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Viscosities of Aqueous Solutions of Sodium Alkanoates

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Viscosities of aqueous solutions of sodium salts of formic acid, acetic acid, propionic acid, and butyric acid were measured in the concentration range 0.01—0.1 mol dm^{-3} at 15, 25, and 35° C. For formate ion, values of B_{st}, the increment of viscosity B-coefficient arising from structural change of water, and of $(\mathrm{d}B_{\mathrm{ion}}/\mathrm{d}T)$, the temperature dependence of ionic B-coefficient, are both nearly zero, indicating that formate ion is neither a structure maker nor a structure breaker. For the alkanoate ions the signs of B_{st} and $(\mathrm{d}B_{\mathrm{ion}}/\mathrm{d}T)$ are positive and negative, respectively. From these facts, alkanoate ions may be concluded to be hydrophobic structure making ions.

It has long been recognized that the water structure around an ion plays an important role with respect to the interionic interactions in water.[1]

In a previous paper[2] concerning the mean activity coefficients ($\gamma_\pm$) of guanidinium salts with hydrophobic carboxylate ions, the order of $\gamma_\pm$ values among these salts was well interpreted by regarding acetate ion as a hydrophobic structure maker, which promotes the water structure by forming an ice-likeness in the vicinity of hydrophobic moiety.

In general, organic ions have more than one functional group besides the ionic residue, such as hydrophobic group and hydrophilic amino or hydroxyl group. These groups also play an important role in interionic interactions in water. In this connection, the simplest example is acetate ion which has the hydrophobic methyl group and the carboxylate ion residue. The structure around the hydrophobic methyl group would be different from that around the carboxylate ion. It has already been known by viscosity[3,4] and NMR measurements[5] that acetate ion is a structure maker. Gurney[3] postulated that the nature of structure promotion by acetate ion was based on the electrostriction of carboxylate ion, on the assumption that the valence electron of oxygen in carboxylate ion is localized. However, this assumption was denied by Spinner on the basis of IR and Raman studies.[6,7] Tamaki reached a similar conclusion from a viscosity study.[4] In the curve of B-coefficient *vs.* alkyl-carbon numbers (C_{n}) of carboxylate ions, the sign of the intercept at $C_{\mathrm{n}}=0$ was positive. Unfortunately, formate ion was excluded in his study.

In order to elucidate the discrepancy between Gurney's and our views concerning the nature of structure promotion by acetate ion, we measured viscosities of aqueous solutions of some alkanoate ions including formate ion at various temperatures. The results indicate that the alkanoate ions studied are hydrophobic structure makers.

Experimental

Materials. Reagent grade sodium and potassium carboxylates obtained from Wako Chemical Co., Ltd. were used without further purification. Salts were dried *in vacuo* over P_2O_5 at room temperature. These salts were dissolved in redistilled and deionized water.

Methods. Viscosity measurements were made with an Ostwald type viscometer with an efflux time of *ca.* 360 s for water at 25 °C. Efflux time was measured with a Seiko stop watch 89 ST down to 0.01 s. At least five readings of efflux time with variation not exceeding ±0.05 s were taken for each solution. Viscosity η was calculated from average efflux time t and density d according to

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

where α and β are the characteristic constants of the viscometer and are determined from the viscosities and densities of water at 15, 25, and 35 °C. The temperature of the thermostat bath was controlled to ±0.03 °C.

Results

Generally the relative viscosity (η_{rel}) of a dilute electrolyte solution can be expressed by the Jones-Dole equation

$$\eta/\eta_0 = \eta_{\mathrm{rel}} = 1 + A\sqrt{c} + Bc, \qquad (1)$$

where η_0 and η are the viscosities of solvent and solution, respectively, and c the molarity of electrolyte. The constant A relates to the interionic interaction of the Debye-Hückel type and is calculated by using molar conductivities of ions. The constant B is a so-called "viscosity B-coefficient" which is closely related to ion-solvent interaction. Equation 1 is valid for concentrations up to about 0.1 mol dm^{-3}. At higher concentrations than 0.1 mol dm^{-3}, an additional term, Dc^2 is required in the right hand side of Eq. 1. In the concentration range studied, the quantity $(\eta_{\mathrm{rel}}-1)/\sqrt{c}$ was plotted against $\sqrt{c}$. The constants A and B were obtained from the intercept and slope, respectively. Figure 1 shows $(\eta_{\mathrm{rel}}-1)/\sqrt{c}$ *vs.* $\sqrt{c}$ curves for some sodium alkanoates at 25 °C. The A values were found to be very small and agree with those calculated by using molar conductivity data reported by Falkenhagen and Vernon.[8]

The B-coefficient of an electrolyte is expressed by the sum of B-coefficients of each ion

$$B = \sum B_{\mathrm{ion}}. \qquad (2)$$

For the determination of B_{ion}, Eq. 2 was used by adopting the convention of Gurney[3] and Kaminsky[9] ($B_{\mathrm{K}^+}=B_{\mathrm{Cl}^-}$). Values of B_{ion} for Na$^+$ and K$^+$ at various temperatures were obtained from Kaminsky's data. B-coefficients of acetate ion obtained from aqueous solutions of sodium, potassium, and guanidinium acetate at 25 °C were 0.242, 0.229, and 0.231, respectively. The values of B_{ion} for the alkanoate ions at 25 °C were in fair agreement with those of Tamaki's work.[4] Table 1 shows the B-coefficients of the carboxylate ions at 15, 25, and 35 °C.

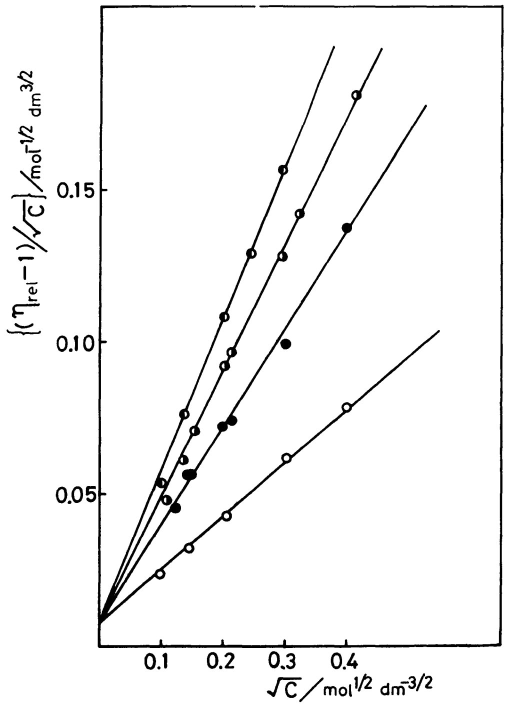

Fig. 1. Relationships between $(\eta_{rel}-1)/\sqrt{c}$ and $\sqrt{c}$ for sodium alkanoates at 25 °C.
○: Sodium formate, ●: sodium acetate, ◑: sodium propionate, ◐: sodium butylate.

Table 1. B-Coefficients of carboxylate ions at various temperatures

Compound	B_{ion}/dm^3 mol^{-1}		
	T/°C 15	25	35
$HCOO^-$	0.084	0.088	0.087
CH_3COO^-	0.264	0.242	0.221
$C_2H_5COO^-$	0.354	0.326	0.302
n-$C_3H_7COO^-$	0.450	0.413	0.393

B_{ion} is usually expressed by the sum of two contributions: 1) the hydrodynamic obstruction effect based on the size and shape of ion (B_{size}), and 2) the change of water structure induced by the addition of ion (B_{st}):

$$B_{ion} = B_{size} + B_{st}. \tag{3}$$

On the other hand, the viscosity of a dilute suspension of spherical colloid is represented by the Einstein equation

$$\eta_{rel} = 1 + 2.5\,\phi, \tag{4}$$

where ϕ is the volume fraction of colloidal particle. Equation 4 is an expression of the hydrodynamic effect of solute in a viscous flow. On the assumption that Eq. 4 is applicable to a solution of low molecular weight and ϕ is equal to the partial molar ionic volume at infinite dilution ($\bar{V}^{\circ}_{ion}$), B_{size} and B_{st} are expressed by

$$B_{size} = 0.0025\,\bar{V}^{\circ}_{ion}, \tag{5}$$

$$B_{st} = B_{ion} - 0.0025\,\bar{V}^{\circ}_{ion}. \tag{6}$$

As mentioned above, the sign and magnitude of B_{st} are regarded as a measure of ion-solvent interaction.

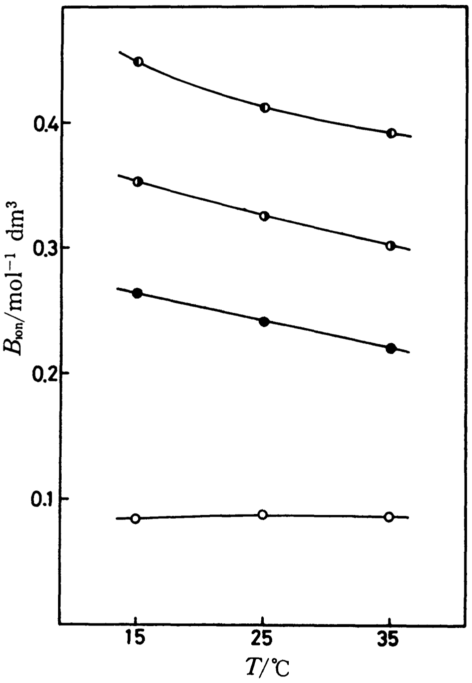

Fig. 2. Relationships between ionic B-coefficients of carboxylate ions and temperatures.
○: Sodium formate, ●: sodium acetate, ◑: sodium propionate, ◐: sodium butylate.

Table 2. The values of B_{st}, dB/dT, and $\bar{V}_0$ of carboxylate ions at 25 °C

Compound	B_{st} dm^3 mol^{-1}	dB_{ion}/dT dm^3 mol^{-1} K^{-1}	$\bar{V}_0$$^{a)}$ dm^3 mol^{-1}
$HCOO^-$	0.009	0.000	31.7
CH_3COO^-	0.127	−0.0022	45.9
$C_2H_5COO^-$	0.178	−0.0025	59.4
n-$C_3H_7COO^-$	0.223	−0.0028	75.9

a) "Water and Aqueous Solutions," ed by R. A. Horne, Wiley Interscience, New York (1972), p. 575.

Additional information on this interaction may be obtained from the sign and magnitude of the temperature dependence of B_{ion} (dB_{ion}/dT). Figure 2 shows the temperature dependence of B_{ion} for carboxylate ions. The values of (dB_{ion}/dT) obtained from the slope of B_{ion} *vs.* temperature curve are shown in Table 2 together with the values of B_{st} and $\bar{V}^{\circ}_{ion}$.

Discussion

The sign and magnitude of B_{st} are considered to reflect the structural change of water by the addition of ion. The ions associated with a large value of B_{st} with positive sign strongly promote the water structure, whereas the ions with a small value of B_{st} with negative sign break the water structure slightly.

As for the temperature dependence of B_{ion}, structure breaking ions should have a positive sign, since the structural water was already broken to a considerable extent by the thermal agitation at a high temperature. Therefore, the absolute value of B_{ion} decreases with temperature increase. From a consideration similar to that for the case of structure breaking ions, the sign of $(\mathrm{d}B_{\mathrm{ion}}/\mathrm{d}T)$ of structure making ions should be negative. Consequently, the structure making ion has a positive sign of B_{st} and a negative sign of $(\mathrm{d}B_{\mathrm{ion}}/\mathrm{d}T)$, and *vice versa* for the structure breaking ion.

However, some ions of intermediate type between the structure maker and breaker do not obey this rule.[10] Judging from the ambiguity in the estimation of solute volume, the sign of $(\mathrm{d}B_{\mathrm{ion}}/\mathrm{d}T)$ would be more reliable than that of B_{st} for the determination of the structure making or breaking effect of the ion.[11,12]

As shown in Table 2, the values of B_{st} and $(\mathrm{d}B_{\mathrm{ion}}/\mathrm{d}T)$ for formate ion are both close to zero, indicating that formate ion is neither a structure maker nor a structure breaker, that is, formate ion hardly influences the water structure. This result is consistent with the conclusion that the valence electron of the carboxylate group is delocalized on the two oxygen atoms,[6,7] because the delocalization of the electron lowers the surface charge density of the carboxylate group and weakens the ionic hydration by the electrostriction.

The signs of B_{st} of the alkanoate ions are positive and their magnitudes increase with the alkyl-chain length. The signs of $(\mathrm{d}B_{\mathrm{ion}}/\mathrm{d}T)$ for the alkanoate ions are negative and their absolute values increase with the alkyl-chain length. These results indicate that the alkanoate ions are structure making ions. By taking into account the fact that formate ion is neither a structure maker nor a structure breaker, we conclude that the nature of the structure making action for these alkanoate ions originates from the alkyl groups which form the ice-like structure around themselves. In conclusion, alkanoate ions are not ionic or hydrophilic structure makers but hydrophobic structure makers.

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