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Solution Properties of Sodium Perfluoroalkanoates. Heats of Solution, Viscosity *B* Coefficients, and Surface Tensions

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The heats of solution, the viscosity *B* coefficients, and the surface activities of sodium perfluoroalkanoates, $F(CF_2)_nCOONa$, n=1—4, 6, 7), in water were measured. The changes in the heat capacity for dissolution in water, ΔC_p^∞, calculated from the heats of solution at 15, 25, and 35 °C, were positive for the salts, and the ΔC_p^∞ values increased with an increase in n. The increment in the ΔC_p^∞ values per CF_2 group was 93 J K^{-1} mol^{-1}. The viscosity *B* coefficients increased with the chain length at a definite temperature, and the increment in the viscosity *B* coefficients per CF_2 group was 0.119 dm^3 mol^{-1} at 25 °C. Further, the viscosity *B* coefficients for all the salts decreased with the increase in the temperature between 15 and 35 °C. Traube factors, as obtained from the surface tensions, were found to be 3.0 for the homologs from C_2 salt to C_7 salt. The results are discussed in comparison with those of sodium alkanoates, $H(CH_2)_nCOONa$.

The behavior of homologous organic monovalent anions, such as alkyl sulfates,[1,2] alkanesulfonates,[3] and dialkyl phosphates,[4] in water were discussed in previous papers. Perfluoroalkanoates are other organic monovalent anions. It is well-known that perfluoroalkanoic acids are considerably more hydrophobic than alkanoic acids. This stronger hydrophobicity of perfluorocarbon compounds leads to a greater lowering of the surface tensions[5] and to lower critical micelle concentration values[6] when compared to hydrocarbon compounds of the same chain length. In the present paper, experimental results will be reported on the temperature dependence of the heats of solution and the viscosity *B* coefficients, and on the surface active properties in water at 25 °C for the homologs of sodium perfluoroalkanoates ($F(CF_2)_nCOONa$, which will be abbreviated as f-C_n). The results will be discussed in comparison with those for homologs of sodium alkanoates ($H(CH_2)_nCOONa$, which will be abbreviated as C_n).

Experimental

Homologs of f-C_n were prepared by the neutralization of the corresponding perfluoroalkanoic acids (97—99%) with a solution of sodium hydroxide, after which the water was evaporated to dryness; the salts were purified several times by recrystallization from benzene-ethanol solutions. The salts of f-C_1 and f-C_2 were hygroscopic; all the salts were dried in vacuo at room temperature 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 obtained samples have no water of crystallization. The homologs of C_n were commercial samples. The salts of C_1 and C_2 were used as received. The other C_n samples were purified by recrystallization from ethanol. All the salts were dried in vacuo at 100 °C for several days. The water was triply distilled.

The heats of solution were measured at 15, 25, and 35 °C using a twin isoperibol calorimeter, TIC-2C, of the Tokyo Riko Co., Ltd., by a method similar to that described in a previous paper.[3]

The viscosities were measured at 15, 25, and 35 °C using an automatic viscometer of the Shibayama Scientific Co., Ltd. The densities were measured using a vibrating-tube densimeter, twin-type SS-D-200, of the Shibayama Scientific Co., Ltd. The details of the procedure were described in a previous paper.[3] The electric conductivities were measured with an LCR meter, AG-4301B, of the Ando Electric Co., Ltd., using a frequency of 1000 Hz.

The surface tensions were measured at 25°C by means of the Wilhelmy method using a CBVP-A3 tensiometer of the Kyowa Kaimenkagaku Co., Ltd.

Results and Discussion

Heats of Solution. Heat-of-solution measurements were carried out in the concentration range of $(1.8—3.6)\times10^{-3}$ mol dm^{-3} (below the critical micelle concentrations). In this concentration range, any dependence of the heat of solution on the concentration is within the limit of experimental error, so the average of three or more measurements has been taken as the heat of solution at an infinite dilution ΔH_s^∞. The ΔH_s^∞ values of f-C_n salts in water are listed in Table 1. The results from the ΔH_s^∞ values were then used to calculate the change in the heat capacity for dissolution at an infinite dilution, ΔC_p^∞:

$$\Delta C_p^\infty = \mathrm{d}\Delta H_s^\infty/\mathrm{d}T, \tag{1}$$

where T is the temperature. The ΔC_p^∞ values obtained at 25 °C are also listed in Table 1.

The sign and magnitude of ΔC_p^∞ can be taken as a relative measure of the structural effect upon the solvent water.[7,8] The ΔC_p^∞ values of common salts indicate negative values, whereas the ΔC_p^∞ values of hydrophobic solutes indicate positive values. As may be seen in Table 1, the ΔC_p^∞ signs of the f-C_n salts are all positive, indicating that these salts behave as structure-makers in water. Figure 1 shows an approximate linear relation between the ΔC_p^∞ values and the number of carbon atoms in the perfluoroalkyl chain, n; the average increment in the ΔC_p^∞ values per

Table 1. Heats of Solution and Heat-Capacity Changes of $F(CF_2)_nCOONa$

n	ΔH_s^∞/kJ mol^{-1}			ΔC_p^∞/J K^{-1}mol^{-1}
	15 °C	25 °C	35 °C	25 °C
1	−9.18±0.10	−8.70±0.02	−7.98±0.02	60±13
2	−12.43±0.10	−11.35±0.04	−9.71±0.03	136±16
3	−9.74±0.02	−7.32±0.03	−5.05±0.02	235±7
4	−6.17±0.10	−3.09±0.10	0.10±0.01	314±24
6	1.89±0.02	7.16±0.02	12.02±0.02	507±6
7	6.61±0.02	12.80±0.02	18.92±0.04	616±7

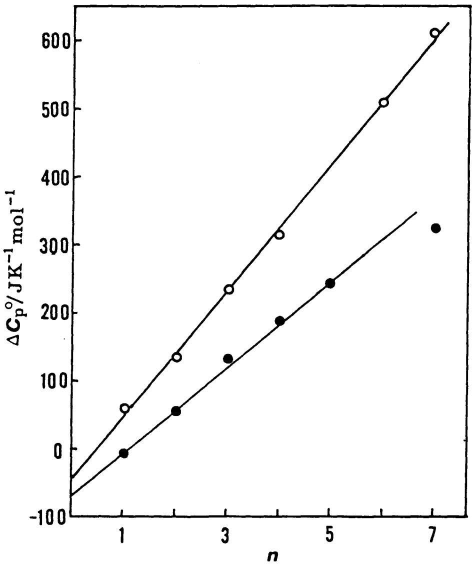

Fig. 1. Plots of ΔC_p^∞ against n.
○, $F(CF_2)_nCOONa$; ●, $H(CH_2)_nCOONa$.[9]

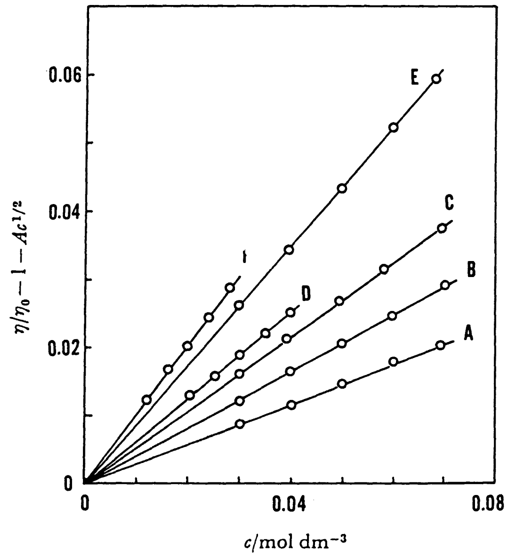

Fig. 2. Plots of $\eta/\eta_0-1-Ac^{1/2}$ against c for $F(CF_2)_n$-COONa at 25 °C.
A, CF_3COONa; B, C_2F_5COONa; C, C_3F_7COONa; D, C_4F_9COONa; E, $C_6F_{13}COONa$; F, $C_7F_{15}COONa$.

CF_2 group is 93 J K^{-1} mol^{-1}. The ΔC_p^∞ values for C_n salts in the temperature range of 25—35 °C, reported by Chaula and Ahluwalia,[9] are also included in Fig. 1. The average increment in ΔC_p^∞ per CH_2 group was reported as 59 J K^{-1}mol^{-1}. Therefore, the increment in the ΔC_p^∞ value per CF_2 group is about 1.6 times that of the CH_2 group.

The Viscosity *B* Coefficients. The viscosity of an aqueous solution of an electrolyte, η, for concentrations up to about 0.1 mol dm^{-3} can be represented by the Jones-Dole equation:[10]

$$\eta/\eta_0 = 1 + Ac^{1/2} + Bc, \tag{2}$$

where η_0 is the viscosity of water, c is the molar concentration, A is a constant related to ion-ion interaction, and B is the viscosity B coefficient. The A constant was interpreted theoretically by Falkenhagen and Vernon;[11] it can be calculated using the data of the limiting equivalent conductivities of the salt, the cation, and the anion. Equation 2 may be converted to:

$$\eta/\eta_0 - 1 - Ac^{1/2} = Bc. \tag{3}$$

When the left-hand side of Eq. 3, using the calculated values of A is plotted against c, the viscosity B coefficient is obtained as the slope of a straight line. The limiting molar conductivities required for the calculation of the A values in Eq. 3 for f-C_n salts were obtained from the measurements of the electric conductivities for aqueous solutions of these salts. The $Ac^{1/2}$ factor in Eq. 3 is relatively small, and the A values are insensitive to the variation in the temperature in the range of 15—35 °C, therefore, the values of A calculated using the limiting molar conductivities at 25 °C were also used for the A values at 15 and 35 °C. The A values for C_n salts were calculated from the limiting molar conductivities in the literature.[12] For example, Fig. 2 shows the results of the plotting of Eq. 3 for the f-C_n series at 25 °C. For each salt, the measurements were carried out in the concentration range below the critical micelle concentration. The values of A and B are listed in Table 2. The viscosities of the C_n salts at 25 °C were reported in a previous paper.[13] In this work, the temperature dependence of the viscosity B coefficients for the C_n series (n=1—7) were reinvestigated by means of a more elaborate method; the B values thus obtained are also included in Table 2. The viscosity B coefficient is related to the ion-solvent interaction and to the size and shape

Table 2. The Values of A, B, and dB/dT

n	A	B			dB/dT
	dm$^{3/2}$ mol$^{-1/2}$	dm^3 mol^{-1}			dm^3 mol^{-1} K^{-1}
		15 °C	25 °C	35 °C	25 °C
		F(CF$_2$)$_n$COONa			
1	0.0082	0.300	0.296	0.279	−0.0011
2	0.00865	0.424	0.418	0.373	−0.0026
3	0.0093	0.586	0.544	0.507	−0.0040
4	0.0096	0.688	0.635	0.589	−0.0050
6	0.0099	0.962	0.875	0.797	−0.0083
7	0.0101	1.141	1.027	0.945	−0.0098
		H(CH$_2$)$_n$COONa			
1	0.0082	0.320	0.317	0.307	−0.00065
2	0.0088	0.423	0.406	0.381	−0.0021
3	0.0092	0.517	0.498	0.463	−0.0027
4	0.0097	0.596	0.555	0.512	−0.0042
5	0.0099	0.687	0.631	0.581	−0.0053
6	0.0104	0.763	0.700	0.645	−0.0059
7	(0.0107)	0.860	0,768	0.724	−0.0068

of the ion, and it is highly specific for the electrolyte and the temperature.[14]

The B values of both homologous series of salts are found to increase with the chain length at a definite temperature. The average increment in the B values per CF$_2$ group for the f-C$_n$ series is larger than the increment in the B values per CH$_2$ group for C$_n$; the values are 0.119 dm^3 mol^{-1} per CF$_2$ group and 0.074 dm^3 mol^{-1} per CH$_2$ group at 25 °C.

The temperature dependence of the B values may be regarded as an index of the solute-solvent interaction; the B values increase with the temperature for a solvent-structure-breaking salt, while they decrease with the temperature for a solvent-structure-making solute.[15] For both the homologous organic salts, it may be seen in Table 2 that the B values decrease as the temperature is raised from 15 to 35 °C; these salts behave as structure-making salts in the water phase. The B values of electrolytes are determined by adding the individual contributions of the ions. Fortunately, the B value of sodium ion is insensitive to the temperature.[16] Therefore, the temperature dependences of the viscosity B coefficients of the sodium salts of both series of organic acids discussed above conveniently reflect the nature of the organic anions, and both F(CF$_2$)$_n$COO$^-$ and H(CH$_2$)$_n$COO$^-$ anions are structure-making ions. The temperature dependence of the viscosity B coefficients at 25 °C, dB/dT, are also listed in Table 2. Previous experimental results of dB/dT are available for C$_1$(−0.0022 dm^3 mol^{-1} K^{-1}), C$_2$(−0.0025 dm^3 mol^{-1} K^{-1}), and C$_3$(−0.0028 dm^3 mol^{-1} K^{-1}).[17] As is evident in Table 2, the dB/dT values for the f-C$_n$ series are smaller than those for the C$_n$ series with the same number of carbon atoms. In Fig. 3 the dB/dT values are plotted against n; the dB/dT values decrease with the number of carbon atoms in the perfluoroalkyl or alkyl chains of both series of salts; this means that the hydrophobic hydration increase with the length of the chains. The average value of dB/dT per CF$_2$ group is −0.00144 dm^3 mol^{-1} K^{-1}, while the value per CH$_2$ group is −0.00102 dm^3 mol^{-1} K^{-1}. These values reflect the stronger hydrophobic nature of the f-C$_n$ series than that of the C$_n$ series.

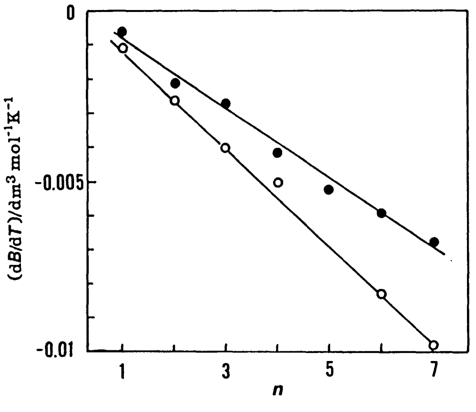

Fig. 3. Plots of dB/dT against n at 25 °C. ○, F(CF$_2$)$_n$COONa; ●, H(CH$_2$)$_n$COONa.

Surface Tensions. Figure 4 shows the surface tensions, γ, of aqueous solutions of the f-C$_n$ series as a function of the logarithmus of the molar concentration at 25 °C. It may be seen that all the salts reduce the surface tension of pure water. The shape of the surface tension-versus-concentration curve for an organic salt in aqueous solutions is considered to give a rough criterion of the behavior of the salt in water; common salt raises the surface tension of water, whereas hydrophobic salt reduces it.[18] Thus, f-C$_n$ salts are excellent hydrophobic structure-makers in water. On the other hand, the surface tensions of aqeous solutions of the C$_n$ series have been reported in the literature;[19] C$_1$ salt raises the surface tensions of pure water, whereas C$_2$ and higher homologous salts reduce

Table 3. Traube Factors, K, for $F(CF_2)_nCOONa$

n	$\gamma=60$ mN m^{-1}		$\gamma=50$ mN m^{-1}		$\gamma=40$ mN m^{-1}	
	c/mol dm^{-3}	K	c/mol dm^{-3}	K	c/mol dm^{-3}	K
2	0.52		1.45			
		3.0		2.8		
3	0.185		0.52		1.15	
		3.0		3.1		3.0
4	0.062		0.17		0.39	
		3.2		3.1		3.1
6	0.0060		0.0175		0.040	
		3.0		3.1		3.3
7	0.0020		0.0056		0.0122	

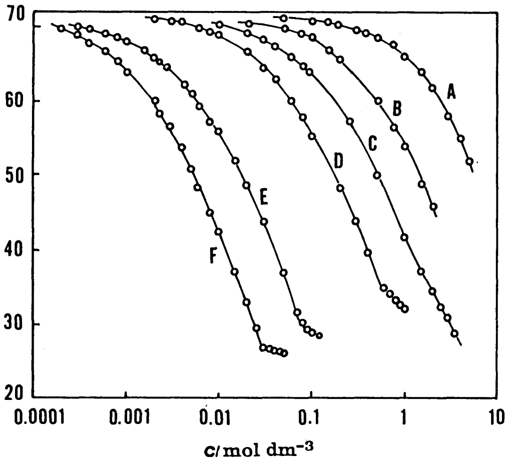

Fig. 4. Plots of surface tensions against c for $F(CF_2)_nCOONa$ at 25 °C.
A, CF_3COONa; B, C_2F_5COONa; C, C_3F_7COONa; D, C_4F_9COONa; E, $C_6F_{13}COONa$; F, $C_7F_{15}COONa$.

the surface tension of water. Therefore, the surface-active properties of the f-C_n series are much more higher than those of the C_n series.

In addition, the critical micelle concentrations can be estimated from the surface-tension-versus-concentration curves in Fig. 4; the values are 0.030 mol dm^{-3} for f-C_7 salt, 0.080 mol dm^{-3} for f-C_6 salt, and 0.55 mol dm^{-3} for f-C_4 salt. However, the critical micelle concentration becomes obscure for f-C_3 salt.

It may be found in Fig. 4 that the concentrations required for an equal lowering of the surface tension diminish by a constant factor for an additional CF_2 group in the perfluorocarbon chain. This is in accord with Traube's rule, which is expressed as;

$$C_n/C_{n+1}=K, \qquad (4)$$

where C_n and C_{n+1} are, respectively, the concentrations for successive members of the series with n and $n+1$ CF_2 groups at an equal lowering of the surface tension; K is termed the Traube factor. The values of K obtained from Fig. 4 are summarized in Table 3. It may be seen in Table 3 that the Traube factors are about 3.0 for the homologs from f-C_2 salt to f-C_7 salt. In a previous paper,[20] for homologous strong electrolytes K was derived as:

$$K=\exp(-\Delta G/2RT), \qquad (5)$$

where ΔG is the free energy of the adsorption of the CF_2 or CH_2 group from water to the surface, R is the gas constant, and T is the temperature. By the substitution of K=3.0 at 25 °C into Eq. 5, ΔG becomes −5.4 kJ mol^{-1}. This value is comparable to those in the literature: −5.4 kJ mol^{-1} reported by Phillips[21] and −5.9 kJ mol^{-1} reported by Davies and Rideal.[22]

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