Volumes and Heat Capacities of Sodium Perfluoroalkanoates in Water

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The apparent molar volumes and heat capacities of sodium perfluoroalkanoates, $NaCF_3(CF_2)_xCOO$, for *x* equal to 0, 1, 2, 4, and 6, were measured in water at 25 °C, and also at 5 and 55 °C in the case of $NaCF_3(CF_2)_6COO$, from densities and heat capacities per unit volume. The CF_2 contribution to the standard partial molar volumes and heat capacities are (23.57 ± 0.05) $cm^3 \cdot mol^{-1}$ and (124 ± 1) $J \cdot K^{-1} \cdot mol^{-1}$, respectively. The data for $NaCF_3(CF_2)_4COO$ and $NaCF_3(CF_2)_6COO$ were analyzed with a mass-action model to obtain the thermodynamic properties of micellization of the surfactants. The volumes and heat capacities of micellization at 25 °C are respectively (8.8 and 11.2) $cm^3 \cdot mol^{-1}$ and (−443 and −587) $J \cdot K^{-1} \cdot mol^{-1}$. At 5 °C, $NaCF_3(CF_2)_6COO$ is too close to the Krafft temperature to obtain data for the surfactant in the micellized form. At 55 °C, the volume and heat capacity of micellization are significantly smaller in magnitude than those at 25 °C.

Introduction

Fluorinated surfactants are of interest since they are much more hydrophobic than the corresponding hydrogenated surfactants. Many physical properties of such surfactants have been investigated in water and, in general, shorter-chain fluorinated surfactants show the same trends as longer-chain hydrogenated surfactants. One interesting feature of such surfactants is their tendency to form two types of mixed micelles with hydrogenated surfactants of the same chain length (Mukerjee and Mysel, 1975; Mukerjee and Yang, 1976; Funasaki and Hada, 1979). Such mixed micelles were investigated in our laboratory through volumes and heat capacities (Perron et al., 1981). Trends in the partial molar volumes and heat capacities of sodium perfluorooctanoate with concentration were presented at 25 °C in this paper, but the actual data were never published. Since then, Tamaki et al. (1990) have reported good volume data at 25 °C for the sodium perfluoroalkanoates in the premicellar region for carbon chains from 1 to 7, while Milioto et al. (1995) and Kato et al. (1992) have reported volume data for sodium perfluorooctanoate over the whole micellar region at 25 °C. However, a recent literature review on the thermodynamic properties of surfactants (Desnoyers and Perron, 1996a,b) shows that little precise data have been published on heat capacities of fluorinated amphiphiles in water. Our early studies were therefore completed and data are presently reported for sodium perfluoroalkanoates ($NaCF_3(CF_2)_xCOO$) in water, for *x* equal to 0, 1, 2, 4, and 6 at 25 °C, and also at 5 and 55 °C in the case of $NaCF_3(CF_2)_6COO$. The apparent molar heat capacities, measured with a flow microcalorimeter (Picker et al., 1971), require precise density data. The apparent molar volumes of the same systems were therefore measured with the same solutions. A comparison of these volumes with those of Tamaki, Milioto, and Kato will serve as a good test of the accuracy of the present data.

Experimental Section

The perfluoro carboxylic acids were purchased either from Pierce Chemicals (Sequanal grade) or from Columbia Organic Chemical Co. The sodium salts were prepared by neutralizing the corresponding acid in water with a 1 molar sodium hydroxide solution to a final pH slightly superior to the equivalence value. The water was removed with a vacuum flash rotary evaporator. At the end of the evaporation, 2-propanol was added to remove the residual water, through the formation of an azeotropic mixture, followed by acetone. The technique of drop injection directly in the vacuum flash evaporator has been used with the surface active solutions. Salts were recrystallized in an acetone−dichloromethane mixture. The salt was dissolved in hot acetone, the solution was filtered, and the dichloromethane was added slowly to the stirred solution. The ratio used was 1:4:*x*, where *x* was decreased as the chain length increased. Typically, its value is 6.5 for proprionate and 2.5 for hexanoate. The filtered salt was dried under vacuum in the presence of P_2O_5. The water content, determined by coulometric Karl Fischer titration (Photovolt Co, Aquatest II), was always less than 0.02%.

All solutions were prepared with distilled deionized water with concentrations expressed in $mol \cdot kg^{-1}$.

The volumetric heat capacities were measured with a Picker flow microcalorimeter (SODEV Model CP-C) (Picker et al., 1971). Essentially, two liquids at the same initial temperature and flowing at the same rate in twin cells are heated. The difference in the applied power ΔW necessary to maintain the final temperature of laboratory cell identical to the reference cell is proportional to the difference in the heat capacity per unit volume, $\Delta\sigma$, of the two liquids. If there is no heat loss (Desnoyers et al., 1976),

$$\frac{\Delta W}{W_o} = \frac{\Delta\sigma}{\sigma_o} \qquad (1)$$

where W_o is the basic power applied to the cells and σ_o is the heat capacity per unit volume of the reference liquid. The difference in specific heat capacity in $J \cdot K^{-1} \cdot g^{-1}$ can be calculated from

$$c_p = (1 + \Delta\sigma/\sigma_o)c_{p,o}d_o/d \qquad (2)$$

where *d* and d_o are the densities of the solution and of the solvent in $g \cdot cm^{-3}$ and $c_{p,o}$ is the heat capacity of the

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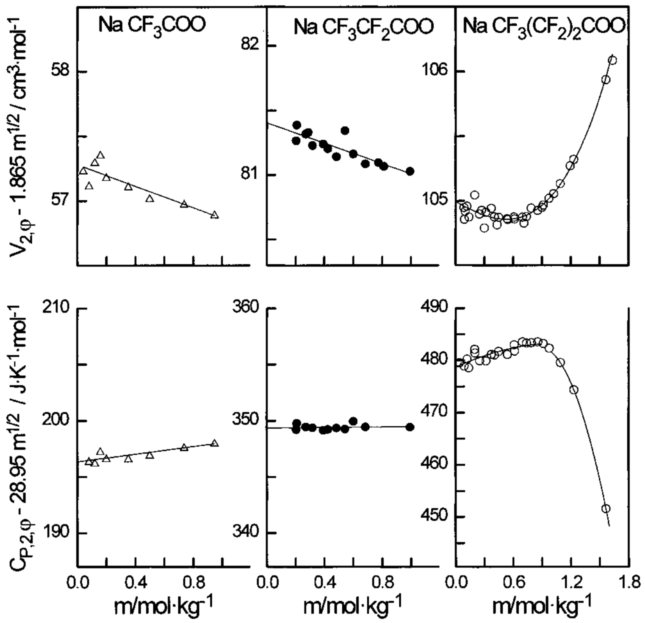

Figure 1. Apparent molar volumes and heat capacities of $NaCF_3$-COO, $NaCF_3(CF_2)COO$, and $NaCF_3(CF_2)_2COO$ in water at 25 °C. Full lines are from the least-squares fit using a polynomial of order 3 in the case of $NaCF_3(CF_2)_2COO$.

reference water in $J{\cdot}K^{-1}{\cdot}g^{-1}$ (Weast, 1990). The differences in heat capacities can be obtained to ±0.5% under the best conditions.

The density is related to the resonance frequency of the U-shaped vibrating capillary tube adapted to the flow regime by Picker et al. (1974). The difference in density between the solution and a reference solvent is given by

$$d - d_o = k(\tau^2 - \tau_o^2) \tag{3}$$

where k is the calibration constant obtained using pure water (Weast, 1990), dry nitrogen (Weast, 1990), and vacuum as references. The calibration constant obtained for various organic liquids against vacuum or nitrogen is slightly different from the one for water and vacuum or nitrogen in the commercial version of the instrument. The densities of nonaqueous solvents should therefore be measured and calibrated against an organic reference solvent. Densities can be measured to $\pm 3 \times 10^{-6}$ $g{\cdot}cm^{-3}$ under the most favorable conditions.

Results and Discussion

The volumes and heat capacities of solutions are usually expressed as apparent molar quantities $Y_{2,\varphi}$. The apparent molar volume of component 2 is calculated from

$$V_{2,\varphi} = \frac{M_2}{d} - \frac{1000(d - d_o)}{m_2 d d_o} \tag{4}$$

where M_2 is the molar mass and m_2 is the molality of component 2, and the apparent molar heat capacity from

$$C_{p,2,\varphi} = M_2 c_p + \frac{1000(c_p - c_{p,o})}{m_2} \tag{5}$$

The difference in densities ($d - d_o$), the relative changes in heat capacities per unit volume ($\Delta\sigma/\sigma_o$), and the derived $V_{2,\varphi}$ and $C_{P,2,\varphi}$ are given in Table 1. The apparent molar quantities of the three lower members of this homologous series were plotted in Figure 1 as a function of molality with a Redlich–Meyer type equation:

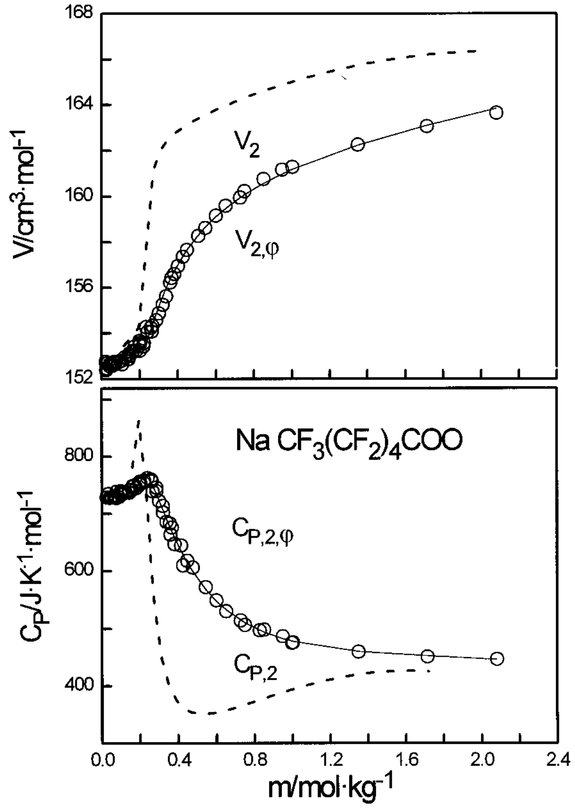

Figure 2. Apparent and partial molar volumes and heat capacities of $NaCF_3(CF_2)_4COO$ in water at 25 °C. The full and broken lines are from the least-squares fit using a mass-action model.

$$Y_{2,\varphi} = Y_2^{o} + y_{DH} m^{1/2} + A_Y^{A} m + ... \tag{6}$$

where y_{DH} is the Debye–Hückel limiting slope for volumes or heat capacities. The derived parameters are given in Table 2 and are compared with available literature values.

The first two members of this homologous series behave as typical short-chain amphiphilic solutes in water, while $NaCF_3(CF_2)_2COO$ shows a tendency for self-association at 25 °C, somewhat like *n*-butanol. The trends with m for $NaCF_3(CF_2)_4COO$ and $NaCF_3(CF_2)_6COO$, shown in Figures 2–4, are those of surfactants. At 5 °C, only the beginning of the micellization process is observed with $NaCF_3(CF_2)_6$-COO since the Krafft temperature, ≈8 °C (Shinoda et al., 1972), is above the solution temperature.

In the mass-action model developed by Desnoyers et al. (1983) for nonionic surfactants and extended to ionic systems (Caron et al., 1985), the concentration dependence of $V_{2,\varphi}$ and $C_{P,2,\varphi}$ has the following form:

$$\begin{aligned} V_{2,\varphi} = {} & \alpha(V_2^{o} + v_{DH}\alpha^{1/2}m^{1/2} + A_V^{A}\alpha m + ...) + \\ & (1 - \alpha)[V_{CMC}^{M} + A_V^{M}(1 - \alpha)(m - CMC) + \\ & B_V^{M}(1 - \alpha)^2(m - CMC)^2 + ...] \end{aligned} \tag{7}$$

and

$$\begin{aligned} C_{P,2,\varphi} = {} & \alpha(C_{P,2}^{o} + c_{DH}\alpha^{1/2}m^{1/2} + A_C^{A}\alpha m + ...) + \\ & (1 - \alpha)[C_{P,CMC}^{M} + A_C^{M}(1 - \alpha)(m - CMC) + \\ & B_C^{M}(1 - \alpha)^2(m - CMC)^2 + ...] + \\ & \frac{\alpha(1 - \alpha)}{1 - \alpha + \alpha/n}\frac{(\Delta H^{M})^2}{RT^2} \end{aligned} \tag{8}$$

where V_2^{o} and $C_{P,2}^{o}$ are the standard infinite dilution partial molar quantities, V_{CMC}^{M} and $C_{P,CMC}^{M}$ are the partial

Table 1. Volumes and Heat Capacities of Sodium Perfluoroalkanoates in Water

m/ mol·kg^{-1}	$10^3(d - d_o)$/ g·cm^{-3}	$V_{2,\varphi}$/ $\text{cm}^3\text{·mol}^{-1}$	$10^3\Delta\sigma/\sigma_o$	$C_{P,2,\varphi}$/ $\text{J·K}^{-1}\text{·mol}^{-1}$	m/ mol·kg^{-1}	$10^3(d - d_o)$/ g·cm^{-3}	$V_{2,\varphi}$/ $\text{cm}^3\text{·mol}^{-1}$	$10^3\Delta\sigma/\sigma_o$	$C_{P,2,\varphi}$/ $\text{J·K}^{-1}\text{·mol}^{-1}$
$NaCF_3COO$ at 25 °C									
0.039 928	3.120	57.61	−0.34	204.5	0.350 36	26.687	58.22	−2.37	213.8
0.080 04	6.238	57.65	−0.68	204.6	0.498 00	37.555	58.34	−2.97	217.4
0.120 02	9.296	57.95	−1.00	206.3	0.736 98	54.664	58.58	−3.66	222.5
0.157 99	12.187	58.10	−1.25	208.8	0.946 52	69.262	58.71	−3.95	226.2
0.199 40	15.360	58.02	−1.52	209.6					
$NaCF_3CF_2COO$ at 25 °C									
0.097 22	9.998	82.29	0.41	361.4	0.484 22	48.204	82.44	2.90	369.5
0.204 77	20.912	82.11	0.97	362.3	0.543 89	53.841	82.53	3.23	370.6
0.209 19	21.329	82.24	0.96	363.0	0.601 67	59.240	82.61	3.86	372.4
0.270 76	27.456	82.29	1.32	364.5	0.685 34	67.026	82.63	4.50	373.4
0.287 77	29.160	82.23	1.60	366.4	0.775 48	75.229	82.74		
0.317 86	32.115	82.28	1.69	365.7	0.812 38	78.576	82.75	5.65	375.8
0.393 16	39.433	82.41	2.17	367.3	0.995 04	94.764	82.89	7.25	378.3
0.424 72	42.489	82.42	2.35	368.1					
$NaCF_3(CF_2)_2COO$ at 25 °C									
0.039 470	5.136	105.29	0.44	485.3	0.543 86	66.710	106.23		
0.087 790	11.348	105.50	1.00	487.5	0.609 55	74.216	106.33	8.57	505.6
0.091 282	11.802	105.42			0.614 33	74.770	106.32	8.51	504.5
0.100 16	12.928	105.51			0.696 70	84.031	106.43	10.0	507.7
0.118 50	15.257	105.60	1.41	490.2	0.712 05	85.769	106.40		
0.136 78	17.570		1.59	489.3	0.738 38	88.651	106.48	10.6	508.2
0.139 20	17.887	105.57			0.788 80	94.142	106.60	11.3	509.1
0.197 69	25.127	106.20	2.44	495.0	0.855 26	101.367	106.65	12.4	510.3
0.200 52	25.540	105.88	2.50	494.4	0.901 65	106.327	106.72		
0.249 53	31.637	105.83	3.12	494.4	0.913 67	107.590	106.75	13.2	510.9
0.272 04	34.390	105.90			0.974 59	113.985	106.86	13.9	510.9
0.300 01	37.844	105.81			1.021 9	118.885	106.94		
0.316 45	39.808	105.96	4.02	496.2	1.090 1	125.842	107.08	14.9	509.8
0.372 01	46.484	106.08	4.86	498.8	1.092 4	126.095	107.07		
0.403 46	50.264	106.06	5.34	499.4	1.194 2	136.229	107.31		
0.432 63	53.747	106.04			1.230 9	139.831	107.39	15.4	506.5
0.447 63	55.493	106.12	6.04	501.1	1.563 7	170.845	108.27	11.8	487.8
0.538 85	66.130	106.23	7.31	502.4	1.633 8	177.018	108.47		
$NaCF_3(CF_2)_4COO$ at 25 °C									
0.021 734	3.968	152.77			0.239 78	42.065	154.06	6.70	763.1
0.023 896	4.370	152.40	0.53	728.1	0.257 34	44.981	154.25	5.97	760.4
0.026 463	4.836	152.48	0.59	728.9	0.262 41	45.874	154.09	6.96	757.5
0.032 383	5.904	152.71			0.265 88	46.390	154.34	6.89	739.5
0.034 556			0.79	735.0	0.285 61	49.391	155.38	6.46	746.2
0.042 874	7.811	152.57	0.94	728.0	0.285 80	49.650	154.58	6.29	740.1
0.043 950	8.001	152.67			0.299 72	51.872	154.88	5.31	722.9
0.049 587	9.018	152.70			0.319 00	54.932	155.26	4.89	714.2
0.052 556	9.554	152.70	1.16	729.3	0.319 78	55.058	155.26	4.07	702.8
0.059 278	10.771	152.60			0.337 72	57.868	155.63	2.89	686.2
0.063 009	11.433	152.75	1.41	730.9	0.355 63			2.48	683.2
0.069 274	12.560	152.72	1.52	729.1	0.358 58	61.038	156.24	1.04	663.8
0.075 825	13.731	152.77	1.63	727.5	0.366 11	62.177	156.44	2.02	676.2
0.089 210	16.124	152.75	1.96	729.6	0.380 39	64.397	156.62	−0.46	647.3
0.099 535	17.956	152.81	2.29	734.4	0.400 13	67.408	156.96		
0.100 77	18.142	153.14	2.41	739.6	0.414 38			−1.21	644.9
0.104 24	18.792	152.81	2.48	737.7	0.425 37	71.219	157.37	−4.32	610.5
0.107 29	19.349	152.66	2.51	735.3	0.446 83	74.445	157.67	−3.84	618.5
0.120 95	21.732	152.92	2.84	737.3	0.475 83			−5.87	606.7
0.124 80	22.387	153.15	2.92	737.8	0.507 07	83.426	158.28		
0.140 69	25.215	152.88			0.543 91	88.815	158.63	−10.6	572.6
0.143 96	25.757	153.10	3.35	737.4	0.599 95	96.859	159.17	−14.9	549.5
0.144 66	25.892	153.01	3.52	741.5	0.651 32	104.091	159.61	−19.0	530.5
0.159 16	28.399	153.18	3.87	742.4	0.727 36	114.724	159.96	−23.7	514.6
0.164 72	29.355	153.25	4.19	747.6	0.749 94	117.701	160.24	−25.8	506.7
0.171 36	30.480	153.42	4.42	749.9	0.827 50	128.187	160.56		
0.180 24	32.048	153.25	4.49	745.4	0.850 78	131.185	160.77	−30.7	498.6
0.198 69	35.147	153.67	5.13	751.5	0.949 43	144.007	161.18	−36.4	486.9
0.200 03	35.461	153.25	5.37	754.2	0.997 03			−40.3	475.7
0.200 53	35.481	153.58	5.30	753.8	1.002 9	150.869	161.30	−40.5	476.3
0.200 16			5.44	756.7	1.349 6	192.456	162.27	−57.3	460.0
0.218 11	38.523	153.44			1.714 2	231.839	163.07	−73.1	451.6
0.221 10	39.000	153.59	6.08	758.8	2.081 8	267.844	163.65	−87.3	447.1
0.233 93	41.023	154.28							

Table 1 (Continued)

m/ mol·kg^{-1}	$10^3(d - d_o)$/ g·cm^{-3}	$V_{2,\varphi}$/ cm^3·mol^{-1}	$10^3\Delta\sigma/\sigma_o$	$C_{P,2,\varphi}$/ J·K^{-1}·mol^{-1}	m/ mol·kg^{-1}	$10^3(d - d_o)$/ g·cm^{-3}	$V_{2,\varphi}$/ cm^3·mol^{-1}	$10^3\Delta\sigma/\sigma_o$	$C_{P,2,\varphi}$/ J·K^{-1}·mol^{-1}
$NaCF_3(CF_2)_6COO$ at 25 °C									
0.004 900	1.157	199.63			0.068 772	15.501	207.38	−1.84	751.0
0.006 008	1.419	199.47	0.21	976.3	0.075 054	16.870	207.72	−2.43	728.3
0.009 902	2.333	199.86			0.077 900	17.483	207.93		
0.009 927	2.243	199.44	0.36	984.2	0.079 747	17.874	208.14	−2.84	716.0
0.011 470	2.703	199.72			0.091 090	20.284		−3.93	687.5
0.013 490	3.177	199.82	0.46	975.5	0.098 901	21.984	209.13	−4.68	699.6
0.013 977	3.287	200.10	0.51	986.4	0.102 20	22.685	209.30	−5.05	661.2
0.014 630	3.443	199.95			0.106 91	23.694	209.42		
0.018 138	4.262	200.12	0.67	988.8	0.128 00	28.152	210.16	−7.36	629.1
0.018 250	4.292	199.87			0.136 05	29.843	210.39		
0.019 669	4.617	200.28	0.78	1001.1	0.142 66	31.213	210.65	−8.75	613.8
0.020 130	4.719	200.59	0.77	996.4	0.154 26	33.612	211.04	−9.86	603.6
0.021 551	5.057	200.30			0.163 18	35.510	210.93	−10.6	598.2
0.022 318	5.240	200.10	0.81	986.0	0.177 35	38.408	211.33	−11.9	590.2
0.025 289	5.936	200.03			0.187 86	40.585	211.42	−12.7	587.3
0.027 423	6.418	200.64	1.08	1001.5	0.189 30	40.893	211.37		
0.029 697	6.938	200.93	1.22	1010.0	0.196 75	42.386	211.64	−13.6	581.2
0.030 472	7.123	200.77	1.32	1018.7	0.199 50	43.011	211.35	−11.4	579.4
0.033 470	7.801	201.32	1.32	1004.8	0.226 47	48.456	211.82		
0.034 833	8.103	201.70	1.29	996.3	0.239 84	51.117	212.08	−17.2	568.8
0.036 900	8.558	202.32	1.12	970.9	0.281 18	59.358	212.35	−20.3	565.3
0.037 604	8.724	202.20			0.283 67	59.843	212.39	−20.9	558.6
0.039 609	9.163	202.77	0.68	917.4	0.284 48	60.030	212.29		
0.040 633	9.384	203.12			0.293 84	61.894	212.27		
0.041 580	9.580	203.62	0.81	930.3	0.321 35	67.188	212.69	−24.0	552.9
0.042 013	9.686	203.45	0.67	915.1	0.359 78	74.597	212.85	−27.2	546.9
0.042 838	9.876	203.42			0.380 79	78.589	212.95	−28.0	555.3
0.043 952	10.108	203.94	0.54	901.2	0.382 64	78.969	212.88	−28.4	551.7
0.045 017	10.342	204.14	0.46	893.8	0.396 98	81.541		−29.4	553.2
0.050 180	11.478	204.89	−0.08	847.2	0.430 78	88.005	213.03		
0.052 332	11.952	205.14			0.469 54	95.102	213.26	−34.5	550.9
0.055 799	12.692	205.92	−0.54	817.4	0.519 60	104.134	213.45	−40.8	525.0
0.057 247	13.020	205.87			0.836 56	157.585	214.02		
0.061 206	13.878	206.39	−1.10	784.0	1.236 9	216.748	214.45	−87.0	521.9
0.068 608	15.478	207.19	−1.82	750.8					
$NaCF_3(CF_2)_6COO$ at 5 °C									
0.009 902	2.423	190.89	0.25	909.0	0.042 013	10.146	192.59	2.87	1098.6
0.019 669	4.802	191.16	0.59	926.0	0.045 017	10.842	193.12	3.12	1105.2
0.030 472	7.424	191.00	0.87	922.6	0.050 180	12.013	194.31	2.82	1055.0
0.033 470			1.07	944.3	0.061206	14.484		2.05	968.3
0.036 900			1.51	982.6	0.068 608	16.140	197.61		
0.039 609	9.598	191.89	2.50	1073.8	0.079 747	18.620	198.86		
0.040 633	9.837	192.07	2.85	1104.0					
$NaCF_3(CF_2)_6COO$ at 55 °C									
0.006 008	1.365	208.25	0.19	990.9	0.068 772	14.840	217.02	−2.32	751.4
0.009 927	2.230	210.67	0.28	985.0	0.075 054	16.133	217.59	−2.94	730.5
0.013 977	3.155	209.35	0.34	963.8	0.098 901	21.041	218.74	−5.00	685.8
0.018 138	4.072	210.44	0.44	969.3	0.128 00	26.977	219.45	−7.49	653.1
0.022 318	4.994	210.99	0.59	980.8	0.163 18	34.037	220.10	−10.3	634.0
0.027 423	6.110	211.76	0.62	968.0	0.293 84	59.278	221.43	−20.7	599.3
0.029 697	6.603	212.11	0.59	958.0	0.199 50	41.176	220.73	−13.4	616.8
0.034 833	7.710	212.90	0.38	923.6	0.382 64	75.660	221.84	−27.4	590.0
0.041 580	9.143	214.07	0.09	891.9	0.547 46	104.433	222.47	−39.2	581.7
0.043 952	9.654	214.21	−0.20	863.8	0.836 56	150.737	222.85	−57.4	579.3
0.055 799	12.130	215.97	−1.20	799.3					

t/°C	d_o/g·cm^{--3}	σ_o/J·K^{-1}·cm^{-3}
5	0.999 964	4.2020
25	0.997 045	4.1672
55	0.985 695	4.1226

molar quantities of the surfactant in the micellar form at the CMC, v_{DH} and c_{DH} are the Debye−Hückel limiting slopes for volumes and heat capacities, A_Y^A, A_Y^M, B_Y^A, etc. are virial coefficients to account for all interactions affecting the properties of the surfactant ion in the monomeric (A) and micellar (M) forms, n is the aggregation number, ΔH^M is the enthalpy of micellization, and α is the fraction of monomers. The last term of eq 8 is the relaxational contribution to heat capacity and accounts for the shift in CMC during a unit change in temperature. The values of α depend on n and m_I, the molality at the inflexion point of α.

The full lines in Figures 2−4 are the fits obtained from the least-squares analysis of the data. The nonideality in the pre- and postmicellar regions is strong with these fluorinated surfactants. To increase the reliability of the micellization parameters, some of the volume parameters in the premicellar region were obtained from eq 6 and fixed

Table 2. Parameters of Eqs 6−8 for the Volumes and Heat Capacities of $NaCF_3(CF_2)_xCOO$ in Water[a]

x	0	1	2	4	6	6	6 (a)	6 (b)
t/°C	25	25	25	25	5	25	55	55
V_2^o	57.28	81.41	105.00	(152.26)	(190.8)	(199.23)	(207.90)	(209)
	57.2^b	81.8^b	104.9^b			199.3^b 200.00^c 200.5^d		
V_{DH}	(1.865)	(1.865)	(1.865)	(1.865)	(1.529)	(1.865)	(2.389)	(2.389)
A_V^A	−0.42	−0.40	−0.42	1.13		(36.20)	(125.00)	78.42
	-0.87^b	-0.75^b	-0.92^b			0^c 0^d		
B_V^A			0.12					
V_{CMC}^M				163.14	206.7	213.55 213.8^c 213.8^d	221.97	221.83
A_V^M				1.25		2.29 0^c 0^d	3.42	3.98
B_V^M				(0)		−1.22	−2.14	−2.65
$n(V)$				(30)	(50)	(50)	(50)	(50)
$m_I(V)$				(0.27)	0.0418	0.0356	0.0400	0.0350
$C_{P,2}^o$	196.3	349.4	478.7	(720)	920	(970)	(989.4)	(980)
c_{DH}	(28.95)	(28.95)	(28.95)	(28.95)		(28.95)	(38.73)	(38.73)
A_C^A	1.7	0.1	8.6	(52.5)		(980)	−1537.7	−642.7
B_C^A			−4.0					
$C_{P,CMC}^M$				328.3		461.2	514.4	542.0
A_C^M				34.4		137.3	137.2	22.0
B_C^M				(0)		−78.8	−102.9	4.4
relax				68.0		27.9	(0)	(0)
$n(C_P)$				(30)		(50)	(50)	(50)
$m_I(C_P)$				(0.27)		(0.0356)	(0.040)	(0.035)

[a] The units of the various parameters are for volumes in $cm^3 \cdot mol^{-1}$, heat capacities in $J \cdot K^{-1} \cdot mol^{-1}$, and m in $mol \cdot kg^{-1}$. [b] Tamaki et al. (1990) for concentrations in $mol \cdot L^{-1}$. [c] Milioto et al. (1995). [d] Kato et al. (1992).

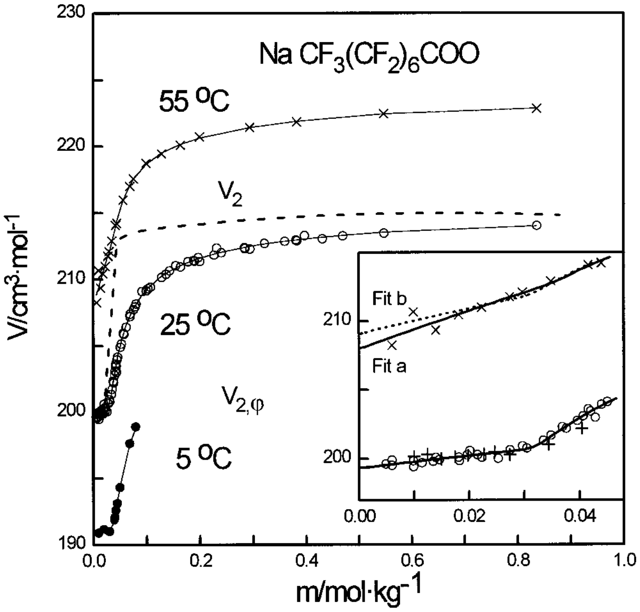

Figure 3. Apparent and partial molar volumes of $NaCF_3(CF_2)_6COO$ in water at 5, 25, and 55 °C: (+) data from Milioto et al. (1995). The fit b was made after elimination of the data point at the lowest concentration.

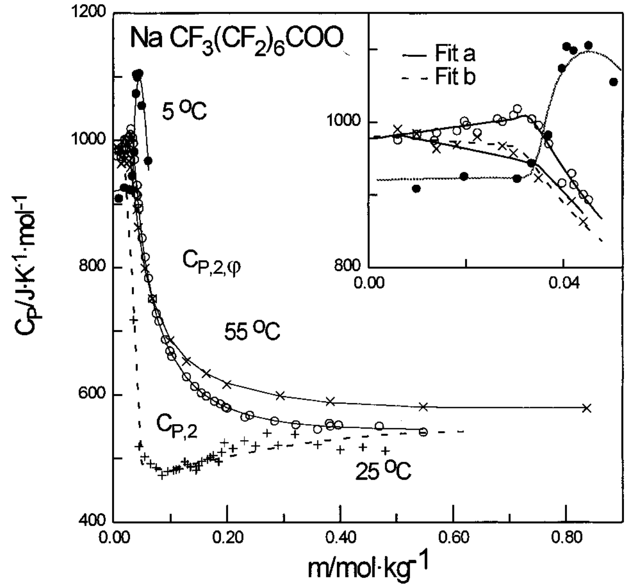

Figure 4. Apparent and partial molar heat capacities of $NaCF_3(CF_2)_6COO$ in water at 5, 25, and 55 °C. + are the partial molar heat capacities determined experimentally.

in the mass-action treatment. Similarly, for $C_{P,2,\varphi}$, in addition to some of the premicellar parameters, the values of n and of m_I are generally assumed to be identical to those derived from volumes. This was not possible in the case of $NaCF_3(CF_2)_4COO$ since the m_I value derived from volumes, 0.3 $mol \cdot kg^{-1}$, gave unrealistic values for $C_{P,CMC}^M$. Since the value of m_I, derived from heat capacities was about 0.265 $mol \cdot kg^{-1}$, this parameter was fixed at 0.27 $mol \cdot kg^{-1}$ for the two properties. There are not enough data points for $NaCF_3(CF_2)_4COO$ at high concentrations to justify the introduction of a B_Y^M term. All the derived parameters and those that were fixed are given in parentheses in Table 2. The agreement between the present volume data and those of Tamaki et al. (1990) of Milioto et al. (1995) and of Kato et al. (1992) is excellent, as can be seen from Table 2 and Figure 3.

If we consider that the main purpose of the mass-action equilibrium (equilibrium constant and aggregation number) is to evaluate the fraction of free monomers α at all concentrations, then eqs 7 and 8 are essentially fitting

Table 3. CF_2 and CH_2 Contributions

	CF_2	CH_2
V_2^o/cm^3·mol^{-1}	23.57 ± 0.05	15.8[a]
V_2^M/cm^3·mol^{-1}	25.4 ± 1.5	16.5[a]
V_2^*/cm^3·mol^{-1}	25[b]	16.3[c]
$C_{P,2}^o$/J·K^{-1}·mol^{-1}	124 ± 1	87.5[a]
$C_{P,2}^M$/J·K^{-1}·mol^{-1}	70 ± 20	35[a]
$C_{P,2}^*$/J·K^{-1}·mol^{-1}	55[d]	31[c]

[a] Desnoyers and Perron (1996a). [b] Grosselli and Ritchey (1975). [c] Trejo et al. (1991). [d] Jin et al. (1994).

equations to obtain, by least squares, the apparent molar volumes and heat capacities of the surfactant in the monomeric and micellar forms (Desnoyers and Perron, 1996a,b).

The standard quantities of micellization, in the pseudophase equilibrium formalism, are defined as the changes in the partial molar quantities at the CMC. To obtain the correct values at the CMC, it is therefore necessary to convert the apparent molar quantities into partial molar quantities. The trends obtained from the least-squares parameters are shown as broken lines in Figures 2−4 and are in excellent agreement with the partial molar quantities derived from a plot of $\Delta(mY_{2,\varphi})/\Delta m$ against the mean molality (see for example the heat capacity in Figure 3). Since in general $Y_2 = \partial(mY_{2,\varphi})/\partial m$, the partial molar quantities of an ionic surfactant into both forms are given by Desnoyers and Perron (1996b)

$$Y^A = Y_2^o + \frac{3}{2} y_{DH} m^{1/2} + 2A_Y^A m + ... \qquad (9)$$

and

$$Y^M = Y_{CMC}^M + 2A_Y^M(m - CMC) + 3B_Y^M(m - CMC)^2 + ... \qquad (10)$$

For the present purpose, the CMC were taken to be identical to m_I, although this parameter is generally slightly larger than the usual CMC values. The magnitude of Y^M can also be estimated from a plot of $Y_{2,\varphi}$ against $1/m$. Such plots generally confirm the values of Y_{CMC}^M given in Table 3. With surfactants having high CMCs and strong interactions in the pre- and postmicellar regions, it is more difficult to obtain reliable Y_{CMC}^M.

The dependences on chain length of V_2^o, V_{CMC}^M, $C_{P,2}^o$, and $C_{P,CMC}^M$ are shown in Figure 5. The CF_2 contributions to these functions were obtained from the slopes of these lines and are compared with the values of the pure liquid solutes, V_2^* and $C_{P,2}^*$, and to the CH_2 group contributions in Table 3. The differences between the CF_2 and CH_2 groups are due primarily to the larger size of the CF_2 group. The values in the micellar state are closer to those of the pure liquids than those at infinite dilution, in agreement with the lyophilic nature of the interior of the micelles.

The thermodynamic functions of micellization ΔY_{CMC}^M, defined as the the difference $Y^M - Y^A$ at the CMC, are given in Table 4. The present ΔV_{CMC}^M of $NaCF_3(CF_2)_6COO$ at 25 °C is slightly smaller than the values obtained by Milioto et al. (1995) and by Kato et al. (1992). The agreement in the experimental $V_{2,\varphi}$ is excellent between different authors, as illustrated for the example in Figure 3 in the case of Milioto et al. The disagreement comes mostly from the method of treating the data in the premicellar region for extrapolation of the partial molar volumes of the monomers to the CMC and partly from a different choice of the CMC.

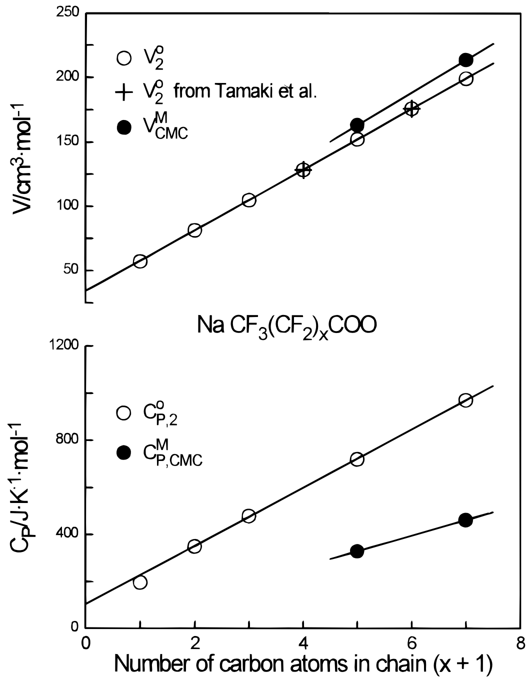

Figure 5. Dependence on chain length $x + 1$ of various thermodynamic parameters of the homologous $NaCF_3(CF_2)_xCOO$ in water at 25 °C.

Table 4. Volumes and Heat Capacities of Micellization

surfactant	t/°C	CMC/ mol·kg^{-1}	ΔV_{CMC}^M/ cm^3·mol^{-1}	$\Delta C_{P,CMC}^M$/ J·K^{-1}·mol^{-1}
$NaCF_3(CF_2)_4COO$	25	0.27	8.8	−443
$NaCF_3(CF_2)_6COO$	25	0.0356	11.2	−587
	25	0.031	13.3[a]	
	25	0.031	12.8[b]	
	25	0.031	11.5	
	55	0.040	3.4	−363

[a] Milioto et al. (1995). [b] Kato et al. (1992).

The importance of having sufficient data points in the pre- and postmicellar regions is well illustrated for the data at 55 °C. The parameters from the fits (a) at 55 °C in Table 2 are based on a plot of $V_{2,\varphi} - v_{DH} m^{1/2}$ versus m in the premicellar region, using all the data points. The ΔV_{CMC}^M obtained, 3.4 cm^3·mol^{-1}, seems small and m_I is somewhat high. If the first data point at 0.006 mol·kg^{-1}, where the uncertainty is large, is removed and the value of V_2^o is fixed at 210 cm^3·mol^{-1}, then the second set of parameters (b) in Table 2 is obtained. The new value of ΔV_{CMC}^M, 6.7 cm^3·mol^{-1}, seems more reasonable, but a different choice of parameters at low concentrations can yield other values for ΔV_{CMC}^M. The same procedure was applied to the heat capacities and again different values for $\Delta C_{P,CMC}^M$ were obtained (see Table 4).

The uncertainty in the ΔY_{CMC}^M values comes from the quantity and quality of data points in the pre- and postmicellar region, from the choice of parameters that were fixed in the application of the mass-action model and from the approximations made in deriving the model. We would estimate the uncertainty on the present micellization functions at 25 °C to 1 cm^3·mol^{-1} and 10 J·K^{-1}·mol^{-1}. These functions show an increase in magnitude with chain length but a decrease with temperature.

The partial molar quantities in the postmicellar region, especially the heat capacities, vary significantly with concentration. This could result from intermolecular interaction between the surfactant molecules in the micelle, but most likely these trends are reflecting the change in shape and size of the micelles with concentration. Similar trends are observed for the hydrogenated alkanoate surfactants in water (DeLisi et al., 1980; Desnoyers and Perron, 1996a), while the partial molar quantities of nonionic surfactants reach constant values in the postmicellar region.

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