BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 2939—2940 (1972)

Heat Capacity Changes of Some Sodium Alkylsulfates in Aqueous Solutions

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(Received January 31, 1972)

Recently, the physical properties of aqueous electrolyte solutions have mainly been discussed in terms of the resultant change in the water structure upon the introduction of ions into water.[1] Small ions, such as lithium, sodium, and fluoride ions, have a net structure-making effect on the water structure, while large ions, such as potassium, chloride, and bromide ions, have a net structure-breaking effect.[1] On the other hand, nonpolar solutes such as hydrocarbons and amphiphilic compounds, such as alkyl alcohols or fatty acids, act as water-structure-making solutes in water; that is, the water molecules form an "iceberg" around nonpolar groups of the molecules.[2] This type of hydration is called "hydrophobic hydration" or "hydration of the second kind."[1]

It seems that it would be interesting to study the strength of hydrophobic hydration for amphiphilic electrolytes, that is, the molecules with both nonpolar and ionized groups. The solute-solvent interaction of this kind of compound is determined from the balance of the two different modes of hydration (ionic hydration and hydrophobic hydration). The object of this paper is to consider the role of alkyl groups in the change in the water structure, in the case of a series of sodium alkylsulfates; this work is based on the experimentally-determined values of the change in the partial molal heat capacity. The method has been applied to tetraalkylammonium salts,[3] sodium tetraphenylboron,[4] aliphatic alcohol,[5] and poly(ethylene glycol) and related compounds.[6]

At a constant pressure, the following relation is derived between the heat of solution at an infinite dilution, ΔH_s^0, and the temperature, T:[7]

$$d\Delta H_s^0/dT = \Delta C_p^0 = \bar{C}_p^0 - C_p^s$$

where ΔC_p^0 is the change in the heat capacity for dissolution, $\bar{C}_p^0$ is the partial molal heat capacity of the solute at an infinite dilution, and C_p^s is the heat capacity of the pure solute. As the C_p^s values of the sulfates are unavailable at present, discussion will be limited to the ΔC_p^0 values in this paper.

Experimental

Materials. The sodium methylsulfate used in this work was prepared from the precipitation by the addition of petroleum benzine to an ethanol solution of commercial sodium methylsulfate monohydrate. Analysis showed the obtained sample was anhydrous. The other sodium alkylsulfates were synthesized by the esterification of the corresponding alcohols by concentrated sulfuric acid, and were neutralized with a concentrated solution of sodium hydroxide. The reaction mixtures were dried in air and extracted with ethanol, and then the products were recrystallized twice from ethanol and dried in a vacuum desiccator. The water was obtained by redistillation from an alkaline permanganate solution.

Apparatus. Heat-of-solution measurements at 10, 25, and 45°C were made with an Ōyodenki Kenkyujo (Tokyo) Model CM-204D1 twin conduction calorimeter. An ampoule containing an aproppriate amount of a sample was mechanically broken into 50 cc of water at a constant temperature. Because of the hygroscopic property of the sodium alkylsulfates used, the samples introduced into ampoules were dried in a vacuum before final weighing. The calorimeter was checked by measuring the heats of solution of potassium chloride. The values thus obtained were within 2% of those reported in the literature.[8]

Results and Discussion

The heat of solution at an infinite dilution is generally obtained by extrapolating the plot of the heat of solution as a function of the concentration (or the square root of the concentration in the case of electrolytes). However, it was found that the results obtained at concentrations below 0.01M showed some scattered values. Thus, the heats of solution at 0.01M, ΔH_s, are presented in Table 1. A correction for the heats of dilution must be made to obtain ΔH_s^0. With sodium chloride, a typical uni-univalent electrolyte, the heat of dilution from a solution at 0.01M to one at an

Table 1. Heats of solution of sodium alkylsulfates at 0.01 M

$ROSO_3Na$	10°C kcal/mol	25°C kcal/mol	45°C kcal/mol	ΔC_p° cal/deg·mol
Methyl	2.30±0.03	2.01±0.02	1.70±0.01	−17
Ethyl	1.20±0.04	1.14±0.02	1.15±0.02	≒0
Propyl	1.23±0.01	1.38±0.02	1.63±0.05	+11
Butyl	1.44±0.02	1.74±0.04	2.20±0.04	+21
Pentyl	1.00±0.05	1.55±0.02	2.33±0.06	+38
Hexyl	1.20±0.04	1.98±0.04	3.08±0.08	+54

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infinite dilution is −0.039 kcal/mol;[9] this value is sometimes comparable with the range of error of this work. The average values of ΔC_p^0 between 10 and 45°C are calculated by assuming that the change in the partial molal heat capacity at 0.01 M is equal to that at an infinite dilution. The ΔC_p^0 values obtained on the basis of this assumption are also listed in Table 1. A procedure similar to this was employed by Greyson and Snell.[10]

As will be seen in Table 1, sodium methylsulfate shows only negative ΔC_p^0 values in the homologous series. Though the ΔC_p^0 or $\bar{C}_p^0$ value of an electrolyte naturally consists of the sum of the contributions of both cation and anion, so far no reliable procedure for assigning a value to the individual ions has been established. The $\bar{C}_p^0$ values, and thus the ΔC_p^0 values, of most simple electrolytes are negative;[11] *e.g.*, the $\bar{C}_p^0$ value of sodium chloride is −22.1 cal/deg·mol at 25°C.[11] As the ΔC_p^0 value of methyl alcohol is 23.1 cal/deg·mol,[5] the methyl group must cause a positive change in the ΔC_p^0 value. The overall change in the partial molal heat capacity of sodium methylsulfate is as low as −17 cal/deg·mol as is shown in Table 1; this means that the methyl salt displays behavior rather similar to that of simple salt in the water phase. In this sense, sodium methylsulfate may be considered to behave as a net structure-breaking salt.

The ΔH_s values of sodium ethylsulfate are virtually independent of the temperature. With this salt, the contributions of the two types of hydration (ionic and hydrophobic) seem to cancel each other out.

The ΔC_p^0 values of sodium propylsulfate and higher homologues are positive; these salts exhibit an excellent water-structure-making effect. The positive ΔC_p^0 values in Table 1 indicate that the promotion of the water structure ("iceberg" formation[2]) around the nonpolar groups of these salts increases with the number of carbon atoms of alkyl chain.

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