Viscosity *B* Coefficients for Some Homologous Series of Organic Electrolytes in Aqueons Solutions. The Effect of Ionic Groups

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The viscosity *B* coefficients for the three homologous series of sodium alkane carboxylates (acetate to butyrate), sodium *n*-alkyl sulfonates (methyl to hexyl), and *n*-alkylammonium chlorides (methyl to hexyl) in aqueous solutions at 25 °C have been determined. The *B* values increase linearly with the number of carbon atoms in the alkyl chains for each homologous series studied in this work, as well as for a homologous series of *n*-alkyl sulfate ions previously studied. In the case of the three kinds of organic anions with the same alkyl groups, the *B* values increase in the order: $-COO^- \gg -SO_3^- > -OSO_3^-$. The ion-solvent interaction effect, as estimated by the combination of the *B* values with the molal volume at an infinite dilution for ions, is positive for each carboxylate ion; however, it is negative for the lower alkyl sulfonate, alkyl sulfate and alkylammonium ions. From these facts, $-COO^-$ may be classified as an "electrostrictive structure-maker," whereas, $-SO_3^-$, $-OSO_3^-$, and $-NH_3^+$ are "electrostrictive structure-breakers." In this connection, the reported specific interactions of these ionic parts with simple counter-ions on the activity coefficients of organic electrolytes, the counter-ion binding of polyelectrolytes, and the effect of counter-ions on the critical micelle concentrations of long-chain electrolytes are briefly discussed on the basis of the change in water structure induced by both cations and anions in water.

A series of measurements of viscosity *B* coefficients for organic electrolytes in aqueous solutions has been performed in this laboratory in order to elucidate the behavior of organic ions in water. In a previous paper,[1)] the results for a homologous series of sodium *n*-alkyl sulfates were reported. This paper will describe the experimental results for the three homologous series of sodium alkane carboxylates, sodium *n*-alkyl sulfonates, and *n*-alkylammonium chloride.

The behavior of ions in water has generally been attributed to the structural change in water upon the introduction of ions into water.[2)] In solutions of electrolytes with large ions, such as K^+, Cl^-, and Br^- ions, these ions will decrease the extent of intermolecular hydrogen-bonding of water in the vicinity of ions; thus, they are "electrostrictive structure-breakers."[2)] On the other hand, in solutions of salts with small ions, such as Li^+, Na^+, and F^- ions, these ions will promote the water structure in the vicinity of ions; thus, they are "electrostrictive structure-makers."[2)] As a third possibility, nonpolar groups are "hydrophobic structure-makers"[2)] in water; that is, the water molecules will form "icebergs" around nonpolar molecules or groups in water.[3)] As amphiphilic organic ions generally consist of both nonpolar and ionic parts, the behavior of these organic ions in water may be interpreted approximately by the balance of two different modes of interaction, namely, hydrophobic hydration due to nonpolar parts and electrostrictive hydration due to ionic parts. The main object of this paper is to discuss the role of ionic parts on the structural influence in water on the basis of the experimental results of the effect of ionic groups on the viscosity *B* coefficients.

Experimental

Sodium acetate and *n*-butyrate were from Wako Pure Chemical Industries, and all the other organic substances were from Tokyo Kasei Kogyo Co. Sodium propionate and *n*-butyrate were recrystallized from ethanol. All the sodium carboxylates were dried at 100 °C. Sodium methyl and ethyl sulfonates were prepared by the neutralization of the corresponding sulfonic acids with a 2 M solution of sodium hydroxide, and then the water was evaporated to dryness. The sodium salts were twice recrystallized from ethanol-water solutions (80% for methyl salt and 90% for ethyl salt). The other sodium alkyl sulfonates were synthesized by a modification[4)] of Strecker method. The *n*-alkyl bromides were added, drop by drop, to the saturated solutions of sodium sulfite at 100 °C, and then the mixtures were dried in air. The sodium salts were extracted with ethanol and were further twice purified by recrystallizing them from ethanol. All the products of sodium alkyl sulfonates were dried *in vacuo* at 100 °C. All the *n*-alkylammonium chlorides except pentyl salt were recrystallized from suitable solvents—*i.e.*, ethanol for methyl salt and an ethanol-benzene solution for the other salts. Pentylammonium chloride was prepared by the neutralization of pentylamine with gaseous hydrogen chloride in benzene; the salt thus prepicitated was recrystallized from an ethanol-benzene solution. All the alkylammonium chlorides were dried in a vacuum desiccator. Water was obtained by redistillation from an alkaline permanganate solutions.

The viscosities were measured at 25 °C by a method similar to that described in a previous paper.[1)] Ubbelohde-type viscosimeters with flow times for water of 800—1200 s were used. The densities were measured in Ostwald pycnometers.

Results and Discussion

The B Values for the Organic Ions. The viscosity of aqueous electrolyte solutions can be expressed by the Jóne-Dole equation:[5)]

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

where η and η_0 are the viscosity of the solution and of the water respectively; *C*, the concentration (molarity); *A*, the constant relating to the ion-ion interaction, and *B*, the viscosity *B* coefficient. The viscosity *B* coefficients can be obtained as slopes of $(\eta/\eta_0-1)/C^{1/2}$ *versus* $C^{1/2}$ plots. In this work generally, the viscosity measurements were made at five different concentrations up to about 0.15 M for each salt; the *B* values thus obtained are summarized in Table 1. The *B* value for sodium acetate is slightly higher than that reported by Padova.[6)] The *B* values for sodium hexanoate[7)] and octanoate[8)] calculated from the re-

Table 1. Viscosity B coefficients for electrolytes at 25°C (in l/mol)

i	R_iCOONa		R_iSO_3Na	R_iNH_3Cl
1	0.343	0.331[a)]	0.213	0.040
2	0.425		0.301	0.125
3	0.505		0.391	0.214
4			0.471	0.290
5		0.680[b)]	0.551	0.360
6			0.637	0.422
7		0.862[c)]		

a) Ref. 6. b) Calculated from the data in Ref. 7. c) Calculated from the data in Ref. 8.

sults published by Campbell *et al.* are included in Table 1.

The viscosity B coefficients of electrolytes are considered to be determined by adding the individual contribution of the solute constituent ions.[9)] Adopting the convention of Gurney[9)] that the ionic B values for K^+ and Cl^- ions are equal, the ionic B values for Na^+ and Cl^- ions become 0.086 and -0.007 respectively.[10)] The ionic viscosity B coefficients, $B_{\rm ion}$, for the series of alkane carboxylate, alkyl sulfonate, and alkylammonium ions thus calculated are listed in Table 2. The B values for the alkylammonium ions are in fairly good agreement with those calculated from the results for alkylammonium bromides by Desnoyers, Arel and Leduc,[11)] assuming that the $B_{\rm ion}$ value for Br^- ion[10)] is -0.032. The data for a series of alkyl sulfate ions reported in the previous paper[1)] are included in Table 2.

The B values for homologous electrolytes are found to increase with the chain length. Fig. 1 shows the relationship between the $B_{\rm ion}$ values of the organic ions and the number of carbon atoms in the alkyl chains. It can be seen in Fig. 1 that the linear relation between the $B_{\rm ion}$ values and the number of carbon atoms holds for each series of homologous electrolytes and that the slopes are nearly equal. If the role of the interaction of the organic ion with water could be separated into the effect of the nonpolar part and that of the ionic part, nearly the same strength of interaction for the nonpolar alkyl group with water could be anticipated for all the homologous organic electrolytes. If this assumption is valid, the difference in the $B_{\rm ion}$ values for the organic ions with the same alkyl groups may be attributed to the interaction of the ionic parts with water. As is evident in Fig. 1, the $B_{\rm ion}$ values for the four types of homologous organic ions with the same alkyl groups are larger in the order: alkane carboxylate ions≫alkyl sulfonate ions>alkyl sulfate ions>alkylammonium ions. However, there remains some uncertainty as to the comparison of the absolute $B_{\rm ion}$ values between the alkylammonium cations and the three other kinds of the organic anions, because the values depend on the convention used in splitting the B values for an electrolyte into the individual values of a cation and an anion. Nevertheless, in the case of the three kinds of organic anions, *i.e.*, alkane carboxylate, alkyl sulfonate, and alkyl sulfate ions, the above sequence of the $B_{\rm ion}$ values is independent of the convention adopted.

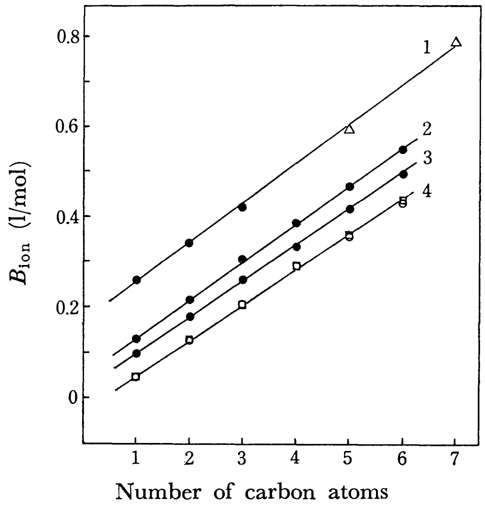

Fig. 1. Plots of viscosity B coefficients for organic ions against number of carbon atoms in the alkyl group. 1: alkane carboxylate ions, 2: alkyl sulfonate ions, 3: alkyl sulfate ions, 4: alkylammonium ions, ●, ○: present work, △: Refs 8 and 9, □ Ref. 11.

The Behavior of $-COO^-$, $-SO_3^-$ and $-OSO_3^-$ in Water. The viscosity B coefficient has been interpreted in terms of the size of the solute or the ion (Einstein effect) and in terms of the solute or ion-solvent interaction.[9,10)] For a comparison of the size of the solutes, the partial molal volumes at an infinite dilution of the electrolytes in water, $\bar{V}^\circ$, are listed in Table 3. The data for alkane carboxylates,[12,13,14)] and some for sulfonates[14)] and sulfates[15)] are cited from the literature. Because of the incompleteness of data in the liter-

Table 2. Ionic viscosity B coefficients at 25°C (in l/mol)

i	R_iCOO^-		$R_iSO_3^-$	$R_iOSO_3^-$	$R_iNH_3^+$	
1	0.257	0.245[a)]	0.127	0.102[d)]	0.047	0.048[e)]
2	0.339		0.215	0.179[d)]	0.132	0.141[e)]
3	0.419		0.305	0.262[d)]	0.221	0.222[e)]
4			0.385	0.337[d)]	0.297	0.298[e)]
5		0.594[b)]	0.465	0.418[d)]	0.368	0.373[e)]
6			0.551	0.496[d)]	0.429	0.446[e)]
7		0.776[c)]				

a) Ref. 6. b) Ref. 7. c) Ref. 8. d) Ref. 1. e) Calculated from the data in Ref. 11 assuming that the B value of bromide ion is -0.032.

TABLE 3. PARTIAL MOLAL VOLUME OF ELECTROLYTES AT INFINITE DILUTION AT 25°C (in cm^3/mol)

i	R_iCOONa			R_iSO_3Na		R_iOSO_3Na		R_iNH_3Cl	
1	38.75$^{a)}$	39.23$^{b)}$	39.31$^{c)}$	54.7	53.88$^{c)}$	63.4		54.5	
2	52.82$^{a)}$		53.71$^{c)}$	68.9	71.56$^{c)}$	81.3	81.1$^{d)}$	71.3	71.23$^{c)}$
3	68.41$^{a)}$	69.19$^{b)}$	69.32$^{c)}$	85.1		96.8		87.5	
4				101.0		113.5	111.7$^{d)}$	103.6	
5			100.58$^{c)}$	117.2		128.5		119.8	
6				133.1		145.3	141.3$^{d)}$	133.2	135.26$^{c)}$

a) Ref. 12. b) Ref. 13. c) Ref. 14. d) Ref. 15.

TABLE 4. ESTIMATION OF THE ION-SOLVENT INTERACTION EFFECTS

i	R_iCOO^-			$R_iSO_3^-$			$R_iOSO_3^-$			$R_iNH_3^+$		
	B_{ion} (l/mol)	$\overline{V}^\circ_{ion}$ (cm^3/mol)	Δ (l/mol)	B_{ion} (l/mol)	$\overline{V}^\circ_{ion}$ (cm^3/mol)	Δ (l/mol)	B_{ion} (l/mol)	$\overline{V}^\circ_{ion}$ (cm^3/mol)	Δ (l/mol)	B_{ion} (l/mol)	$\overline{V}^\circ_{ion}$ (cm^3/mol)	Δ (l/mol)
1	0.257	45.9	0.142	0.127	61.3	−0.026	0.102	70.0	−0.073	0.047	31.3	−0.031
2	0.339	60.3	0.188	0.215	75.5	0.026	0.179	87.9	−0.041	0.132	48.0	0.012
3	0.419	75.9	0.229	0.305	91.7	0.076	0.262	103.4	0.004	0.221	64.3	0.060
4				0.385	107.6	0.116	0.337	120.1	0.037	0.297	80.4	0.096
5	0.594	107.2	0.326	0.465	123.8	0.156	0.418	135.1	0.080	0.368	96.6	0.126
6				0.551	139.7	0.202	0.496	151.9	0.116	0.429	110.0	0.154

ature, the $\overline{V}^\circ$ values for alkyl sulfonates and sulfates are calculated from the present density data by the use of the standard procedure.$^{16)}$ Our density measurements are not very accurate, as they were for the calculation of the viscosity. However, these volume data are still instructive for the following discussion. The $\overline{V}^\circ$ values of electrolytes are also composed of the sum of the contributions from both cations and anions. Unfortunately, there has been some controversy about the absolute values of ions, $\overline{V}^\circ_{ion}$.$^{16)}$ If we use −5.4 cm^3/mol as the $\overline{V}^\circ_{ion}$ value of H^+ ion at 25 °C, recommended by Millero,$^{16)}$ the $\overline{V}^\circ_{ion}$ values of Na^+ and Cl^- ions become −6.6 and 12.4 cm^3/mol respectively.$^{16)}$ The $\overline{V}^\circ_{ion}$ values thus calculated are listed in Table 4. Figure 2 represents an approximate linear relation between the B_{ion} values and the $\overline{V}^\circ_{ion}$ values. A similar relation has frequently been reported.$^{11,15,17)}$

The viscosity of a dilute suspension of spherical colloids is given by the Einstein equation:$^{18)}$

$$\eta = \eta_0(1+2.5\phi) \qquad (2)$$

where ϕ is the volume fraction of colloids. Though the coefficient of 2.5 in Eq. (2) becomes slightly varied in the case of elongated solutes,$^{19)}$ an approximate attempt assuming the spherical form will be made in this paper. For the solution, the B coefficient can be related to $\overline{V}^\circ$ expressed in cm^3/mol:

$$B = 0.0025\,\overline{V}^\circ \qquad (3)$$

Thus, the contribution from the Einstein effect in the B_{ion} values is equal to 0.0025 $\overline{V}^\circ_{ion}$. Desnoyers and Perron$^{20)}$ showed that the values, $B-0.0025\,\overline{V}^\circ$, is a measure of the solute-solvent interation. Similarly, the ion-solvent interaction effect, Δ, for organic ions can be derived by the equation:$^{20)}$

$$\Delta = B_{ion} - 0.0025\,\overline{V}^\circ_{ion} \qquad (4)$$

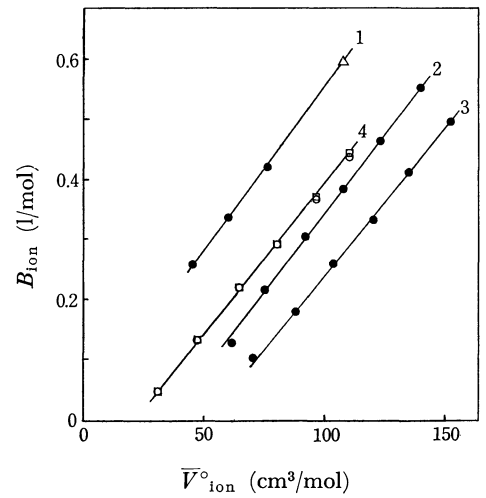

Fig. 2. Plots of viscosity B coefficients for organic ions against molal volumes for ions at infinite dilution.
1: alkane carboxylate ions, 2: alkyl sulfonate ions, 3: alkyl sulfate ions, 4: alkylammonium ions, ●, ○ present work, △: Ref. 8, □: Ref. 11.

It may be noted that the Δ values are of a semi-quantitative nature, because the absolute values of Δ depend on the two conventions adopted for splitting the B values and the $\overline{V}^\circ$ values into the respective ionic B_{ion} and $\overline{V}^\circ_{ion}$ values.

As is indicated in Table 4, the Δ values are positive for all the carboxylate ions. Further, it has been reported that alkane carboxylic acids have rather small B values, those for acetic, propionic, and butyric acids being 0.117, 0.190, and 0.250 respectively.$^{21)}$ The large difference in the B values between carboxylic acids and carboxylate ions may be interpreted in terms of the strong tendency of the carboxylate anion to orientate the water molecules around the ions.[9] Therefore, it may be concluded that the $-COO^-$ ionic part acts as an "electrostrictive structure-maker" in the water phase.

On the other hand, the $-SO_3^-$ ionic part and the $-OSO_3^-$ ionic part have quite small B values. With the lower members of sulfonates and sulfates, the Δ values are negative, as is shown in Table 4. Therefore, it may be assumed that these two anionic parts are "electrostrictive structure-breakers" in water. The structure-breaking properties of sulfonate ions have been discussed by Uedaira and Uedaira[22] on the basis of their conductivity measurements, and by Katayama *et al.*[23] on the basis of their partial molal measurements.

The Behavior of $-NH_3^+$ in Water. The $\bar{V}^\circ$ values for alkylammonium chlorides and the $\bar{V}^\circ_{\text{ion}}$ values for alkylammonium ions are listed in Tables 3 and 4 respectively. Table 4 indicates a negative Δ value for methylammonium ion. From this fact, the $-NH_3^+$ ionic part is considered to be an "electrostrictive structure-breaker." This is probably supported by the fact that simple ammonium ion has a net structure-breaking effect.[9]

Specific Interactions of the $-COO^-$, $-SO_3^-$, $-OSO_3^-$ and $-NH_3^+$ Ionic Parts with Other Simple Counter-ions. There are several phenomena which indicate the characteristic behavior of the $-COO^-$, $-SO_3^-$, $-OSO_3^-$ and $-NH_3^+$ ionic parts in water, particularly with regard to the interaction of these ionic parts with other simple counter-ions. The mean ionic activity coefficients, γ, for the alkali metal salts of acetic acid for a given concentration decrease in the order: $Li^+ < Na^+ < K^+$.[24] On the other hand, the γ values for the salts of *p*-toluensulfonic acid[24] as well as the salts of methyl and ethyl sulfonic acids[25] in dilute solutions increase in the order: $Li^+ > Na^+ > K^+$. The variation in the order of the ionic activity coefficients has been discussed by Gurney[9] and by Frank.[26] The theory of Gurney and Frank implies that an anion and a cation with similar structural influences—both being structure-makers or both structure-breakers—will attract each other, whereas if an anion and a cation have different structural tendencies, they will repel each other. Among the cations, Li^+ is a strong, and Na^+, a weak structure-maker, while K^+, slightly structure-breaking. As has been explained above, the $-COO^-$ ionic part is believed to be a structure-maker, while the $-SO_3^-$ ionic part, a structure-breaker. Therefore, the lithium salt of carboxylic acid, a "maker-maker" salt, and the potassium salt of sulfonic acid, a "breaker-breaker" salt, will give lower-lying activity coefficient *versus* concentration curves because of the tendency toward more attraction between cations and anions. At the opposite extreme, the potassium salt of carboxylic acid, a "breaker-maker" salt, and the lithium salt of sulfonic acid, a "maker-breaker" salt, will give higher-lying curves because of the greater escaping tendency between cations and anions. Steigman and Dobrow[27] also discussed the ionic activity coefficients along the same lines.

With polyelectrolytes, the counter-ions are bound to poly-ions because of the strong electrostatic potential of poly-ions.[28] This phenomenon is called "counter-ion binding". There are characteristic sequences of simple counter-ions with regard to the degree of binding to the poly-ions. In the case of the alkali metal salts of polyacrylic acid, the degree of binding decreases with the size of the counter-ion: $Li^+ > Na^+ > K^+$.[29] With polyvinyl- and polystyrenesulfonates, on the other hand, the degree of binding increases with the size of the ion: $Li^+ < Na^+ < K^+$.[24] This characteristic feature may also be interpreted in terms of the structural influences by ions in water. In the case of the "like-like" combinations in the structural influences of both cations and anions, such as lithium polyacrylate and potassium polyvinyl- and polystyrenesulfonates, cations and anions will attract each other more. Conversely, in the case of the incompatible combinations in the structural influences of cations and anions, such as potassium polyacrylate and lithium polyvinyl- and polystyrene-sulfonates, the resultant phenomenon will result in a stronger repulsive force.

The amphiphilic salts containing an alkyl group, higher than octyl, have a tendency to form micelles in aqueous solutions. The critical micelle concentration (CMC) is a measure of the solute-solvent interaction. The CMC value depends mainly on the oleophilic group. However, there are some specific effects of ionic species. In the case of the alkali metal salts of dodecyl sulfuric acid, the CMC values decrease with size of the cations: $Li^+ > Na^+ > K^+$.[30] In the case of the alkali metal salts of long-chain carboxylic acid, the CMC values are in the order: $Li^+ < Na^+ < K^+$.[31] Further, the CMC values for dodecylammonium halides are in the order: $I^- < Br^- < Cl^-$.[32] In view of the structural influences in water induced by both cations and anions, the degree of counter-ion binding at the surface of ionic micelles will be in the order of $Li^+ < Na^+ < K^+$ in the case of the alkali metal salts of dodecyl sulfuric acid, whereas the order will be reversed in the case of the alkali metal salts of alkane carboxylic acid: further, it will be in the order of $I^- > Br^- > Cl^-$ in the case of dodecylammonium halides. With increased binding of counter-ions the contribution of the electric free energy in the micelle formation per monomer will be reduced, thus resulting in the easier formation of the aggregates at lower concentrations.

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