Transport Properties for Aqueous Solution of Sodium Sulfonate Surfactants

1. Mutual Diffusion Measurements: Evaluation of the Equilibrium Parameters for the Micellization Process

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Isothermal mutual diffusion coefficients (D) have been measured for binary aqueous solutions of sodium alkylsulfonates at 25°C. The diffusion coefficient values drop as the concentration of micelles in the system increases. As the length of the hydrocarbon chain increases, the observed drop in D becomes increasingly sharp and shifts to lower concentrations. When the micellization process is treated as a chemical equilibrium, diffusion coefficients lead to the calculation of the thermodynamic parameters association number, n, and the equilibrium constant, K. These parameters are briefly discussed in connection with the alkyl chain length of the surfactants. © 1999 Academic Press

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INTRODUCTION

Ionic surfactants are widely used as solubilizers and emulsifiers (1). In these practical applications, diffusion due to chemical concentration gradients (mutual diffusion) is quite important. For example, this kind of diffusion occurs when aqueous detergents solubilize organic compounds. However, most of the literature on diffusion in surfactant solutions is devoted to intradiffusion coefficients ($\mathscr{D}$), which are related to the Brownian motion of the species in a system with a uniform chemical composition (2–6).

In a binary solution, intradiffusion coefficients are an n concentration-weighted average of the diffusion coefficients of monomer surfactant and micelle (3). In contrast, the mutual diffusion coefficient (D) is an n^2 concentration-weighted average of the diffusivity of the species present in the system, where n is the aggregation number (7). This is true for both nonionic and ionic surfactants. Although in this latter case the expression for D is complicated by the presence of counterions, they impose the necessary electroneutrality condition on the motion of various ions. This important feature favors the

obtaining of information on the equilibrium properties from the behavior of D with surfactant concentration.

The chemical equilibrium model is one physical interpretation of micelle diffusion present in the literature (9, 10). Using it and the fundamental transport equations, it is possible to relate the binary diffusion coefficient to equilibrium properties, such as the equilibrium constant (K), aggregation number (n), and condensed counterion number (q) (10). The concentration dependence of diffusion coefficients can be explained by analyzing the effect of micelle formation on the chemical potential gradient (driving force) and on overall mobility (10).

This treatment leads to an equation where D is a function of the diffusion coefficients of the actual species present in solution (monomer surfactant, micelle, and free Na$^+$ counterions) and equilibrium parameters of the micellization process. In principle it is possible to fit this equation to the experimental data to calculate equilibrium parameters. However, the large number of adjustable parameters makes this quite difficult.

In this paper we report mutual diffusion coefficients for binary aqueous solutions of alkyl sulfonate sodium salts [CH$_3$–(CH$_2$)$_{n-1}$–SO$_3$Na, C$_n$SNa] with an odd number of carbon atoms in the chain. The measurements have been made over a wide range of surfactant concentrations to study the effect of aggregation on D. Finally, the mutual diffusion coefficients were combined with intradiffusion coefficients of the micelle, $\mathscr{D}_M$, in order to get the equilibrium parameters.

Note that the paper presented here is a part of a more extensive work on sodium alkyl sulfonate binary solutions. All the intradiffusion coefficients presented here are given in Reference 11.

EXPERIMENTAL

Materials. Sodium pentylsulfonate (C$_5$SNa), sodium heptylsulfonate (C$_7$SNa), and sodium nonylsulfonate (C$_9$SNa)

were purchased from Sigma Chemical Co. (98.5% purity); sodium undecylsulfonate ($C_{11}SNa$) was purchased from Tokyo Kasei (98% purity). All chemicals were dried under vacuum before use and used without further treatment.

The molecular weights of C_5SNa, C_7SNa, C_9SNa, and $C_{11}SNa$ were assumed to be 174.20, 202.25, 230.30, and 258.36 g mol^{-1}, respectively.

Density measurements. The density of each solution used in a mutual diffusion run was measured with an Anton Paar Model 602 densimeter. The temperature of the densimeter was regulated at $25.00 \pm 0.01°C$.

The density meter was calibrated using air at known pressure and humidity and double-distilled water (assumed density 0.997044 kg dm^{-3}) as the references. All the experimental densities are collected in Table 1.

Diffusion measurements. The mutual diffusion coefficients were measured by a Gouy diffusiometer (8) automated to scan Gouy fringe patterns and record fringe positions during each experiment. A Model II fx Macintosh computer was used to control the scanning apparatus and calculate the fringe minima from fringe intensity profiles (12). The light source was a Unifas PHA SE 0.8-mW neon–helium laser operating at 632.8 nm. The temperature was regulated at 25.00 ± 0.01.

The diffusion coefficients were calculated by a set of programs well described in the literature (13, 14). Table 2 collects experimental diffusion coefficients for each surfactant. The corresponding diffusion coefficients at infinite dilution are collected in Table 3. They were calculated with Nernst's equation,

$$D^{\infty} = \frac{RT}{\mathscr{F}^2} \frac{2\lambda_+^{\infty}\lambda_-^{\infty}}{(\lambda_+^{\infty} + \lambda_-^{\infty})}, \qquad [1]$$

where λ_-^{∞}, λ_+^{∞} are the limiting ionic conductivities of anionic surfactant and sodium ion, respectively, and $\mathscr{F}$ is the Faraday constant. The limiting ionic conductivities λ_-^{∞} were obtained through a least-squares fit of literature data (15), and λ_+^{∞} for the Na^+ ions was assumed to be 50.10 cm^2 S mol^{-1} (16).

RESULTS AND DISCUSSION

Sodium sulfonates are completely dissociated in dilute aqueous solutions, but as the micelles are ionic, association definitely occurs between sodium counterions and micelle polyions. For moderately short hydrocarbon chain surfactants, such as those presented in this paper, the micellization process can be described in terms of the chemical equilibrium (17, 18)

$$nS^- + qM^+ = (S_nM_q)^{-(n-q)}, \qquad [2]$$
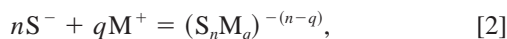
with equilibrium constant

$$K = \frac{[S_n^-M_q^+]}{[S^-]^n[M^+]^q}, \qquad [3]$$

where n and q are the aggregation number and the number of counterions bound to each micelle, respectively, and ideal behavior is assumed.

Figures 1 and 2 show the behavior of the diffusion coefficients of the various surfactants as a function of the square root of the surfactant concentration. The diffusion behavior of micellar electrolytes can be explained by studying the changes of mobility and thermodynamic factors through the micellization process. Mutual diffusion coefficients are given by

$$D = \mathscr{M}\left(C \frac{\partial \mu}{\partial C} \right), \qquad [4]$$

where $\mathscr{M}$, μ, and C are the mobility, the chemical potential of the surfactant, and the surfactant concentration, respectively.

With the chemical equilibrium approximation for the micellization process, and assuming that micelles are a monodisperse species, Evans (9) and Leaist (10) derived an explicit equation for the thermodynamic factor and mobility,

$$\left(C \frac{\partial \mu}{\partial C} \right) = B(C) = RTC \frac{C_1 + C_2 + (n-q)^2 C_M}{C_1 C_2 + q^2 C_1 C_M + n^2 C_2 C_M} \quad [5]$$

and

$$\mathscr{M} = \frac{1}{RTC} \frac{C_1 C_2 D_1 D_2 + q^2 C_1 C_M D_1 D_M + n^2 C_2 C_M D_2 D_M}{C_1 D_1 + C_2 D_2 + (n-q)^2 C_M D_M}, \qquad [6]$$

so that

$$D = \frac{C_1 C_2 D_1 D_2 + q^2 C_1 C_M D_1 D_M + n^2 C_2 C_M D_2 D_M}{C_1 D_1 + C_2 D_2 + (n-q)^2 C_M D_M}$$
$$\times \frac{C_1 + C_2 + (n-q)^2 C_M}{C_1 C_2 + q^2 C_1 C_M + n^2 C_2 C_M}, \qquad [7]$$

where subscripts 1, 2, and M refer to the monomer anion $C_N S^-$, the free Na^+, and the micelle, respectively, and $C = C_1 + nC_M$.

Since the transport of a micelle offers less frictional resistance than the transport of the separate monomers, the mobility of the total surfactant component (Eq. [6]) increases when the system is dominated by the presence of micelles. In contrast, the thermodynamic factor (Eq. [5]) decreases with increasing surfactant concentration (see Fig. 3) because an increase in the

TABLE 1
Density Data for the Binary System Alkyl Sulfonate–Water at 25°C

C$_5$SNa				C$_7$SNa		C$_9$SNa		C$_{11}$SNa	
m (mol kg^{-1})	d (kg dm^{-3})	m (mol kg^{-1})	d (kg dm^{-3})	m (mol kg^{-1})	d (kg dm^{-3})	m (mol kg^{-1})	d (kg dm^{-3})	m (mol kg^{-1})	d (kg dm^{-3})
0.00000	0.997044	0.34619	1.016036	0.00000	0.997044	0.00000	0.997044	0.00000	0.997044
0.00375	0.997271	0.39444	1.018551	0.02813	0.998575	0.01033	0.997575	0.00060	0.997071
0.01088	0.997623	0.43415	1.020670	0.07744	1.001154	0.02646	0.998320	0.00328	0.997194
0.01237	0.997756	0.45145	1.021518	0.12683	1.003694	0.04022	0.999054	0.00746	0.997393
0.01325	0.997819	0.45607	1.021701	0.17042	1.005863	0.05175	0.999666	0.01992	0.997989
0.02020	0.998200	0.49225	1.023468	0.20917	1.007730	0.06455	1.000180	0.02642	0.998236
0.02200	0.998259	0.52630	1.025192	0.25496	1.009955	0.06721	1.000463	0.03034	0.998413
0.02843	0.998711	0.54200	1.026035	0.27500	1.010837	0.06742	1.000513	0.03571	0.998599
0.02914	0.998705	0.54703	1.026302	0.32499	1.013198	0.07301	1.000682	0.04283	0.998856
0.03004	0.998807	0.60187	1.028905	0.33772	1.013823	0.07620	1.001038	0.05840	0.999417
0.03516	0.999056	0.62362	1.029757	0.35320	1.014518	0.08267	1.001124	0.06363	0.999596
0.04136	0.999472	0.63388	1.030378	0.37556	1.015434	0.09018	1.001526	0.06365	0.999604
0.05002	0.999927	0.63989	1.030658	0.38053	1.015625	0.09935	1.001849	0.07843	1.000081
0.05624	1.000257	0.68939	1.033120	0.42497	1.017476	0.10485	1.002077	0.09709	1.000793
0.05859	1.000497	0.72969	1.035046	0.42554	1.017334	0.10698	1.002134	0.12844	1.001906
0.06679	1.000776	0.77671	1.037245	0.45088	1.018497	0.11517	1.002429		
0.06869	1.000874	0.84547	1.040458	0.47481	1.019398	0.13575	1.003406		
0.07226	1.001187	0.85653	1.040825	0.47529	1.019453	0.16451	1.004333		
0.07279	1.001213	0.92430	1.043924	0.52468	1.021357	0.23597	1.007028		
0.07639	1.001405	0.94051	1.044666	0.54256	1.022078	0.27942	1.008581		
0.08702	1.002064	0.97371	1.046090	0.57306	1.023102	0.32002	1.010041		
0.09101	1.002134	1.01177	1.047577	0.58800	1.023771	0.36395	1.011704		
0.09154	1.002263	1.02365	1.048243	0.62206	1.024953	0.42021	1.013392		
0.09207	1.002282	1.03194	1.048538	0.68505	1.027256	0.46364	1.014991		
0.09882	1.002736	1.10227	1.051535	0.84158	1.032736	0.53112	1.017231		
0.09896	1.002745	1.11783	1.051987	0.97493	1.037323	0.75432	1.024090		
0.11158	1.003392	1.22307	1.056370	0.97493	1.037323	0.86112	1.027330		
0.11415	1.003533	1.24973	1.057395	1.16909	1.042997	1.04511	1.032670		
0.11928	1.003704	1.28470	1.059509	1.16909	1.042997				
0.12817	1.004245	1.35306	1.061537	1.23067	1.044846				
0.13551	1.004633	1.35729	1.061534	1.23067	1.044846				
0.14199	1.005201	1.41260	1.063450	1.99566	1.065932				
0.14337	1.004997	1.41422	1.064416	2.78637	1.083195				
0.15024	1.005489	1.42449	1.063899						
0.15700	1.005903	1.43106	1.064235						
0.19724	1.008067	1.53972	1.068053						
0.19908	1.008149	1.59386	1.070117						
0.20120	1.008226	1.67950	1.072882						
0.21849	1.009415	2.69629	1.103570						
0.22485	1.009558	3.17506	1.115019						
0.25400	1.011073	3.21686	1.116733						
0.29691	1.013444	3.39001	1.119571						
0.34301	1.015894	3.58380	1.123825						
0.34532	1.016185	3.95880	1.130966						

micelle concentration causes a decrease in the total number of particles in the system, which lowers the free energy gradient, i.e., the driving force for diffusion.

The balance of these two effects is responsible for the diffusion coefficients' behavior.

From a qualitative point of view it is possible to recognize three regions in the diffusion coefficients' behavior (see the inset in Fig. 1). In the first region, at low concentration, the system is characterized by the presence of the monomer salt. D is given by the diffusion coefficient of the aggregate surfactant; its value decreases slightly and can be extrapolated at infinite dilution as a linear function of the square root of concentration. In the second region, there is a sharp decrease of the diffusion coefficient; here the D value is due to the contribution of the

TABLE 2
Diffusion Data for the Systems C$_5$SNa–Water, C$_7$SNa–Water, C$_9$SNa–Water, and C$_{11}$SNa–Water at 25°C

m_{bottom} (mol kg^{-1})	m_{top} (mol kg^{-1})	C_{av} (mol dm^{-3})	ΔC (mol dm^{-3})	J_m	$D \times 10^5$ (cm^2 s^{-1})
			C$_5$SNa–water		
0.08702	0.00375	0.04480	0.08212	68.29	0.9297
0.09882	0.01237	0.05484	0.08506	72.57	0.9176
0.14199	0.05624	0.09744	0.08350	72.78	0.9094
0.21849	0.11928	0.16475	0.09501	78.56	0.9041
0.34301	0.25400	0.28706	0.08268	69.67	0.8895
0.43415	0.34532	0.37089	0.08076	69.51	0.8636
0.54200	0.45145	0.46696	0.08031	65.79	0.8443
0.72969	0.63989	0.63019	0.07626	64.40	0.8147
0.94051	0.84547	0.80286	0.07698	62.34	0.7672
1.11783	1.01177	0.93933	0.08265	66.49	0.6854
1.28470	1.20038	1.07523	0.06316	50.59	0.5790
1.41422	1.35306	1.17936	0.04441	30.80	0.4901
1.67950	1.59386	1.35804	0.05884	42.22	0.3727
2.02870	1.95300	1.59236	0.04820	35.22	0.3012
3.17506	3.01952	2.22160	0.07897	52.00	0.2932
			C$_7$SNa–water		
0.07276	0.02813	0.04985	0.04384	45.55	0.8766
0.12683	0.07744	0.10023	0.04778	48.93	0.8412
0.17042	0.12818	0.14558	0.04030	41.10	0.8381
0.25496	0.20917	0.22357	0.04262	43.27	0.7946
0.33557	0.25986	0.28397	0.06911	73.49	0.7253
0.32499	0.27500	0.28615	0.04560	46.07	0.7199
0.35320	0.31281	0.31615	0.03649	36.38	0.6038
0.38053	0.33772	0.33964	0.03837	37.01	0.4782
0.42554	0.37556	0.37653	0.04425	39.35	0.3593
0.47481	0.42497	0.41989	0.04348	40.59	0.3011
0.54256	0.45088	0.46028	0.07888	74.05	0.2705
0.52468	0.47529	0.46328	0.04246	39.33	0.2703
0.62206	0.57306	0.54596	0.04093	37.26	0.2572
0.84158	0.77299	0.71581	0.05390	49.44	0.2541
1.04648	0.97493	0.87115	0.05309	48.44	0.2592
1.23067	1.16909	1.00799	0.04340	40.16	0.2765
			C$_9$SNa–water		
0.04022	0.01033	0.02504	0.02953	36.10	0.8408
0.06455	0.02646	0.04494	0.03736	44.38	0.7958
0.06742	0.03441	0.05026	0.03232	41.68	0.7981
0.07620	0.04459	0.05953	0.03084	36.06	0.8075
0.08999	0.05175	0.06970	0.03716	45.77	0.8209
0.09018	0.05812	0.07291	0.03112	36.98	0.8049
0.09935	0.06721	0.08175	0.03109	36.73	0.5098
0.10698	0.07301	0.08824	0.03279	38.19	0.3031
0.11517	0.08267	0.09684	0.03127	35.51	0.2454
0.13575	0.10485	0.11733	0.02950	32.85	0.2200
0.23597	0.16451	0.19232	0.06621	73.50	0.2611
0.32002	0.27942	0.28296	0.03625	39.91	0.3113
0.42021	0.36395	0.36400	0.04858	51.82	0.3470
0.53112	0.46364	0.45321	0.05615	60.81	0.3713
0.57203	0.52671	0.49617	0.03704	41.21	0.3590
			C$_{11}$SNa–water		
0.019916	0.00060	0.01018	0.01918	27.66	0.7927
0.063653	0.03571	0.04896	0.02727	35.44	0.2239
0.078432	0.04283	0.05960	0.03457	44.09	0.2463
0.092910	0.05840	0.07414	0.03329	43.37	0.2837
0.128437	0.09113	0.10682	0.03546	49.39	0.3412

Note. m_{bottom}, molality of bottom solution for each diffusion run; m_{top}, molality of top solution; C_{av}, average concentration; ΔC, concentration difference between bottom and top solutions ($C_{bottom} - C_{top}$); J_m, total number of Gouy fringes, in terms of refractive index difference; Δn, between bottom and top solutions at the He–Ne laser red light ($\lambda = 632.8$ nm), $J_m = 3.951 \times 10^6 \, \Delta n$.

TABLE 3
Intradiffusion and Limit Mutual Diffusion Coefficients
of Sodium Alkyl Sulfonate at 25°C

n_c	$\mathscr{D}_M \times 10^5$ $(cm^2\ s^{-1})$	$D^\infty \times 10^5$ $(cm^2\ s^{-1})$
5	0.17	1.010
6	0.17	0.972^a
7	0.17	0.946
9	0.14	0.886
11	0.11	0.830

Note. $\mathscr{D}_M$ from Ref. 11. D^∞ from Eq. [1].
[a] From Ref. 19.

faster monomer surfactant and the slower micelle. In the third region the system is dominated by the presence of the micelles and, depending on the alkyl chain length, D is constant or increases with the surfactants' concentration.

For C$_7$SNa, C$_9$SNa, and C$_{11}$SNa, in fact, the mutual diffusion coefficients at high surfactant concentration increase by the dragging effect of the faster sodium counterion on the slower micelle species (9, 10). This is obviously related to the charge of the micelle ($q - n$).

In the case of C$_5$SNa, the higher value of the CMC causes a significant presence of surfactant monomer, even at high micelle concentration. Within the explored concentration the monomer species acts as an added electrolyte so that the presence of free counterions is always large enough to damp the dragging effect of the faster sodium ion, thus preventing the D increase (19–21). The same effect was found for the C$_6$SNa solutions (19).

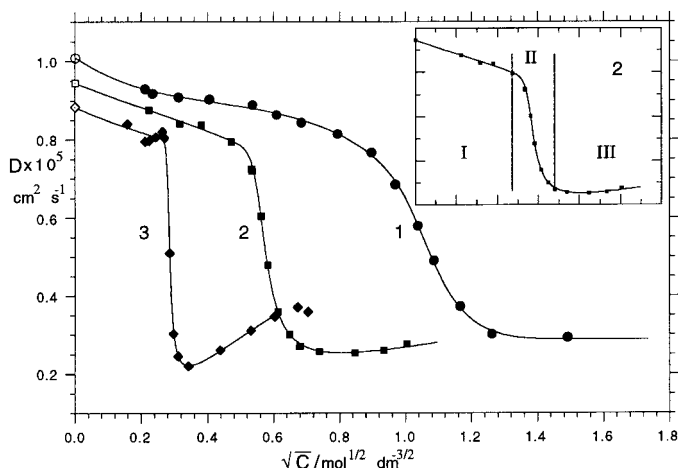As mentioned above, Eq. [7] can be fitted to the experimen-

FIG. 2. Diffusion coefficients of C$_{11}$SNa in aqueous solution at 25°C. Full lines, data computed through Eq. [7].

tal diffusion coefficients by an iteration procedure involving both Eq. [3] and Eq. [7] to obtain the equilibrium parameters n, q, and K. However, because of the high number of adjustable parameters (D_1, D_2, D_M, q, n, K) the fitting of Eq. [7] to the experimental diffusion coefficients is quite poor.

To avoid this, it is more useful to make the following approximations.

(i) The diffusion coefficient, D_2, of sodium counterion can be evaluated in the whole range of explored concentration by the equation (22, 23)

$$D_2 \times 10^5\ (cm^2\ s^{-1}) = 1.334 - 0.779C_2^{1/2} + 1.635C_2$$
$$- 1.789C_2^{3/2} + 0.989C_2^2 - 0.2148C_2^{5/2}, \quad [8]$$

where C_2 is the concentration of the free sodium ion.

The above equation was computed from the experimental

FIG. 1. Diffusion coefficients of aqueous sodium alkyl sulfonates solutions at 25°C: 1, C$_5$SNa; 2, C$_7$SNa; 3, C$_9$SNa (inset, diffusion coefficients of C$_7$SNa, the different behavior as concentration increases is evidenced). Full lines, data computed through Eq. [7].
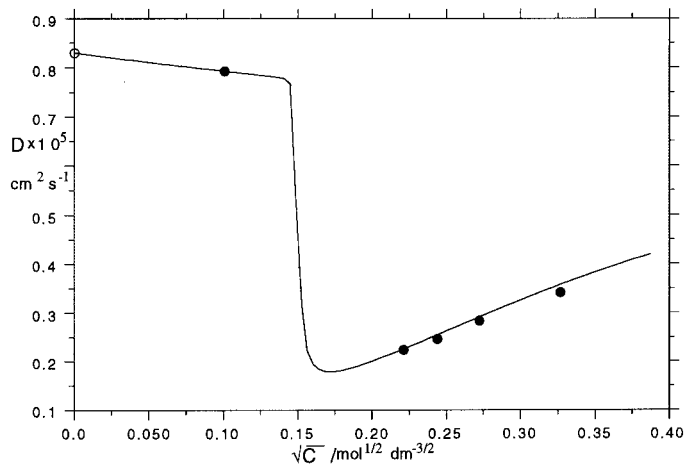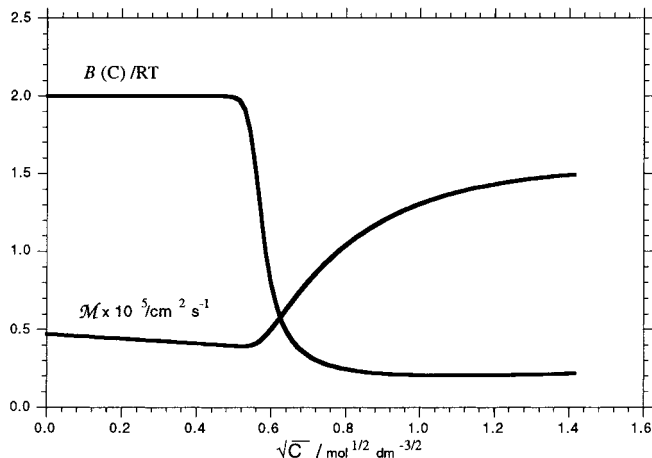
FIG. 3. Comparison of mobility (Eq. [6]) and thermodynamic factor (Eq. [5]) for the C$_7$SNa solutions.

diffusion coefficients of NaCl at 25°C (22) using literature transference data (23) to separate the Na^+ ion contribution from that of the Cl^- ion according to the Nernst–Hartley equation.

(ii) The diffusion coefficient of the monomer surfactant anion can be evaluated from the behavior of D_1 in the range of concentrations where the system is dominated by the presence of monomer surfactant. A reasonable approximation is to extend Eq. [8] to the whole range of concentrations taking into account the actual C_1 concentration given by Eq. [3]. D_1 can be computed from the experimental diffusion coefficients, D, using the Nernst–Hartley equation for 1–1 electrolytes,

$$D = \frac{2D_1 D_2}{D_1 + D_2}, \qquad [9]$$

where D_2 is given by Eq. [8].

The following equations were fitted to the experimental D_1 in the moderate dilute solution of the various surfactants examined:

$$D_1 \times 10^5 \ (cm^2 \ s^{-1}) = 0.8110 - 0.4339 C_1^{1/2} + 0.7923 C_1$$
$$- 0.6824 C_1^{3/2} \quad (C_5 SNa) \quad [10]$$

$$D_1 \times 10^5 \ (cm^2 \ s^{-1}) = 0.7319 - 0.1728 C_1^{1/2}$$
$$+ 0.2196 C_1 \quad (C_7 SNa) \quad [11]$$

$$D_1 \times 10^5 \ (cm^2 \ s^{-1}) = 0.6628 - 0.2246 C_1^{1/2}. \quad (C_9 SNa). \quad [12]$$

(iii) Optimization of the iterative process still needs a value of D_M. The evaluation of D_M is possible by experimental mutual diffusion techniques only for nonionic and short alkyl electrolyte surfactants. In both cases the diffusion coefficients do not increase in the micellar region (19).

The values used here for D_M were the limiting values of intradiffusion coefficients obtained by the pulsed gradient spin-echo (PGSE) NMR technique, following the signal of tetra-methylsilane (TMS) dissolved in the micelle (see companion paper, Ref. 11). In fact, it is possible in principle to assume that at infinite dilution the intradiffusion coefficient approaches the micelle interdiffusion coefficient (8, 24, 25):

TABLE 4
Equilibrium Parameters of the Micellization Process for the Sodium Alkyl Sulfonate Binary Systems at 25°C

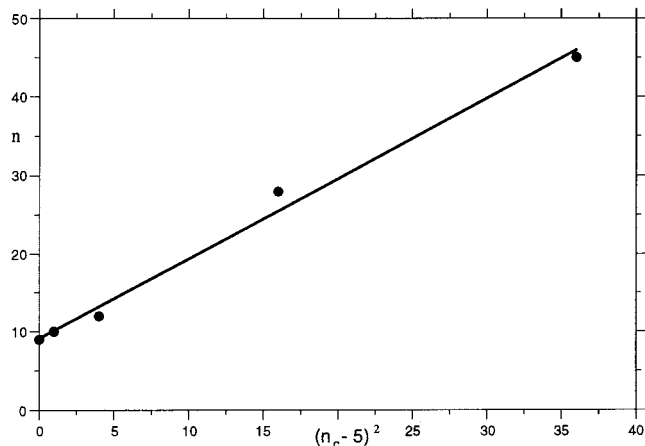| n_c	n	q/n	$\ln K$	$\Delta G°$ (kJ mol^{-1})
5	9	0.6	−7.00	1.93
6	10[a]	0.8	3.91[a]	−0.79
7	12	0.8	18.19	−3.76
9	28	0.8	119.79	−10.60
11	45	0.8	297.14	−16.36

[a] From Ref. 19.

FIG. 4. Graph of Eq. [14]. Relation between the aggregation number, n, and the number of methylene groups in the alkyl chain of sodium sulfonates.

$$\lim_{C_M \to 0} D_M = \mathscr{D}_M. \qquad [13]$$

According to Eq. [13] the intradiffusion coefficient $\mathscr{D}_M$ measured by the NMR technique extrapolated to the hypothetical CMC (chosen at the concentration where the D sharply decreases) should correspond to the mutual diffusion coefficients of the micelle.

We assume these values for D_M and consider them to be independent of surfactant concentration in the fitting of Eq. [7]. The D_M values are collected in Table 3.

The equilibrium parameters n, q, and K are now obtained from Eqs. [3] and [7] for each sodium alkyl sulfonate–water system. Those values are given in Table 4.

EQUILIBRIUM PARAMETERS

Inspection of Table 4 shows that the equilibrium parameters, n and K, increase along the sulfonate series. This is reasonable taking into account that the micellization process is dominated by the hydrophobic interaction among the surfactant molecules. This interaction of course increases with the length of the alkyl chain.

Aggregation numbers n. The following equation fits the n values with the number of carbons, n_c (see Fig. 4);

$$n = (9 \pm 1) + (1.02 \pm 0.06)(n_c - 5)^2 \qquad (n_c \geq 5). \quad [14]$$

Ratio q/n. This value is quite constant for the higher n_c values in the series and equal to 0.8. The large value of q/n is indicative of the polyelectrolyte behavior of micelles. In fact, where the aggregation number becomes large enough, the charge density on the micelle surface also becomes large enough to promote the counterions' condensation effect described for polyelectrolyte solutions (26–28).
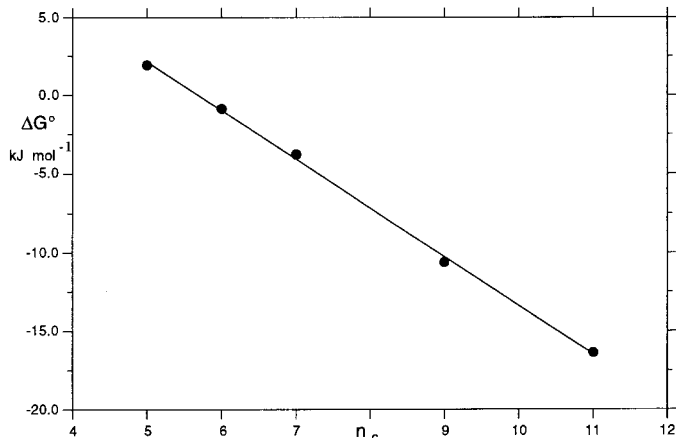
FIG. 5. Standard free energy of micellization (data from Table 4).

The lower q/n value found for the C_5SNa surfactant ($q/n = 0.6$) may be related to a lower charge density of the micelle surface. It does not promote a dragging effect, as should be expected, because the high concentration of monomer species in solution damps this effect, as noted before.

Equilibrium constant.   The equilibrium constant increases in the series as well as the absolute value of the standard Gibbs free energy of micellization (see Table 4). $\Delta G°$ for the micellization process refers to 1 mol of surfactant:

$$S^- + \frac{q}{n}\,Na^+ = \frac{1}{n}\,(S_nNa_q)^{-(n-q)}. \qquad [15]$$
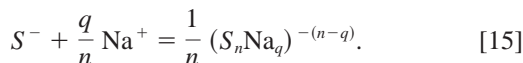
It was calculated by using the expression

$$\Delta G° = -\frac{RT}{n}\ln K. \qquad [16]$$

Inspection of Fig. 5 shows that the $\Delta G°$ is a linear function of the carbon chain:

$$\Delta G°\ (kJ\ mol^{-1}) = (17.9 \pm 0.8) - (3.15 \pm 0.15)n_c. \qquad [17]$$

From this equation it is possible to compute the contribution of each methylene group to the total $\Delta G°$ of the process: $\Delta G°_{CH_2} = -3.15 \pm 0.15\ kJ\ mol^{-1}$. This datum is in quite good agreement with the corresponding value found for the polyoxyethylene chains: $\Delta G°_{CH_2} = -2.8\ kJ\ mol^{-1}$ (29, 30) (see Fig. 5).

Finally, treating the micellization process of the alkylsulfonates surfactant systems according to the phase separation model, it is possible to determine the values of CMC. The logarithms of these values, reported in the companion paper, Ref. 11, are a linear function of the number, n_c, of carbon atoms in the hydrocarbon chain:

$$\log_{10}(CMC) = 1.45(\pm 0.04) - 0.284(\pm 0.005)n_c. \qquad [18]$$

We note that the slope is 0.5 for nonionic surfactants (18), while it is 0.29–0.30 for the ionic (19) ones in good agreement with our value.

Finally, for the $C_{11}SNa$ system it was not possible to measure the D in the whole range of concentration. The analysis of runs was quite difficult in the region where the diffusion coefficients decrease sharply. The Gouy fringe pattern showed an unusual shape, probably due to the high concentration dependence of D in that region. Therefore, the equilibrium parameters for this system were evaluated by extrapolation of those measured for the other members of the series. The diffusion coefficients were fitted reasonably well by Eq. [7] using the following parameters: $D_1 \times 10^5 = 0.6027 - 0.2437C_1^{1/2}$, $D_M \times 10^5 = 0.110\ cm^2\ s^{-1}$, $n = 45$, $q = 36$, $\ln K = 56$ (K in $dm^{44}\ mol^{-44}$).

CONCLUSION

This paper has provided mutual diffusion coefficients for an important class of ionic surfactants.

The micellization process can be easily followed by analyzing the diffusion behavior in terms of the chemical equilibrium model. The values of the mutual diffusion coefficients, found by means of some reasonable approximations, can lead to a good determination of the equilibrium parameters K, n, and q.

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