BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 1551—1552 (1973)

Viscosity *B* Coefficients for Some Alkyl Sulfates in Aqueous Solutions

Kunio Tamaki, Yōko Ōhara, and Yoshio Isomura
Department of Chemistry, Yokohama City University, Kanazawa-ku, Yokohama 236

(Received May 29, 1972)

In the previous paper,[1] the change in the partial molal heat capacity of a homologous series of sodium alkyl sulfates has been discussed in terms of the change in water structure for the dissolution of the solutes into water. This paper will drscribe our experimental findings on the viscosity of sodium alkyl sulfates in aqueous solutions.

Experimental

The viscosities were measured in Ubbelohde-type viscosimeters with flow times for water at 25 °C of about 800 s in a constant-temperature bath controlled to ±0.01 °C of the specified temperature. It was found that the kinetic energy correction was negligible in this work. The densities were measured in Ostwald pycnometers. The relative viscosities were calculated in the usual manner, using the data on the flow time and the density. The sodium alkyl sulfates used were the same samples as those described in the previous paper.[1]

Results and Discussion

The viscosity of an aqueous solution of electrolytes, η, can be represented by the Jones-Dole equation:[2]

$$\eta/\eta_0 = 1 + AC^{1/2} + BC \tag{1}$$

where η_0 is the viscosity of water, C is the concentration (molality), A is the constant related to the ion-ion interaction, and B is the viscosity B coefficient. Equation (1) is thus converted to:

$$(\eta/\eta_0 - 1)/C^{1/2} = A + BC^{1/2} \tag{2}$$

When the left-hand side of Eq. (2) is plotted against $C^{1/2}$, the viscosity B coefficient is obtained as the slope of a linear line. For example, Fig. 1 shows the results of the plotting of Eq. (2) at 25 °C. The values of the viscosity B coefficient thus obtained are summarized in Table 1. The estimated error in the B values is ±0.005. The constant, A, was theoretically interpreted by Falkenhagen and can be calculat-

---

[1] K. Tamaki, Y. Isomura, and Y. Ōhara, This Bulletin, **45**, 2939 (1972).

[2] G. Jones and M. Dole, *J. Amer. Chem. Soc.*, **51**, 1950 (1929).

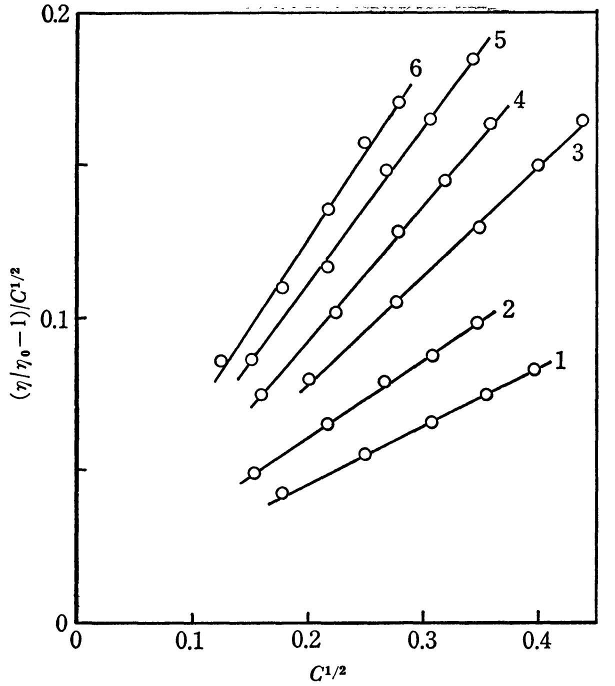

Fig. 1. $(\eta/\eta_0-1)/C^{1/2}$ *vs.* $C^{1/2}$ plot at 25 °C. 1, methyl; 2, ethyl; 3, propyl; 4, butyl; 5, pentyl; 6, hexyl.

Table 1. Viscosity B coefficient for sodium alkyl sulfates at several temperatures

Compound	10 °C	25 °C	35 °C	45 °C	50 °C
Methyl	—	0.188	0.190	—	0.200
Ethyl	0.263	0.265	—	—	0.270
Propyl	—	0.348	0.340	0.327	—
Butyl	—	0.423	—	—	—
Pentyl	—	0.504	0.457	—	—
Hexyl	—	0.582	—	—	—

ed using the data of the limiting equivalent conductivity of the salt, cation, and anion.[3] In this work, the electrical conductivities were measured with a Yokogawa BVZ-13A audio-frequency bridge using a frequency of 1000 Hz. In general, the calculated values of A were found to be in good agreement with those obtained from the semi-empirical Eq. (2).

The B values for the homologous sodium alkyl sulfates increase linearly with the number of carbon atoms in the alkyl chains at 25 °C. The average increment per methylene group is 0.079. Similar relations have been observed for homologous alkylammonium bromides[4] and for homologous amino acids, $NH_3^+(CH_2)_x COO^-$.[5] The increments per methylene group were 0.080 at 25 °C for the alkylammonium bromides[4] and 0.084 at 25 °C for the amino acids.[5] The contribution permethylene group to the viscosity B coefficient is considered to be about 0.080 at 25 °C.

As far as we are aware, there has been no report of a negative B coefficient for organic electrolytes in water.[4–8] This suggests the water-structure-making effect for all organic electrolytes, if we adopt the view of Gurney,[9] the B coefficient being interpreted in terms of a specific ion-solvent interaction. However, the viscosity B coefficient consists of the contribution from the ion-solvent interaction plus the contribution from the size of the ion (Einstein effect).[10] Large molecular ions such as organic ions may be expected to have a large viscosity increment arising from the Einstein effect.[10] With regard to the temperature dependence of the B values, this Einstein effect will remain fairly constant and better criteria for structure influences will be obtained.[10] Kay *et al.*[6] reported an increase in the viscosity B coefficient with the temperature for a structure-breaking ion such as tetramethylammonium salt and a decrease for a structure-making salt, such as tetrapropyl- and tetrabutylammonium salts. A similar relation has been reported for the homologous amino acids.[5] It may be seen in Table 1 that the methyl salt, a structure-breaking solute,[1] shows a slight increase in B value with the increase in the temperature between 25 and 50 °C, and that the ethyl salt, a borderline solute,[1] is rather insensitive to the temperature between 10 and 50 °C. On the other hand, for propyl salt, which is classified as a structure-making solute,[1] the B value decreases slightly with the temperature between 25 and 45 °C. A more remarkable decrease was found in the range of 25—35 °C for pentyl salt, which is an excellent structure-making solute.[1] On comparing these facts with those given in the previous paper,[1] it may be concluded for the homologous sodium alkyl sulfates that there is a close relationship between the temperature dependence of the viscosity B coefficient and the change in the partial molal heat capacity.[1]

The B values listed in Table 1 are naturally made up of the sum of the contributions from both sodium and alkyl sulfate ions. Fortunately, the B values of the sodium ion is practically constant between 15 and 42.5 °C.[10] Therefore, the temperature dependence of the viscosity B coefficient of the sodium salts discussed above conveniently reflects the nature of the alkyl sulfate anions.

---

3) H. S. Harnd and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd ed, Reinhold, New York (1958), p. 240.

4) J. E. Desnoyers, M. Arel and P-A. Leduc, *Can. J. Chem.* **47**, 547 (1969).

5) W. Devine and B. M. Lowe, *J. Chem. Soc., A*, **1971**, 2113.

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

7) C. T. Robertson and H. J. V. Tyrell, *J. Chem. Soc., A*, **1969**, 1938.

8) B. M. Lowe and H. M. Rendall, *Trans. Faraday Soc.*, **67**, 2318 (1971).

9) R. W. Gurney, "Ionic Processes in Solution," McGraw-Hill, New York (1953), p. 159.

10) R. H. Stokes and R. Mills, "Viscosity of Electrolytes and Related Properties," Pergamon, Oxford (1965), p. 39.