Partial Molar Volumes of Sodium Perfluoroalkanoates and Lithium Perfluoro-1-alkanesulfonates in Aqueous Solutions

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Synopsis. The densities of aqueous solutions of sodium perfluoroalkanoates, $F(CF_2)_nCOONa$ (n=1—4, 6, 7) and lithium perfluoro-1-alkanesulfonates, $F(CF_2)_nSO_3Li$ (n=1, 4, 8) were measured at 25 °C, and the limiting partial molar volumes were calculated. The assignment of group partial molar volumes is discussed.

It is well-known that the limiting partial molar volumes of organic solutes can be approximately represented by the additivity of group partial molar volumes.[1] The volumetric properties of perfluoroalkane compounds have received less attention. In our previous paper,[2] the solution properties such as heats of solution, viscosity B coefficients, and surface tensions of homologous sodium perfluoroalkanoates were reported. This paper describes the experimental results of the limiting partial molar volumes for homologous sodium perfluoroalkanoates and some lithium perfluoro-1-alkanesulfonates. Also, assignments of the group partial molar volumes of CF_2 and CF_3 are given.

Experimental

The homologs of sodium perfluoroalkanoates were the same samples as those described in a previous paper.[2] CF_3SO_3Li and $C_8F_{17}SO_3Li$ were prepared by neutralizing the corresponding acids with a solution of lithium hydroxide. CF_3SO_3H was from Tokyo Kasei Kogyo Ltd., and $C_8F_{17}SO_3H$ was prepared from the potassium salt (Dainihon Ink and Chemicals, Inc.) by distillation from concentrated sulfuric acid.[3] $C_4F_9SO_3Li$ was prepared by a reaction between perfluoro-1-butanesulfonyl fluoride (Aldrich) with a concentrated solution of lithium hydroxide.[3] The obtained salts were purified several times by recrystallization from benzene-ethyl acetate solutions. 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 99.8% for CF_3SO_3Li, 96% for $C_4F_9SO_3Li$, and 99% for $C_8F_{17}SO_3Li$. The water was triply distilled. The solutions were made by weight.

The densities were measured at 25 °C to $\pm3\times10^{-6}$ g cm^{-3} using a vibrating-tube densimeter, twin-type SS-D-200, of the Shibayama Scientific Co., Ltd. Details of the procedure were described in a previous paper.[4]

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 equation:[5]

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

where c is the molar concentration in mol dm^{-3}: $\phi_v{}^0$ is the limitimg value, which is identical to the limiting partial molar volume, V^0; A_v, and B_v are constants. The value of the constant A_v is 1.868 cm^3 dm$^{3/2}$ mol$^{-3/2}$ for water at 25 °C.[5] The values of V^0 were obtained from the relation $\phi_v-1.868\ c^{1/2}$ versus c. Measurements were carried out in a concentration range below the critical micelle concentrations. The critical micelle concentrations at 25 °C for C_4F_9COONa, $C_6F_{13}COONa$, and $C_7F_{15}COONa$ are 0.55, 0.080, and 0.030 mol dm^{-3} respectively.[2] The critical micelle concentrations at 25 °C for $C_4F_9SO_3Li$ and $C_8F_{17}SO_3Li$ were determined to 0.10 and 0.0065 mol dm^{-3}, respectively, by measurements of surface tension. The obtained values of V^0 and B_v are summarized in Table 1.

Assignment of Group Partial Molar Volumes. From the additivity rule, the V^0 values for $F(CF_2)_nCOONa$ and $F(CF_2)_nSO_3Li$ can respectively be experessed by the following equations:

$$V^0 = V^0(CF_3) + (n-1)\,V^0(CF_2) + V^0(COO^-) + V^0(Na^+), \tag{3}$$

$$V^0 = V^0(CF_3) + (n-1)\,V^0(CF_2) + V^0(SO_3{}^-) + V^0(Li^+). \tag{4}$$

The values of $V^0(Na^+)$ and $V^0(Li^+)$ become −6.6 and −6.3 cm^3 mol^{-1}, respectively, if we use −5.4 cm^3 mol^{-1} as the $V^0(H^+)$ value at 25 °C, recommended by Millero.[6]

As indicated in Table 1, the V^0 values increase as the perfluoroalkyl-chain length increases. The V^0 values for $F(CF_2)_nCOONa$ listed in Table 1 are fitted by a least-square method to the following equation:

Table 1. Limiting Partial Molar Volumes at 25 °c

n	V^0/cm^3 mol^{-1}	B_v/cm^3 dm^3 mol^{-2}
	$F(CF_2)_nCOONa$	
1	57.2	−0.87
2	81.8	−0.75
3	104.9	−0.92
4	128.5	−1.82
6	175.9	−0.84
7	199.3	—
	$F(CF_2)_nSO_3Li$	
1	74.7	−2.9
4	146.5	−2.6
8	238	—

$$V^0/\text{cm}^3\,\text{mol}^{-1} = 34 + 23.63\,n. \quad (5)$$

We can therefore estimate that the $V^0(CF_2)$ value is 23.6 $cm^3\,mol^{-1}$.

The values of $V^0(COO^-)$ and $V^0(SO_3^-)$ were calculated using the V^0 values for hydrocarbon compounds from the literature. For this purpose, it is necessary to assign the values of $V^0(CH_3)$ and $V^0(CH_2)$. The $V^0(CH_3)$ value is given by the difference;

$$V^0(\text{CH}_3) = V^0[\text{H}(\text{CH}_2)_n\text{X}] - V^0[(\text{CH}_2)_{2n-2}\text{X}_2/2], \quad (6)$$

where X is the terminal group such as COONa or OH. Sakurai[7] reported the V^0 values of the homologs of $H(CH_2)_nCOONa$ and $(CH_2)_n(COONa)_2$. The mean value of $V^0(CH_3)$ calculated from the data at 25 °C reported by Sakurai[7] is 26.2 $cm^3\,mol^{-1}$. Nakajima et al.[8] reported that $V^0(CH_3)$=26.4 $cm^3\,mol^{-1}$ on the basis of their V^0 values for the homologs of $H(CH_2)_nOH$ and $(CH_2)_n(OH)_2$. Therefore, we can estimate the $V^0(CH_3)$ value as being 26.3 $cm^3\,mol^{-1}$.

The $V^0(CH_2)$ value can be calculated from the V^0 values for homologous organic compounds. For example, the V^0 values reported by Sakurai[7] are fitted to the following equations:

$$V^0/\text{cm}^3\,\text{mol}^{-1} = 22.73 + 15.54\,n, \quad (7)$$

for $H(CH_2)_nCOONa$ (n=2—6), and

$$V^0/\text{cm}^3\,\text{mol}^{-1} = 22.95 + 15.76\,n, \quad (8)$$

for $(CH_2)_n(COONa)_2$ (n=3, 4, 6, 8). Therefore, the mean value of $V^0(CH_2)$ is estimated to be 15.7 $cm^3\,mol^{-1}$.

The $V^0(COO^-)$ value, calculated from the data of V^0 for $H(CH_2)_nCOONa$ reported by Sakurai[7] using the values of $V^0(CH_3)$, $V^0(CH_2)$, and $V^0(Na^+)$, becomes 18.3 $cm^3\,mol^{-1}$.

Table 2. Group Partial Molar Volumes at 25 °C

Group	$V^0/cm^3\,mol^{-1}$
CF_2	23.6
CF_3	46.1
CH_2	15.7
CH_3	26.2
COO^-	18.3
SO_3^-	34.0
Na^+	−6.6
Li^+	−6.3

We can now estimate the $V^0(CF_3)$ value from Eq. 3, using the values of $V^0(CF_2)$, $V^0(COO^-)$, and $V^0(Na^+)$. The mean value of $V^0(CF_3)$ becomes 46.1 $cm^3\,mol^{-1}$.

The $V^0(SO_3^-)$ value can be calculated from the data of V^0 for the homologs of $H(CH_2)_nSO_3Na$ (n=1—6) reported in a previous paper[4] using the values of $V_0(CH_3)$, $V^0(CH_2)$, and $V^0(Na^+)$. For these homologous salts, the V^0 values are fitted to

$$V^0/\text{cm}^3\,\text{mol}^{-1} = 37.84 + 15.83\,n. \quad (9)$$

Therefore, the $V^0(CH_2)$ value is 15.8 $cm^3\,mol^{-1}$ for these homologous salts. Then, the mean value of $V^0(SO_3^-)$ becomes 34.0 $cm^3\,mol^{-1}$. All of the values of group partial molar volumes estimated above are summarized in Table 2.

The V^0 Values of $F(CF_2)_nSO_3Li$. The V^0 values for $F(CF_2)_nSO_3Li$ can be estimated from Eq. 4, using the group partial molar volumes listed in Table 2. The calculated values of V^0 for CF_3SO_3Li, $C_4F_9SO_3Li$, $C_8F_{17}SO_3Li$ are 73.8, 144.6, and 239 $cm^3\,mol^{-1}$, respectively. The values of CF_3SO_3Li and $C_8F_{17}SO_3Li$ are in fairly good agreement with the experimental values of 74.7 and 238 $cm^3\,mol^{-1}$, respectively, as is listed in Table 1. With $C_4F_9SO_3Li$, the experimental value is somewhat larger than the calculated value. This discrepancy is probably due to the sample, since $C_4F_9SO_3Li$ is difficult to purify.

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