

Viscosities of Aqueous Solutions of Alkanoic Acids

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Viscosities of aqueous solutions of alkanoic acids including formic acid were measured by an Ostwald type viscometer at 15, 25, and 35 °C, and the viscosity B -coefficient and the temperature dependence of B -coefficient, dB/dT , were calculated. From the signs and the magnitudes of B_{st} , increment of B -coefficient arising from the change of water structure, and dB/dT , it was concluded that formic acid was a hydrophilic structure breaker, while acetic acid was neither a structure maker nor a structure breaker. Both propionic acid and butyric acid were the hydrophobic structure makers. The mechanism of structure breaking effect of carboxyl group was briefly discussed.

Various nonelectrolytes which have the groups such as $-OH$, $-NH_2$, and $>CO$ form the hydrogen bond with water molecules in aqueous solutions, and more or less cause the change of the structure of water depending on the size and shape of the molecule. Urea and monosaccharides, for instance, are typical nonelectrolytes capable of hydrogen bond formation with water molecules. But their effects on the structure of water are quite different. Urea increases the water activity,¹⁾ while glucose decreases it in aqueous solution.²⁾ This fact seems to be related to the geometry of the hydrogen bond between nonelectrolyte molecule and water molecule, and that between water molecules. Carboxyl group is also capable of forming hydrogen bond. Judging from the conformation of carboxyl group, the orientation of hydrogen bonds between carboxyl group and water molecules would not fit the orientation of hydrogen bond in the tridymite-like structure of water.

In a previous paper,³⁾ the effects of alkanoate ions on the structure of water were investigated by measuring the viscosities of aqueous solutions and it was concluded that the structure making effects of alkanoate ions did not arise from the hydration of carboxylate groups by the electrostriction, but from the hydrophobic hydration of alkyl groups. In other words, carboxylate group hardly influences the structure of water.

From these points of view, the viscosities of aqueous solutions of a homologous series of alkanoic acids including formic acid were determined at various temperatures. Based on the viscosity B -coefficients and their temperature dependences, the effects of alkanoic acids on the structure of water were discussed.

Experimental

Materials. Reagent grade alkanoic acids and hydrochloric acid were purchased from Nakarai Chemical Co. Ltd., and were used without further purification. These compounds were dissolved in water purified by redistillation and deionization with ion exchange resin.

Method. Viscosity measurement was carried out by an Ostwald type viscometer with an efflux time of *ca.* 360 s for water at 25 °C. Efflux time was measured with the Seiko stop watch 89 T to 0.01 s. At least five readings of the efflux time with variations not exceeding ± 0.05 s were taken for each solution. Kinetic correction of viscometer was made by using the following equation:

$$\eta/d = \alpha t - \beta/t,$$

where η and d are the viscosity and density of the solution, t the efflux time in second. Pure water at 15, 25, and 35 °C was used as standard, and linear relation was obtained between η/dt and $1/t^2$. The values of α and β obtained from the intercept and the slope were $2.628 \times 10^3 \text{ cP g}^{-1} \text{ cm}^3 \text{ s}^{-1}$ and $15.00 \text{ cP g}^{-1} \text{ cm}^3 \text{ s}$, respectively. The effect of kinetic correction on the relative viscosity was observed in the high concentration region, and the difference of η_{rel} values before and after correction were within 0.3–0.5%. The temperature of the thermostat bath was controlled within ± 0.03 °C.

Results

The relative viscosity, η_{rel} , of a nonelectrolyte solution below 0.1 mol dm^{-3} is expressed by Eq. 1.

$$\eta_{rel} = \eta/\eta_0 = 1 + Bc, \quad (1)$$

where η and η_0 are the viscosities of solution and solvent, respectively, and B is the viscosity B -coefficient, and c is the concentration in mol dm^{-3} . At higher concentration than 0.1 mol dm^{-3} , η_{rel} of nonelectrolyte is described by Eq. 2.

$$\eta_{rel} = 1 + Bc + Dc^2, \quad (2)$$

where D is a characteristic constant of the solute.

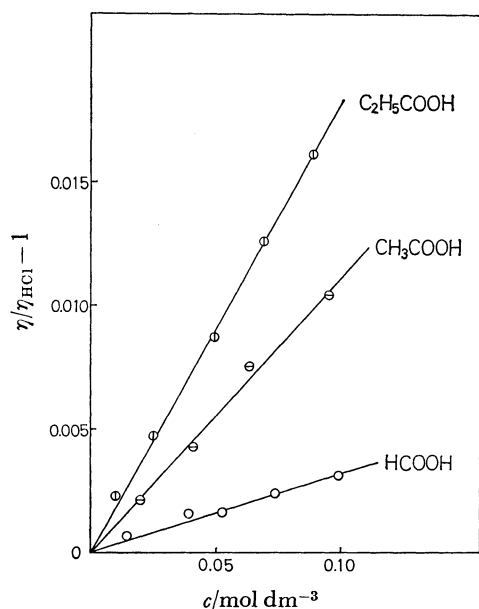
Alkanoic acid dissociates into proton and alkanoate anion in water. The alkanoic acids used in this experiment are formic acid, acetic acid, propionic acid and butyric acid, and their pK_a values are between 3.7–4.9 at 25 °C. Therefore, in dilute solution of alkanoic acid the dissociated ions also contribute to the viscosity of the solution. To remove the contribution of the dissociated species from the solution viscosity, two kinds of experiments were carried out. The viscosity of each alkanoic acid dissolved in 0.01 mol dm^{-3} aqueous solution of hydrochloric acid was determined by using 0.01 mol dm^{-3} of hydrochloric acid as a reference solution. The B -coefficient of the alkanoic acid was obtained from Eq. 3.

$$\eta/\eta_{HCl} = 1 + B'c, \quad (3)$$

where η and η_{HCl} are the viscosity of 0.01 mol dm^{-3} HCl solution of the alkanoic acid and that of 0.01 mol dm^{-3} HCl solution, respectively. B' -coefficient in Eq. 3 is the B -coefficient of alkanoic acid in aqueous 0.01 mol dm^{-3} HCl solution, where the amount of dissociated species of alkanoic acid is negligible. As shown in Fig. 1, linear relationships were obtained

TABLE 1. B AND D COEFFICIENTS OF ALKANOIC ACIDS AT VARIOUS TEMPERATURES

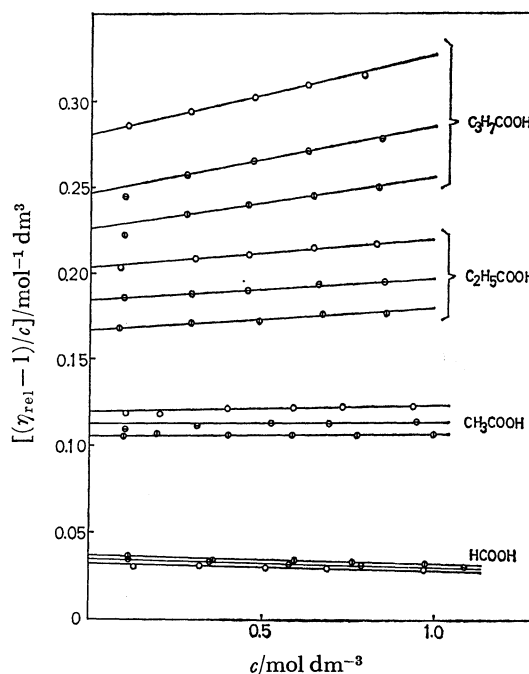
	$T/^{\circ}\text{C}$	HCOOH	CH_3COOH	$\text{C}_2\text{H}_5\text{COOH}$	$\text{C}_3\text{H}_7\text{COOH}$
$B'/\text{mol}^{-1} \text{ dm}^3$	25	0.032	0.111	0.184	—
$B/\text{mol}^{-1} \text{ dm}^3$	15	0.032	0.120	0.204	0.281
	25	0.035	0.113	0.185	0.247
	35	0.037	0.106	0.168	0.226
$D/\text{mol}^{-2} \text{ dm}^6$	15	-0.003	0.004	0.016	0.046
	25	-0.003	0.002	0.013	0.038
	35	-0.005	0.002	0.013	0.030

Fig. 1. Relationships between $\eta/\eta_{\text{HCl}} - 1$ and c for alkanolic acids at 25 °C.○: HCOOH, ⊖: CH_3COOH , ⊕: $\text{C}_2\text{H}_5\text{COOH}$.

between $(\eta/\eta_{\text{HCl}} - 1)$ and c . B' values obtained from the slope are shown in Table 1.

At higher concentration than 0.1 mol dm⁻³, where the concentration of dissociated species is considered to be negligible as compared to the undissociated species, Eq. 2 was applied to the determination of B -coefficients. Linear relationships were obtained between $(\eta/\eta_0 - 1)/c$ and c at 15, 25, and 35 °C as seen in Fig. 2. B and D coefficients obtained from the intercepts and the slopes are shown in Table 1. B values agree with B' values for three alkanolic acids at 25 °C, indicating that at higher concentration than 0.1 mol dm⁻³ the contribution of dissociated species to B -coefficient is negligible. Consequently it is evident that B and D values obtained from the measurements in high concentration region are those for undissociated species. These B values at 25 °C are also in fair agreement with Rupley's values,⁴⁾ which were calculated from the η values described in International Critical Table.

As stated previously,³⁾ B value of nonelectrolyte consists of two terms, B_{size} and B_{st} . B_{size} is the contribution of hydrodynamic obstruction effect of solute to B value and is usually evaluated from Einstein's viscosity equation for spherical colloidal particle on the assumption that the effective rigid volume of the solute is equal to the partial molal volume of the solute

Fig. 2. Relationships between $(\eta_{\text{rel}} - 1)/c$ and c for alkanolic acids at various temperatures.

○: 15 °C, ⊖: 25 °C, ⊕: 35 °C.

at infinite dilution. Thus B_{st} , the contribution of solute to the structure of water, is determined from Eq. 4.

$$B_{\text{st}} = B - 0.0025\bar{V}^{\circ}, \quad (4)$$

where \bar{V}° is generally the partial molal volume of solute at infinite dilution, but in this case we used the partial molal volume of undissociated species as \bar{V}° .⁹⁾ B value vs. \bar{V}° curves for alkanoate ions and alkanolic acids are shown in Fig. 3 together with Einstein's relation ($0.0025\bar{V}^{\circ}$). The solutes with the points above the dotted line are considered to be structure makers. B_{st} values obtained from Eq. 4 are shown in Table 2.

Another and more reliable criterion for the judgement of the solute effect on the structure of water is the sign and magnitude of temperature dependence of B value, dB/dT .³⁾ The values of dB/dT of four kinds of alkanolic acids at 25 °C obtained from the slopes in Fig. 4 are shown in Table 2 together with the values of B , B_{st} , and \bar{V}° .

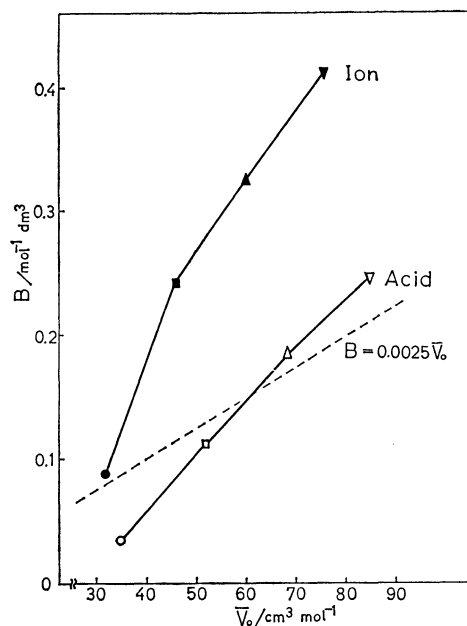
Discussion

As for formic acid, the sign of B_{st} is negative, while the sign of dB/dT is positive, indicating that it is a

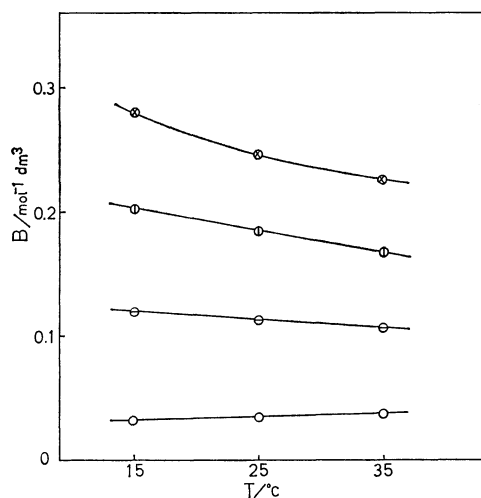
TABLE 2. B , B_{st} , dB/dT , AND \bar{V}° OF ALKANOIC ACIDS AT 25 °C

	HCOOH	CH ₃ COOH	C ₂ H ₅ COOH	C ₃ H ₇ COOH
$B/\text{mol}^{-1} \text{ dm}^3$	0.035	0.113	0.185	0.247
$B_{st}/\text{mol}^{-1} \text{ dm}^3$	-0.052	-0.017	0.015	0.035
$(dB/dT)/\text{mol}^{-1} \text{ dm}^3 \text{ K}^{-1}$	0.0003	-0.0007	-0.0018	-0.0027
$\bar{V}^\circ/\text{cm}^3 \text{ mol}^{-1}$ a)	34.7	51.9	67.9	84.7

a) Ref. 9.

Fig. 3. Relationships between B -coefficients and \bar{V}° at 25 °C.

○: HCOOH, □: CH₃COOH, △: C₂H₅COOH, ▽: C₃H₇COOH, ●: HCOO⁻, ■: CH₃COO⁻, ▲: C₂H₅COO⁻, ▼: C₃H₇COO⁻.

Fig. 4. Temperature dependences of B -coefficients for alkanolic acids.

○: HCOOH, ⊖: CH₃COOH, ⊕: C₂H₅COOH, ⊗: C₃H₇COOH.

structure breaker. The result that both values of B_{st} and of dB/dT for acetic acid are negative seems to be inconsistent with the criterion that structure maker

has the positive sign of B_{st} and negative sign of dB/dT , and *vice versa* for structure breaker. However, judging from the absolute values of B_{st} and dB/dT , acetic acid may be neither a structure maker nor a structure breaker. Applying the criterion to propionic acid and butyric acid, both fall under the category of structure maker. The signs and magnitudes of B_{st} and dB/dT for a homologous series of alkanolic acids indicate that structure making effect of propionic acid and butyric acid originates from the hydrophobic group and not from the carboxyl group, because structure making effect of alkanolic acids increases with alkyl chain-length, and because formic acid with no alkyl group is clearly a structure breaker. From the similar study for sodium alkanolates, methyl group of acetate ion was found to increase the structure of water.³⁾ Therefore carboxyl group should be a structure breaker. The structure breaking effect of carboxyl group compensates for the structure making effect of methyl group in acetic acid, because the values of B_{st} and dB/dT are nearly zero for acetic acid. Propionic acid and butyric acid are hydrophobic structure makers.

D -coefficients of four alkanolic acids at 15, 25, and 35 °C are shown in Table 1. The variations of D -coefficients with alkyl chain-length and temperature are similar to those of B -coefficients except the temperature dependence of the coefficients for formic acid. Thomas extended the Einstein equation and showed that for colloidal suspensions the η_{rel} is given by⁵⁾

$$\eta_{rel} = 1 + 2.5\phi + 10.05\phi^2 \\ = 1 + 2.5 \times 10^{-3} Vc + 10.05 \times 10^{-6} \bar{V}^\circ c^2, \quad (5)$$

where ϕ and V are the volume fraction and the molar volume of solute and c the concentration of solute in mol dm^{-3} . By assuming that $D = 10.05 \times 10^{-6} \bar{V}^\circ c^2$, the values of D -coefficients at 25 °C were found to be 0.012, 0.027, 0.046, and 0.072 for formic acid, acetic acid, propionic acid, and butyric acid, respectively. Thomas's relation predicts the correct order of D -coefficient. But the magnitudes are too large, especially for formic acid and acetic acid. This fact suggests that D -coefficient relates to the volume of the solute, but another effect also contributes to the magnitude of D -coefficient.

Desnoyers *et al.*⁶⁾ pointed out that the solute-solute structural interaction and the solute-solvent interaction which were not accounted for by Bc term would greatly influence the magnitude of D -coefficient. As stated above, the structure making effects of propionic acid and butyric acid come from the hydrophobic hydration of alkyl-chain. The hydrophobic hydration increases with the solute concentration, resulting in the increase

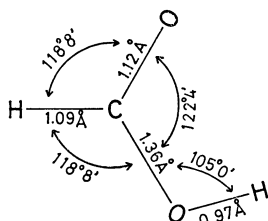


Fig. 5. Molecular structure of formic acid.

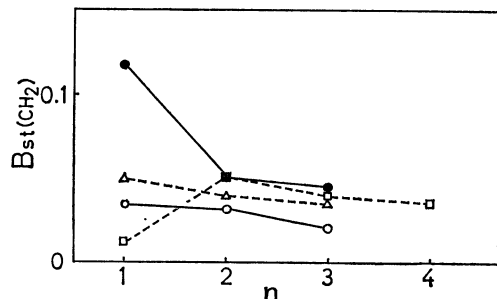


Fig. 6. Relationships between $B_{st}(\text{CH}_2)$ and alkyl-carbon numbers for various alkyl derivatives at 25°C. ●: $\text{H}(\text{CH}_2)_n\text{COO}^-$, ○: $\text{H}(\text{CH}_2)_n\text{COOH}$, □: $\text{H}(\text{CH}_2)_n\text{NH}_3^{+a)}$, △: $\text{H}(\text{CH}_2)_n\text{CONH}_2^{b)}$.

a) Calculated from the data in Ref. 10, b) Ref. 11.

of the solution viscosity and consequently D -coefficient of solute. Such a structural interaction increases with alkyl chain-length and decreases with the increase of temperature. The small values of D -coefficients for formic acid and acetic acid may be due to an absence of such interaction.

Carboxyl group forms hydrogen bond with water like urea and saccharides. It is, however, important whether the formation of hydrogen bond between carboxyl group and water molecule promote the hydrogen bond between water molecules. The structure breaking effect of carboxyl group may be related to its molecular structure. The orientation of hydrogen bond in pure water may be tetrahedral as seen in the tridymite structure of ice. The molecular structure of formic acid is shown in Fig. 5 as a typical example of carboxyl group.⁷⁾ Roughly speaking, all atoms are in a plane, and three bond angles around the central carbon atom are nearly 120°. The structure of carboxyl group of alkyl homologous is similar to that of formic acid. Such a configuration of carboxyl group can

hardly fit with the tridymite-like structure of water. In other words, the formation of hydrogen bonds between carboxyl group and adjacent water molecules would cause the disruption of hydrogen bond network of water. The situation is quite similar to urea.

The contribution of a methylene group to the value of B_{st} estimated from Eq. 6 is shown in Fig. 6.

$$B_{st}(\text{CH}_2) = B_{st}[\text{H}(\text{CH}_2)_n\text{X}] - B_{st}[\text{H}(\text{CH}_2)_{n-1}\text{X}], \quad (6)$$

where X is the terminal functional group shown in Fig. 6. The $B_{st}(\text{CH}_2)$ value of the methylene group adjacent to the terminal ionic group was more influenced than that of nonionic group. The small value of $B_{st}(\text{CH}_2)$ of methylammonium ion reflects the strong electrostriction of ammonium ion as pointed out by Zana.⁸⁾ It seems that the values of $B_{st}(\text{CH}_2)$ of these four kinds of alkyl derivatives converge to around 0.02–0.03 with increase of alkyl carbon chain.

In conclusion, carboxyl group is a weak structure breaker in contrast to carboxylate group, which is neither a structure maker nor a structure breaker. As for the alkanolic acids, the structure breaking effect of carboxyl group compensates for the hydrophobic structure making effect of methyl group of acetic acid, and alkanolic acids with more than two methylene groups become hydrophobic structure makers.

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