqrt{c}$  against  $c$ . These values are also shown in Table 1. The probable error in the  $\phi_V^0$  values is  $\pm 1$  ml/mole in the present study.

†The degrees of dissociation for these acids do not exceed the value of 2% in the studied concentration range, hence the correction for ionization was thought to be negligible.

The  $\bar{V}_2^{0E}$  values obtained in this work, on comparison with those reported for alcohol<sup>16</sup> and amines<sup>17</sup>, show that  $\bar{V}_2^{0E}$  for methyl to butyl alcohols are in the range  $-2.0$  to  $-6.0$  ml/mole and for corresponding amines  $-6.0$  to  $-10.0$  ml/mole, while the corresponding acids show values of  $-5.5$  to  $-8.0$  ml/mole. Thus, it can be said that the acids have comparatively more pronounced effect on solvent water than alcohols which have similar effect as the amines. Since  $\bar{V}_2^{0E}$  represents the effect of solute-solvent interactions, this analysis clearly points out (although acid molecules have four proton accepting sites while amines have two)<sup>16</sup> the loss of acid molecules in the cavities of solvent water. This tendency of the solute molecules to cause hydrophobic hydration increases with increase in chain length up to butyric acid and then appears a saturation effect in the case of valeric acid.

It has been established that the concentration variation of  $\phi_V$  represents the solute-solute interaction. The study of  $d\phi_V/dc$  (Table 1) also shows that formic and acetic acid molecules appear to be structure breakers while butyric and valeric acids are structure forming solutes (the former have positive values and the latter negative values). King<sup>11</sup> has explained the negative slope for butyric acid in terms of its dimerization in solution. On similar grounds, the negative  $d\phi_V/dc$  value for valeric acid can also be explained.

Table 1 shows that each addition of  $-\text{CH}_2$  group contributes about 17.0 ml/mole volume to  $\bar{V}_2^0$ . This value of  $\bar{V}_2^0$  ( $-\text{CH}_2$ ) is in close agreement with that of alcohols, amines and hydrocarbons<sup>16</sup>. Thus it can be said that acid molecules exert similar effect on water structure as the amines and alcohols. The lower members of the homologue appear to be structure breakers to a slight extent while the higher members have structure forming tendency.

The above conclusions drawn on the basis of volumetric behaviour are substantially supported by the viscosity behaviour of these acids in water. The acids are characterized (Table 1) by comparatively high  $B$  coefficient values when compared with alcohols<sup>18</sup>, but the values are similar to those of amines<sup>19</sup>. Again one can note that as the chain length (hydrophobic character) increases, viscosity  $B$  coefficient increases in magnitude for alcohols and amines, while a saturation effect occurs in the case of acids.

The plot  $\phi_V - 1.868 \sqrt{c}$  for sodium valerate passes through a minimum at a concentration of 0.5-0.6 moles litre<sup>-1</sup>. Desnoyers and Arel<sup>6</sup> have explained the occurrence of minimum in  $\phi_V$  for alkyl ammonium salts in water on the basis of hydrophobic hydration (before minimum) and micellization (after minimum). Seen in this light the cmc value for sodium valerate is 0.5 mole litre<sup>-1</sup> which is in excellent agreement with the value reported from osmotic coefficient study of this salt<sup>20</sup>.

From the viscosity behaviour of this salt, it can be seen that viscosity  $B$  coefficient is very high. Subtracting the  $B$  coefficient value of sodium ion (0.08)<sup>12</sup> from the total, one can obtain the value for valerate ion (0.72). When this value is compared with the value for acetate ion (0.25)<sup>12</sup>, it can be said that valerate ion is a strong structure former than acetate ion, which is expected since the hydrophobic residue in valerate ion is more strong than acetate ion. The comparison of ionic  $B$  coefficient with molecular  $B$  coefficients shows that ions have very high values (acetic acid = 0.12, valeric acid = 0.26). The behaviour of acetate ion has been explained by Gurney<sup>12</sup> on the basis that acetate ion is stabilized by forming stronger hydrogen bonds than the acid molecule. The same explanation can be applied to explain the behaviour of valerate ion. Thus strong ion-solvent interactions should lead to higher  $B$  coefficient for anion than that of the parent molecule which is indeed the case.

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## Kinetics & Mechanism of Oxidation of Isobutyric & Diglycolic Acids by Manganic Ion†

P. ELAYAPERUMAL, T. BALAKRISHNAN\* & M. SANTAPPA  
Physical Chemistry Department, University of Madras  
Madras 600025

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The kinetics of oxidation of isobutyric acid (IBA) and diglycolic acid (DGA) have been carried out in the temperature range 15-45° in aqueous sulphuric acid medium. The reaction is overall second order-first order with respect to each reactant. The absence of spectral changes of manganese(III) acetate on adding diglycolic acid and isobutyric acid confirms the outer-sphere interaction of the substrate and the oxidant. The energy of activation and other thermodynamic parameters have been evaluated and discussed. A mechanism involving free radical intermediate is proposed.

THE kinetics of oxidation of alcohols, carboxylic acids, ketones and aldehydes by manganese(III) have been widely studied. Manganese(III) pyrophosphate<sup>1</sup>, manganese(III) sulphate<sup>2</sup>, manganese(III) perchlorate<sup>3,4</sup> and manganese(III) acetate<sup>5,6</sup> have been used as oxidants. Manganese(III) acetate has been mostly used in non-aqueous medium. The kinetics of reaction of manganese(III) perchlorate with isobutyric acid has been studied by Wells *et al.*<sup>3</sup> But no detailed kinetic study has so far been made for the oxidation of isobutyric acid (IBA) and diglycolic acid (DGA) by manganese(III) acetate in aqueous medium.

Manganese(III) acetate was prepared as per the literature procedure<sup>5</sup>. Isobutyric acid was purified by distillation under reduced pressure. Diglycolic acid (Fluka), sulphuric acid (Basynt, AR, sp. gr. 1.8), sodium bisulphate (E. Merck) and manganese(II) acetate (LR, BDH) were used as such.

The reaction system consisted of manganese(III) acetate ( $4 \times 10^{-3}M$ ), substrate (0.04 to 0.4M),  $[H^+]$  (2.5M) with a total volume of 50 ml and at an ionic strength of 2.6M. All the components except manganese(III) acetate were placed in a reaction flask which was thermostated. At definite intervals, after adding manganese(III) acetate, 2 ml aliquots were taken and run into 2% potassium iodide solution to arrest the reaction. The resulting solution of iodine was titrated against standard sodium thiosulphate solution.

At constant [substrate],  $[H_2SO_4]$  (2.5M),  $\mu$  (2.6M) and temperature, a first order dependence with respect to  $[Mn^{3+}]$  was observed. The plot of  $-R_{Mn}$  versus  $[Mn^{3+}]$  was linear with zero intercept (Fig. 1). At constant  $[Mn^{3+}]$  (0.004M),  $[H_2SO_4]$  (2.5M),  $\mu$  (2.6M) and temperature variation of excess of [substrate] gave increasing rates with increasing [substrate]<sub>0</sub>. From the linear plots of  $\log [Mn^{3+}]$  versus time, the pseudo unimolecular

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