364 BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 364—368 (1973) [Vol. 46, No. 2

The Viscosities of Aqueous Sodium Alkylsulfate and Alkyltrimethylammonium Bromide Solutions

Mitsuru Tanaka, Shoji Kaneshina,* Wataru Nishimoto,* and Hiroyuki Takabatake*

Department of Chemistry, Faculty of Science, Fukuoka University, Nanakuma, Fukuoka

**Department of Chemical Engineering, Faculty of Engineering, Tokushima University, Minamijōsanjima-chō, Tokushima*

(Received April 21, 1972)

The viscosities of aqueous solutions of sodium alkylsulfate and alkyltrimethylammonium bromide have been measured at various temperatures from 5 to 55°C. The viscosity data have been interpreted in terms of the Jones-Dole equation, and the viscosity *B* coefficients for the alkylsulfate and alkyltrimethylammonium ions at various temperatures have been calculated. The *B* values for these ions are all positive; they decrease with an increase in the temperature and increase linearly with an increase in the alkyl-chain length. The increment of *B* is found to be 0.076/$-CH_2-$ at 25°C. The energy and the entropy of activation for the viscous flow at 25°C have been calculated for these ions; they increase with an increase in the alkyl-chain length. This behavior of the *B* coefficient, and the energy and the entropy of activation for the viscous flow may be interpreted by saying that the longer-chain ions promote the hydrogen-bond structure of water around the hydrocarbon chain of these ions, while shorter-chain ions, *e.g.*, ethylsulfate and ethyltrimethylammonium ions, behave instead as structure breakers because of the predominance of the disordering effect on the water around the ionic head. The viscosities of micellar solutions have also been measured. The volume of micelles as a hydrodynamic moving unit in solution has been estimated.

The viscosities of aqueous surfactant solutions have been measured by many investigators in order to obtain information about the micelle-forming properties.[1)]

Gurney,[2)] Kaminsky,[3)] and Nightingale[4)] have emphasized that the *B* coefficients of the Jones-Dole equation of viscosity[5)] provide significant informations about the nature of ion-solvent interaction. The division of the *B* value of electrolytes into individual ionic values has been attempted by Gurney.[2)] Kaminsky has extended this treatment to a wide temperature range.[3)] Further, Nightingale[4)] has indicated that the influence of strong electrolytes upon the viscosity of the solvent can be interpreted as a rate process, and that the energy and entropy of activation for a viscous flow can be estimated for a number of ions; on the basis of such estimates, he has discussed the nature of the ion-solvent interaction.

Having a molecule composed of a hydrophilic ionic head and a hydrophobic long-chain tail is a characteristic of an ionic surfactant. With respect to the hydrophobic interaction between water and a hydrocarbon chain, there have been many experimental and theoretical studies, especially by Nemethy and Scheraga.[6)]

In this paper, the interaction between long-chain ions and solvent water will be discussed on the basis of the ionic *B* coefficients and the energy and entropy of activation for the viscous flow of two homologues of surface-active substances, sodium alkylsulfates and alkyltrimethylammonium bromides.

Experimental

Materials. The homologous series of *n*-alkanols and *n*-alkylbromides used in the preparation of sodium *n*-alkylsulfates and *n*-alkyltrimethylammonium bromides with 2 to 12 carbon atoms were all found by gas chromatography to be pure. All the salts gave correct elemental analyses.

Sodium Alkylsulfates: The reaction mixture obtained by treating *n*-alkanols with chlorosulfonic acid was extracted with ether and then neutralized with sodium hydroxide. The longer-chain compounds were obtained from the ether layer, and the shorter compounds, from the water layer. The sodium alkylsulfates thus obtained were recrystallized from an acetone-methanol mixture.

Alkyltrimethylammonium Bromides: These compounds were prepared by the reaction of the corresponding *n*-alkylbromides with trimethylamine. They were purified by recrystallization from acetone.

The critical micelle concentrations (CMC) of surfactants with an alkyl chain from 8 to 12 carbon atoms were determined by means of surface-tension and electric-conductivity measurements; the CMC's obtained by both methods were in good agreement with those from other sources.[7)] The surface tension *vs.* concentration curves did not exhibit a minimum in the vicinity of the CMC.

Measurement of Viscosity. All the measurements of viscosity were carried out at a constant temperature between 5 and 55°C (±0.01°C). All the solutions were prepared on a molal basis. Two Geist-Cannon type viscometers with a flow time of *ca.* 500 s for water at 25°C were employed. The viscometers were carefully cleaned, rinsed with distilled water and methanol, and dried before they were filled with a solution and immersed in a thermostat. The solutions were filtered before being introduced into the viscometers in order to remove dust, *etc.* The error in the flow time was 0.1 s. Two viscometers were calibrated with pure water and 20% and 30% sucrose solutions by means of Eq. (1):

---

1) L. M. Kushner, B. C. Duncan, and J. I. Hoffman, *J. Res. Natl. Bur. Stand.*, **49**, 85 (1952). N. Sata and K. Tyuzyo, This Bulletin, **26**, 177 (1953). P. Mukerjee, *J. Colloid Sci.*, **19**, 722 (1964). Y. Iwadare and T. Suzawa, *Nippon Kagaku Zasshi*, **90**, 1106 (1969).

2) R. W. Gurner, "Ionic Processes in Solution," McGraw-Hill Book Co., New York, N. Y., (1953).

3) M. Kaminsky, *Discuss. Faraday Soc.*, **24**, 171 (1957).

4) E. R. Nightingale, Jr., and R. F. Benck, *J. Phys. Chem.*, **63**, 1777 (1959).

5) G. Jones and M. Dole, *J. Amer. Chem. Soc.*, **51**, 2950 (1929).

6) G. Nemethy and H. A. Scheraga, *J. Chem. Phys.*, **36**, 3401 (1962).

7) K. Shinoda, T. Nakagawa, B. Tamamushi, and T. Isemura, "Colloidal Surfactants," Academic Press, New York, N. Y., (1963), p. 36.

$$\frac{\eta}{\rho} = Kt - \frac{L}{t} \tag{1}$$

where η is the absolute viscosity, ρ is the density, and t is the flow time. The characteristic constants of the viscometers, K and L, were 1.592×10^{-5} and 1.36×10^{-2} for one, and 1.613×10^{-5} and 0.75×10^{-2} for the other, respectively. For the absolute viscosities of water, and 20% and 30% sucrose solutions at 25°C, we used 0.008903, 0.01701, and 0.02741 poise[8] respectively. The densities are 0.99707, 1.07940, and 1.12512 g/ml[9] respectively. The densities of the solutions were measured at a given temperature with *ca.* 6-ml pycnometer; the error of measurement was within ±0.0001 g/ml.

Results and Discussion

The viscosities of the solutions were computed by means of Eq. (1). It was found that the $\rho=\rho_0(1+\alpha m)$ equation held for the densities of aqueous solutions of sodium alkylsulfate and alkyltrimethylammonium bromide over a wide range of concentrations and temperatures, where m is the molal concentration; ρ_0, the density of pure water, and α, a constant.

The viscosity data have been analyzed by means of the Jones-Dole equation[10]:

$$\eta_r = 1 + A\sqrt{m} + Bm \tag{2}$$

where $\eta_r(=\eta/\eta_0)$ is the relative viscosity of a solution and where A and B are constants characteristic of the solute electrolyte. Eq. (2) can, then, be rewritten as:

$$\frac{(\eta_r-1)}{\sqrt{m}} = A + B\sqrt{m} \tag{3}$$

The A coefficient represents the contribution from interionic electrostatic force.[11] The B coefficient is said to be a measure of the effective hydrodynamic volume of the solvated ions,[12] and to denote the order or disorder introduced by the ions into the solvent structure.

Plots of $(\eta_r-1)/\sqrt{m}$ *vs.* $\sqrt{m}$ for aqueous solutions of sodium alkylsulfate and alkyltrimethylammonium bromide at 25°C are given in Fig. 1. The A intercepts obtained were small in every case; at most they amounted to 0.01 in the aqueous solutions studied. The plots of Eq. (3) were found to be linear up to concentrations of 0.1 molality for solutions of salts with hydrocarbon chains shorter than the octyl compound, and up to the CMC for solutions of micelle-forming salts with a hydrocarbon chain of from 8 to 12 carbon atoms. The B coefficients obtained at various temperatures are presented in Table 1.

Viscosity B Coefficient. For a satisfactory discussion of the temperature dependence of the viscosity B coefficients, the individual B values of the component ions are needed. The division of the B coefficients into individual ionic values is a rather arbitrary process, because there is no quantity corresponding to the transport numbers used in ionic mobility assignments. Gurney[2] has computed the ionic B coefficients in aqueous solutions by equating the contributions of the K^+ and Cl^- ions to the B coefficient of KCl at 25°C. Kaminsky has extended this treatment to the temperature range from 15 to 45°C,[3] and obtained ionic values in good agreement with those reported by Cox and Walfenden[13] that were based on the mobility difference for the Li^+ and IO_3^- ions. We have followed Kaminsky's procedure and have used his data for the Na^+ and Br^- ions. The ionic B coefficients for the alkylsulfate and alkyltrimethylammonium ions thus obtained are given in Table 2.

B coefficients for the relatively small alkali and halide ions in an aqueous solution decrease with an

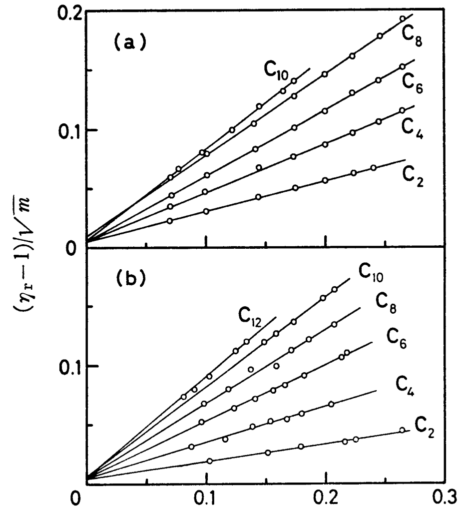

Fig. 1. Plots of $(\eta_r-1)/\sqrt{m}$ *vs.* $\sqrt{m}$ at 25°C. (a): sodium alkylsulfate, (b): alkyltrimethylammonium bromide.

Table 1. Viscosity B coefficients at various temperatures

Salt	Temperature, °C				
	5	15	25	35	55
C_2SO_4Na		0.26	0.25	0.24	0.23
C_4SO_4Na		0.43	0.41	0.39	0.37
C_6SO_4Na		0.61	0.56	0.52	0.49
C_8SO_4Na	0.85	0.77	0.71	0.65	0.56
$C_{10}SO_4Na$	0.90	0.83	0.77	0.71	
$C_{12}SO_4Na$	0.95	0.89			
		15	25	40	
C_2Me_3NBr		0.16	0.16	0.16	
C_4Me_3NBr		0.36	0.31	0.28	
C_6Me_3NBr		0.53	0.45	0.43	
C_8Me_3NBr		0.70	0.61	0.57	
$C_{10}Me_3NBr$		0.88	0.76	0.70	
$C_{12}Me_3NBr$		1.07	0.91	0.76	

---

[8] J. R. Coe and T. B. Godfrey, *J. Appl. Phys.*, **15**, 625 (1944).

[9] L. W. Tilton and K. Taylor, *J. Res. Natl. Bur. Stand.*, **18**, 205 (1937).

[10] The molarity is used instead of the molality in the original Jones-Dole equation. But A and B obtained are almost the same in very dilute solution.

[11] H. Falkenhagen and E. L. Vernon, *Physik. Z.*, **33**, 140 (1932).

[12] E. R. Nightingale, Jr., *J. Phys. Chem.*, **63**, 1381 (1959).

[13] W. M. Cox and J. H. Wolfenden, *Proc. Roy. Soc. Ser. A*, **145**, 475 (1934).

TABLE 2. IONIC B COEFFICIENTS AT VARIOUS TEMPERATURES

Ion	Temperature, °C				
	5	15	25	35	55
$C_2SO_4^-$		0.17	0.16	0.15	0.14
$C_4SO_4^-$		0.34	0.32	0.30	0.28
$C_6SO_4^-$		0.52	0.47	0.43	0.40
$C_8SO_4^-$	0.76	0.68	0.62	0.56	0.47
$C_{10}SO_4^-$	0.81	0.74	0.68	0.62	
$C_{12}SO_4^-$	0.86	0.80			
Na^+	0.09	0.09	0.09	0.09	0.09
		15	25	40	
$C_2Me_3N^+$		0.22	0.20	0.18	
$C_4Me_3N^+$		0.42	0.35	0.30	
$C_6Me_3N^+$		0.59	0.49	0.45	
$C_8Me_3N^+$		0.76	0.65	0.59	
$C_{10}Me_3N^+$		0.94	0.80	0.72	
$C_{12}Me_3N^+$		1.13	0.95	0.78	
Br^-		−0.06	−0.04	−0.02	

increase in the ionic size, often to negative values, and in such cases B increases with an increase in the temperature.[2)] These ions are known as structure breakers. On the other hand, large molecular ions such as the tetraalkylammonium ions have large and positive B values.[14,15)] Assuming that the viscosity of an electrolytic solution at a constant temperature can be interpreted by Einstein's equation[16)]:

$$\eta_r = 1 + 2.5\phi \qquad (4)$$

where ϕ is the volume fraction of the salts, and by combining with Eq. (2), Eq. (4) becomes:

$$2.5\phi = A\sqrt{m} + Bm \qquad (5)$$

The $A\sqrt{m}$ term can safely be neglected in comparison with Bm in the present solution. Since also $\phi = C\overline{V}$ $(=C\sum\bar{v}_i)$, where C is the molarity, $\overline{V}$ and $\bar{v}_i$ are the partial molar volumes of the solute electrolyte and the i-th ions in solution respectively, and since $C \simeq m$, we obtain:

$$2.5\,\overline{V} = B \qquad (6)$$

$$2.5\,\bar{v}_i = B_i \qquad (7)$$

where: $$\sum B_i = B \qquad (8)$$

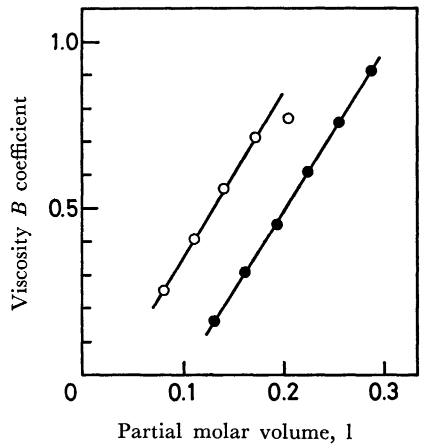

Fig. 2. Plots of viscosity B coefficients *vs.* partial molar volume of long chain salts at 25°C; sodium alkylsulfate (○), alkyltrimethylammonium bromide (●).

TABLE 3. PARTIAL MOLAR VOLUME OF LONG CHAIN SALTS AT 25°C

n	Partial molar volume, ml	
	C_nSO_4Na	C_nMe_3NBr
2	81.1	131.6
4	111.7	162.6
6	141.3	193.6
8	172.6	223.7[17)]
10	204.1[17)]	255.4[17)]
12	234.4[17)]	287.0[17)]

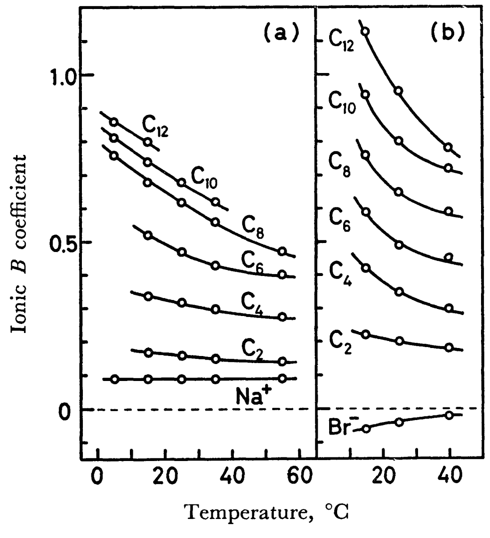

Fig. 3. Temperature dependence of ionic B values. (a): alkylsulfate and sodium ions, (b): alkyltrimethylammonium and bromide ions.

Therefore, if the viscosity of an electrolytic solution can be explained by Einstein's equation, the viscosity B coefficient should be approximately linear with the partial molar volume of the solute, *i.e.*, the ionic size. A plot of B *vs.* $\overline{V}$ for sodium alkylsulfate and alkyltrimethylammonium bromide is found to be linear, as is shown in Fig. 2, where the partial molar volumes of the long-chain salts used are given in Table 3. The slopes of these straight lines, however, are not equal to 2.5, but are about two times it. The B coefficient decreases with the increase in the temperature, as will be mentioned later, whereas $\overline{V}$ slightly increases with the increase in the temperature according to our unpublished data. Such behavior can not be accounted for only by the Einstein effect.

The B coefficients for alkylsulfate and alkyltrimethylammonium ions decrease with an increase in the tem-

---

14) E. R. Nightingale, Jr., *J. Phys. Chem.*, **66**, 894 (1962).

15) R. L. Key, T. Vituccio, C. Zawoyski, and D. F. Evans, *J. Phys. Chem.*, **70**, 2336 (1966).

16) A. Einstein, *Ann. Physik*, **19**, 289 (1906); **34**, 591 (1911).

17) J. M. Corkill, J. F. Goodman, and T. Walker, *Trans. Faraday Soc.*, **63**, 768 (1967).

perature, and the longer the alkyl chain length, the larger the negative temperature coefficient of B values, as is shown in Fig. 3. This tendency is similar to that for the tetraalkylammonium ions.[14,15] On the other hand, the B coefficient of a strong inorganic electrolyte increases with an increase in the temperature.[2] Therefore, the decrease in the B coefficient of these long-chain ions can be attributed to the interaction between the solvent water and the hydrocarbon part of the chain ions. The negative temperature coefficient of the B for the chain ion may be explained by the fact that these long-chain ions cause the water around the hydrocarbon part to become more ice-like than normal water,[18,19] and that this "ice-likeness" or "iceberg"[6] melts as the temperature is raised, causing the ionic B coefficient to be lowered.

The variation in the ionic B coefficient with the alkyl chain length is shown in Fig. 4. The ionic B coefficients of two homologous salts increase with an increase in the chain length at each temperature. This increase can be attributed to the Einstein effect of the additional methylene group and to the highly ordered "iceberg" structure around the hydrocarbon tail of the long-chain ions. The increase in the ionic B coefficient with the chain length is linear at 15 and 25°C except for alkylsulfate with carbon atoms larger than 8; the increments per methylene group are 0.076 for the alkylsulfate ion and 0.075 for the alkyltrimethylammonium ion at 25°C. At 15°C they are 0.085 and 0.091 respectively. Thus, these values are independent of the ionic heads of long-chain ions at a constant temperature. The plots of B values *vs.* the chain length for the alkylsulfate ion are found to be bent suddenly at the carbon number of 8, as is shown in Fig. 4, whereas this is not observed for the alkyltrimethylammonium ion.

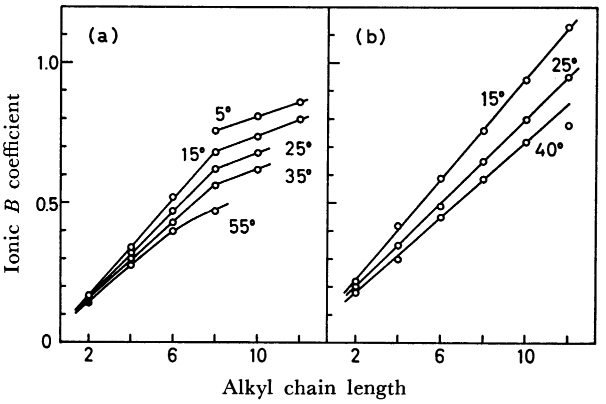

Fig. 4. Ionic B values at various temperature as a function of alkyl chain length. (a): alkylsulfate ions, (b): alkyltrimethylammonium ions.

Energy and Entropy of Activation for the Viscous Flow. The energy of activation for the viscous flow, $E^{\neq}$, according to the theory of absolute reaction rates presented by Eyring *et al.*,[20] is given by:

$$E^{\neq} = R\frac{\mathrm{d}\ln\eta}{\mathrm{d}\,(1/T)} \tag{9}$$

For an associated liquid such as water, the plot of ln η *vs.* $1/T$ is not linear; *i.e.*, $E^{\neq}$ varies with the temperature. By substituting Eq. (2) into Eq. (9), and by neglecting the $A\sqrt{m}$ term in Eq. (2), it follows that:

$$E^{\neq} = R\frac{\mathrm{d}\ln\eta_0}{\mathrm{d}(1/T)} + \frac{R}{1+Bm}\frac{\mathrm{d}(1+Bm)}{\mathrm{d}(1/T)} \tag{10}$$

where the first term of the right-hand side is identical with the energy of activation for the solvent water, $E_0^{\neq}$. Assuming that the difference between the activation energy of a solution and a solvent is equal to the activation energy for the flow of the solute, $\Delta E^{\neq}$, it follows that:

$$\Delta E^{\neq} = E^{\neq} - E_0^{\neq} = \frac{R}{1+Bm}\frac{\mathrm{d}(1+Bm)}{\mathrm{d}(1/T)} \tag{11}$$

The free energy of activation for the viscous flow is given by:

$$\Delta G^{\neq} = RT\ln\frac{\eta V}{hN} \tag{12}$$

where h is the Planck constant, N is the Avogadro number, and V is the molar volume of the moving unit. Subtracting the activation free energy for the solvent, $\Delta G_0^{\neq}$, from Eq. (12), the activation free energy for the flow of the solute is given by:

$$\Delta\Delta G^{\neq} = \Delta G^{\neq} - \Delta G_0^{\neq} = RT\ln\frac{\eta V}{\eta_0 V_0} \tag{13}$$

Since the activation enthalpy can safely be assumed not to differ appreciably from the activation energy, the entropy of activation of the solute, $\Delta\Delta S^{\neq}$, may also be calculated as:

$$\Delta\Delta S^{\neq} = \frac{\Delta E^{\neq} - \Delta\Delta G^{\neq}}{T} \tag{14}$$

Nightingale[4] has shown that the activation quantities of the solute can be represented by the following formulae:

$$\Delta E^{\neq} = \sum \nu_i \Delta E_i^{\neq},\ \Delta\Delta S^{\neq} = \sum \nu_i \Delta\Delta S_i^{\neq} \tag{15}$$

where $\Delta E_i^{\neq}$ and $\Delta\Delta S_i^{\neq}$ are the energy and the entropy of activation for the ionic components, and where ν_i is the number of ions per molecule of salt. He further assumed, in a manner similar to that in the evaluation of the ionic B coefficients, that the activation energy for the flow of the K^+ ion in solutions was approximately equal to that of the Cl^- ion. Following Nightingale's procedure, and using his data for the Na^+ and Br^- ions, the energies and entropies of activation for the flow of alkylsulfate and alkyltrimethylammonium ions were determined to be as is shown in Table 4.[21] It can be seen from Table 4 that the activation energies for the ions under consideration are all positive, that they in-

---

[18] H. S. Frank and M. W. Evans, *J. Chem. Phys.*, **13**, 507 (1945).

[19] H. S. Frank and W. Y. Wen, *Discuss. Faraday Soc.*, **24**, 133 (1957).

[20] S. Glasstone, K. J. Laidler, and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., New York, N. Y., (1941).

[21] These values are based on the solution of 1 mol/kg in order to be compared with Nightingale's data, consequently that for the ions with alkyl chain longer than C_8 may be imaginary because of the micelles to be already formed at lower concentrations.

TABLE 4. IONIC ACTIVATION ENERGY AND ENTROPY FOR VISCOUS FLOW AT 25°C

Ion	$\Delta E_i^{\neq}$(cal)	$\Delta\Delta S_i^{\neq}$(e.u.)
$C_2SO_4^-$	120	−0.11
$C_4SO_4^-$	230	−0.03
$C_6SO_4^-$	440	0.44
$C_8SO_4^-$	610	0.77
$C_{10}SO_4^-$	580	0.56
Na^+	20	0.05
$C_2Me_3N^+$	240	0.40
$C_4Me_3N^+$	620	1.35
$C_6Me_3N^+$	720	1.45
$C_8Me_3N^+$	880	1.67
$C_{10}Me_3N^+$	1090	2.21
$C_{12}Me_3N^+$	1530	3.45
Br^-	−240	−0.85

crease with the increase in the chain length of ions, and that, unlike those for ethylsulfate and butylsulfate, the activation entropies for the other ions considered are positive. These results confirm the interpretation of the negative temperature coefficient of ionic B values. That is, those ions which have a positive activation energy and a positive viscosity B coefficient increase the viscosity of water by increasing the ice-like structure apo-surface.[22] However, the ethylsulfate ion, which has a negative activation entropy, is weakly peri-surface hydrated and scarcely increases the B value at all because of the order-destroying effect of the ionic head. These results, when considered along with the temperature dependence of the B values, indicate that the alkylsulfate and alkyltrimethylammonium ions with longer alkyl chains are structure makers and that ethylsulfate and ethyltrimethylammonium ions are structure breakers, while for the butylsulfate ion the two effects appear to cancel each other out.

Viscosity of Miceller Solutions. It seems likely that, in dilute aqueous solutions of association colloides, the micelles are reasonably spherical. The viscosity of these solutions may be represented by Einstein's equation. The concentration of micelles composed of n molecules, C_m(mol/l), is given by:

$$C_m = \frac{C - \mathrm{CMC}}{n} \tag{16}$$

The hydrodynamic volume of the micelle, V_m (l/mol), is given by:

$$V_m = \frac{n(\bar{v}_m + n_h v_h)}{1000} \tag{17}$$

where $\bar{v}_m$ (ml/mol) is the partial molar volume of the surfactant in the micellar state; v_h(ml/mol), the molar volume of water hydrated, and n_h, the number of moles of the hydrated water per mole of the surfactant.

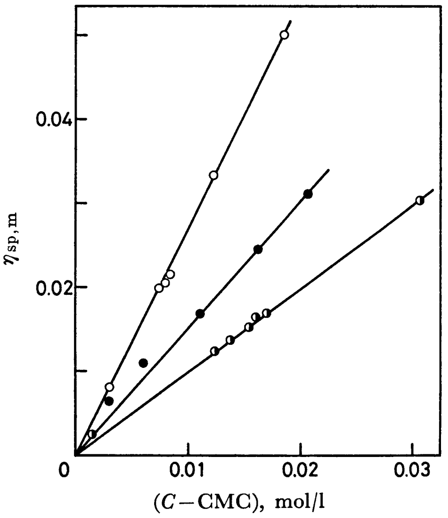

Fig. 5. Plots of $\eta_{sp,m}$ *vs.* $(C-\mathrm{CMC})$ for the micellar solution at 25°C; sodium decylsulfate (●), sodium dodecylsulfate (○), decyltrimethylammonium bromide (◑).

TABLE 5. HYDRODYNAMIC VOLUME FOR MICELLES

Surfactant	$\bar{v}_m + n_h v_h$	$\bar{v}_m$[17]	n_h
$C_{10}Me_3NBr$	397	262.3	7—8
$C_{10}SO_4Na$	604	212.5	21—22
$C_{12}SO_4Na$	1108	246.2	47—48

In a micellar solution the viscosity of the solvent, η_0, should be replaced by the viscosity of the solution at the CMC $\eta_m{}^0$; then Eq. (4) becomes:

$$\eta_{sp,m} = \frac{\eta}{\eta_m{}^0} - 1 = \frac{\bar{v}_m + n_h v_h}{400}(C - \mathrm{CMC}) \tag{18}$$

A plot of $\eta_{sp,m}$ *vs.* (C-CMC) gives a straight line, as is shown in Fig. 5. The hydrodynamic volume of the micelle may be estimated from these slopes. The values of V_m thus obtained are presented in Table 5, together with the values of $\bar{v}_m$ and n_h. It can be seen from Table 5 that, in a homologous series, the longer the chain length, the larger the hydration number. However, n_h is larger than one would expect. Because the micelles of these ionic surfactants carry an electric charge in aqueous solutions, an electroviscous effect is always included as part of the measured intrinsic viscosity. Parker and Wasik[23] have shown that the intrinsic viscosities for sodium dodecylsulfate (SDS) in water and 0.2 M sodium chloride should differ by a factor of 2.3. Courchene,[24] with correction for the electroviscous effect, estimated 12 as the number of water for each surfactant molecule in the micelle. In this paper, the hydration number of SDS micelles in water is calculated to be about 13—14 from a similar correction for the electroviscous effect; this is in fair agreement with Courchene's value.

---

[22] Literally—away from the surface on the ion. While peri-surface means at and round-about the ionic surface. Ref. 10.

[23] R. A. Parker and S. P. Wasik, *J. Phys. Chem.*, **62**, 967 (1958).

[24] W. L. Courchene, *ibid.*, **68**, 1870 (1964).