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Partial Molar Volumes of Sodium Alkyl Sulfates and Disodium α,ω-Alkanediyl Disulfates in Aqueous Solutions

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Synopsis. The densities of aqueous solutions of sodium alkyl sulfates, $H(CH_2)_nSO_4Na$ (n=1—6, 8, 10, 12) and disodium α,ω-alkanediyl disulfates, $NaO_4S(CH_2)_nSO_4Na$ (n=2—4, 6, 8, 10) were measured at 25 °C, and the limiting partial molar volumes were calculated. The group partial molar volume of SO_4^- was estimated to be 44.0 cm^3 mol^{-1}.

The limiting partial molar volumes of organic solutes can be approximately represented by the additivity of the group partial molar volumes.[1] In a previous paper,[2] the limiting partial molar volumes for homologous sodium perfluoroalkanoates were reported. This paper is concerned with the limiting partial molar volumes for homologous sodium alkyl sulfates and disodium α,ω-alkanediyl disulfates in aqueous solutions. The assignments of the group partial molar volumes of SO_4^- are given.

Experimental

Sodium dodecyl sulfate was of SU grade from Tokyo Kasei Kogyo Co., Ltd. The other homologs of sodium alkyl sulfates were synthesized by esterification of the corresponding alcohols (Tokyo Kasei Kogyo Co., Ltd.) using concentrated sulfuric acid below 10 °C. The solutions were neutralized with a solution of sodium hydroxide. The reaction mixtures were dried in air and extracted with ethanol. The obtained salts were purified several times by recrystallization from ethanol. All of the salts were dried in vacuo at 100 °C for several days, and the molecular weights were checked by means of volumetric analysis. A known amount of a sample was dissolved in water and passed through an ion-exchange resin in the hydrogen form; the eluent was titrated with a standard NaOH solution. It was found that the purities were better than 99.5%. Disodium α,ω-alkanediyl disulfates were the same samples as described in a previous paper.[3] The water was triply distilled. The solutions were made by weight.

The densities were measured at 25 °C to $\pm 3\times10^{-6}$ g cm^{-3} using a vibrating-tube densimeter (Anton Paar DMA 60). The apparatus constant of the meter was determined using water and dry air as standard substances; their densities were taken from the literature.[4,5]

Results and Discussion

Apparent Molar Volumes. The apparent molar volumes, ϕ_v, in cm^3 mol^{-1} were calculated from the densities using the following equation:

$$\phi_v = \frac{1000(\rho_0-\rho)}{m\rho\rho_0} + \frac{M}{\rho}, \tag{1}$$

where m is the molal concentration, M the molar mass in g mol^{-1}, and ρ_0 and ρ the densities in g cm^{-3} of water and of a solution, respectively. The apparent molar volume of the electrolytes is given by the following equation:[6]

$$\phi_v = \phi_v^0 + A_v c^{1/2} + B_v c, \tag{2}$$

where c is the molar concentration in mol dm^{-3}; ϕ_v^0 is the limiting value, which is identical to the limiting partial molar volume, V^0; A_v and B_v are constants. The values of constant A_v for water at 25 °C are 1.868 and 9.706 cm^3 dm$^{3/2}$ mol$^{-3/2}$ for 1-1 and 2-1 electrolytes, respectively.[6] The values of V^0 were obtained from the relation $\phi_v - A_v c^{1/2}$ versus c. For example, Fig. 1 shows the results of plotting Eq. 2 for the series of sodium alkyl sulfates. It was found that the values of $\phi_v - A_v c^{1/2}$ for both homologs were only slightly dependent on c. Measurements for sodium decyl sulfate, and dodecyl sulfate were carried out over a concentration range below the critical micelle concentrations and the average values of $\phi_v - A_v c^{1/2}$ were taken to V^0. The obtained values of

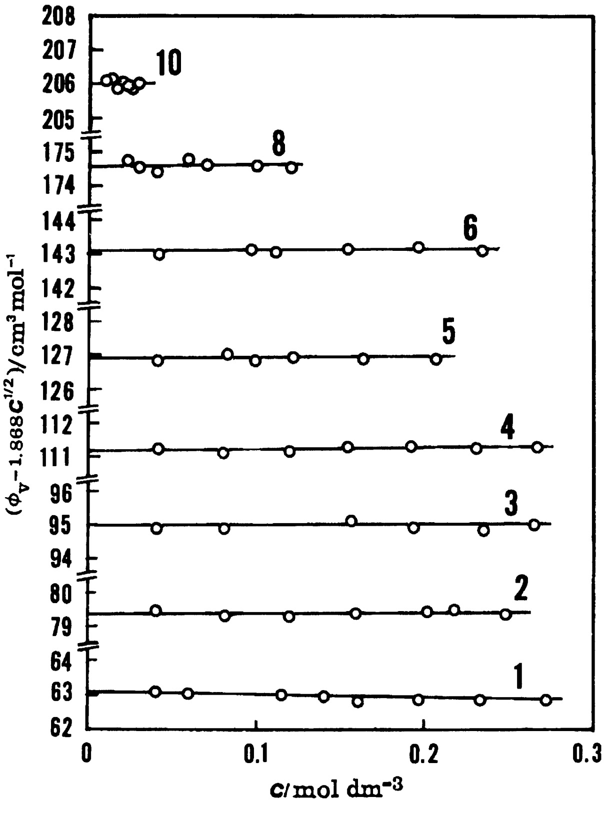

Fig. 1. Apparent molar volumes of $H(CH_2)_nSO_4Na$ at 25 °C. 1, methyl; 2, ethyl; 3, propyl; 4, butyl; 5, pentyl; 6, hexyl; 8, octyl; 10, decyl.

Table 1. Limiting Partial Molar Volumes at 25 °C

n	$V^0/\mathrm{cm^3\,mol^{-1}}$				
	$H(CH_2)_nSO_4Na$				
1	63.1	$62.6^{a)}$			
2	79.4	$77.6^{a)}$		$81.1^{c)}$	
3	95.0	$92.9^{a)}$		$96.2^{c)}$	
4	111.2		$110.0^{b)}$	$111.7^{c)}$	
5	126.9	$124.4^{a)}$		$128.4^{c)}$	
6	143.0	$139.9^{a)}$		$141.3^{c)}$	
8	174.5	$173.3^{a)}$	$173.1^{b)}$	$172.6^{c)}$	
10	206.0		$205.5^{b)}$	$204.1^{d)}$	
12	237.0	$238.0^{a)}$	$238.0^{b)}$	$234.4^{d)}$	$236.8^{e)}$
	$NaO_4S(CH_2)_nSO_4Na$				
2	105.5				
3	122.9				
4	137.2				
6	171.1				
8	199.3				
10	231.2				

a) Ref. 7, b) Ref. 8, c) Ref. 9, d) Ref. 10, e) Ref. 11.

V^0 are summarized in Table 1 along with other relevant literature data. The some scatter in the literature data probably results from the samples and experimental techniques used. In this work, the samples were repeatedly recrystallized and the purities were checked.

Assignment of Group Partial Molar Volumes. From the additivity rule, the V^0 values for $H(CH_2)_nSO_4Na$ and $NaO_4S(CH_2)_nSO_4Na$ can respectively be expressed by the following equations:

$$V^0 = V^0(CH_3) + (n-1)V^0(CH_2) + V^0(SO_4Na) \tag{3}$$

and

$$V^0 = nV^0(CH_2) + 2V^0(SO_4Na). \tag{4}$$

The $V^0(CH_3)$ value is given by the following difference:

$$V^0(CH_3) = V^0[H(CH_2)_nSO_4Na] - V^0[(CH_2)_{2n-2}(SO_4)_2]/2. \tag{5}$$

The mean value of $V^0(CH_3)$ calculated from the data obtained in this work is 26.6 $\mathrm{cm^3\,mol^{-1}}$. This value is in fairly good agreement with 26.3 $\mathrm{cm^3\,mol^{-1}}$ reported in a previous paper.[2)]

As indicated in Table 1, the V^0 values increase as the alkyl or polymethylene chain length increases. The V^0 values for $H(CH_2)_nSO_4Na$ and $NaO_4S(CH_2)_nSO_4Na$ obtained in this work were respectively fitted by a least-square method to the following equations:

$$V^0/\mathrm{cm^3\,mol^{-1}} = 47.72 + 15.81n \tag{6}$$

and

$$V^0/\mathrm{cm^3\,mol^{-1}} = 75.33 + 15.62n. \tag{7}$$

We can therefore estimate the $V^0(CH_2)$ values as 15.7 $\mathrm{cm^3\,mol^{-1}}$.

The $V^0(SO_4Na)$ value can be estimated by two approaches. For the homolog of $NaO_4S(CH_2)_nSO_4Na$, the $V^0(SO_4Na)$ values can be calculated using the value of $V^0(CH_2)$=15.6 $\mathrm{cm^3\,mol^{-1}}$. The mean value of $V^0(SO_4Na)$ becomes 37.8 $\mathrm{cm^3\,mol^{-1}}$. The $V^0(SO_4Na)$ value is also calculated from the data of V^0 for $H(CH_2)_nSO_4Na$ using the values of $V^0(CH_3)$=26.6 $\mathrm{cm^3\,mol^{-1}}$ and $V^0(CH_2)$=15.8 $\mathrm{cm^3\,mol^{-1}}$: the value becomes 37.0 $\mathrm{cm^3\,mol^{-1}}$. We can therefore estimate that the mean value of $V^0(SO_4Na)$ is 37.4 $\mathrm{cm^3\,mol^{-1}}$.

The $V^0(Na^+)$ value becomes -6.6 $\mathrm{cm^3\,mol^{-1}}$ if we use -5.4 $\mathrm{cm^3\,mol^{-1}}$ as the $V^0(H^+)$ value at 25 °C, as recommended by Millero.[12)] Then, the $V^0(SO_4^-)$ value becomes 44.0 $\mathrm{cm^3\,mol^{-1}}$.

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