

Surface and Thermodynamic Parameters of Sodium *N*-Acyl Sarcosinate Surfactant Solutions

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ABSTRACT: Surface tension as a function of concentration and temperature was measured for solutions of *N*-acyl sarcosinates, $\text{RCON}(\text{CH}_3)\text{CH}_2\text{COONa}$. From the intersection points in the $(\gamma\text{-log } c)$ curves, the critical micelle concentration (CMC) was determined at 20, 35, 50, and 65°C. Structural effects on the CMC, maximum surface excess, and the minimum area per molecule at the aqueous solution/air interface are discussed. The free energy, enthalpy, and entropy of micellization and adsorption of surfactant solutions also were investigated. *JAOCS* 74, 43–47 (1997).

KEY WORDS: Gibb's equation, *N*-acyl sarcosinates, surface excess, surface properties, thermodynamic parameters.

N-acyl sarcosinates are marketed under the name Medialan. Sarcosine is used extensively in various phases of the chemical industry, notably as an intermediate in the Rapidogen series of fast cotton dyestuffs (1). *N*-acyl sarcosinate salts make small-particle emulsions and are suitable for cosmetics (2). A toothpaste that contains a C_{8-20} fatty acid sarcosinate has good foaming properties, stability, and consistency in the presence of carboxenates (3,4). The improvement in cleaning and lathering properties of medicated skin cleaners and wound cleaners is achieved by the incorporation of fatty *N*-acyl sarcosinates surfactants (5). They have been particularly favored for personal use because of their mild feel, so they are used in shampoos, bubble-bath pastes, washing creams, aerosols, and synthetic bars (6–9). Numerous investigators have dealt with sarcosinates and their applications as wetting (10,11), flooding, and reducing agents (12,13), and as corrosion inhibitors (14).

The present study deals with the structural effects of *N*-acyl sarcosinates with 12, 14, 16, and 18 carbon atoms on the surface and thermodynamic properties of their solutions by following the methodology of Rosen and colleagues (15,16).

EXPERIMENTAL PROCEDURES

Preparation and purification of *N*-acyl sarcosinates, namely lauroyl, myristoyl, palmitoyl, stearoyl and oleoyl sarcosinates, were prepared according to El-Sukkary *et al.* (17).

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Surface tension was measured with a DuNouy Tensiometer (Kruss Type 8451) for various concentrations of the surfactants (from 1×10^{-5} to 2×10^{-5} mol/L) and at different temperatures (20, 35, 50, and 60°C). Doubly distilled water from an all-glass apparatus with a surface tension of 72.8 dyne/cm at 25°C was used to prepare all solutions.

An electrical conductivity meter (Type 522; Crison Instrument, S.A.) was used to measure the conductivity of the various surfactant solutions. Their concentrations were similar to those of the surface tension measurements (from 1×10^{-5} to 2×10^{-5} mol/L).

RESULTS AND DISCUSSION

Surface tension γ Variations of the surface tension γ values at 20, 35, 50, and 65°C, obtained for various concentrations of aqueous solutions of Na-*N*-lauroyl sarcosinate, Na-*N*-myristoyl sarcosinate, Na-*N*-palmitoyl sarcosinate, Na-*N*-stearoyl sarcosinate and Na-*N*-oleoyl sarcosinate, **I_{a-e}** respectively, are represented in Figure 1A–E. Sharp decreases in surface tension are observed as the activity (concentration) increases, then the curves break rather rapidly at still relatively low concentrations and continue to decrease slowly as the concentrations increase. From the intersection points in the $\gamma\text{-log } c$ curves, the critical micelle concentration (CMC) was determined at each temperature (Table 1). The obtained CMC of the synthesized surfactants show a decreasing trend with increasing temperature. This can be accounted for by thermal effects that decrease hydration of the hydrophilic groups, which favors micellization.

The log CMC values were plotted against their total carbon number of the hydrophobic part C_n . Figure 2 shows that the relation of $\log \text{CMC}-C_n$ is linear for sarcosinate surfactants that contain 12, 14, and 16 carbon atoms in the hydrophobic part, according to Kleven's equation (18). For Na-*N*-stearoyl sarcosinate and Na-*N*-oleoyl sarcosinate, the CMC no longer decreases. This may be due to coiling of these long chains in water.

Electrical conductivity. When the equivalent conductance of sodium *N*-acyl sarcosinate surfactant solutions is plotted against the square root of the concentration (Fig. 3), the curves slope sharply downward in diluted solution. Lauroyl sarcosinate shows no break at all. As the hydrophobic chain

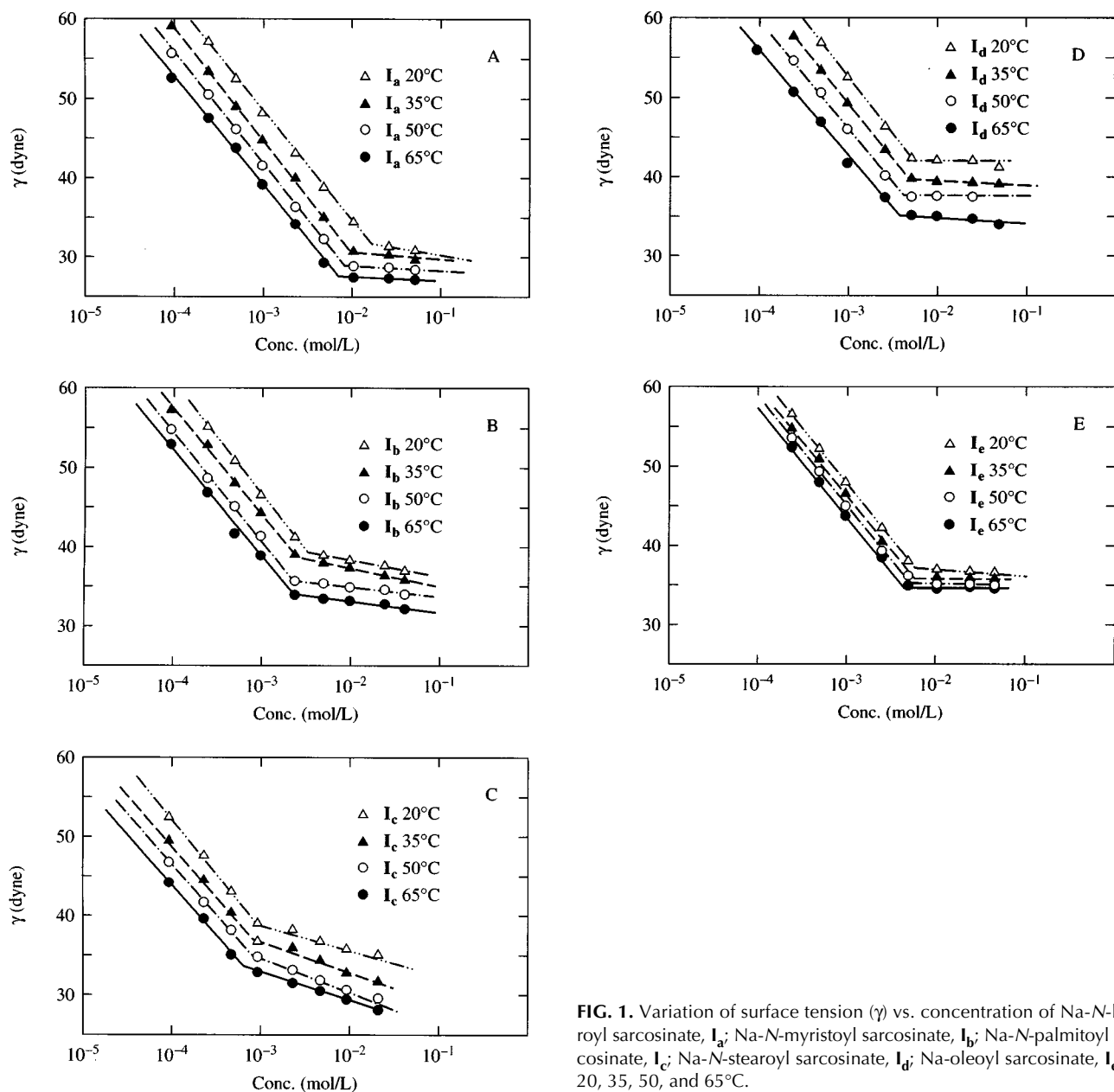


FIG. 1. Variation of surface tension (γ) vs. concentration of Na-*N*-lauryl sarcosinate, I_a ; Na-*N*-myristoyl sarcosinate, I_b ; Na-*N*-palmitoyl sarcosinate, I_c ; Na-*N*-stearoyl sarcosinate, I_d ; Na-*N*-oleoyl sarcosinate, I_e ; at 20, 35, 50, and 65°C.

increases in the homologous series, a break in the slope of the curve occurs at a concentration range at which ionic micelles begin to form rapidly, i.e., the critical concentration. The critical range is sharper as the chainlength increases and has lower concentration values. Figure 3 also shows that, as the temperature increases, the slope in the pre-critical point occurs at almost the same concentrations.

However, the CMC decreases with increasing temperature for the plots of γ -log c curves, as indicated in Figure 1A-E). Conversely, by plotting equivalent conductance vs. the square root of the concentration (Fig. 3), the critical range increases with increasing temperature. Evidently, temperature is not an important factor for determining CMC by the electrical conductivity method.

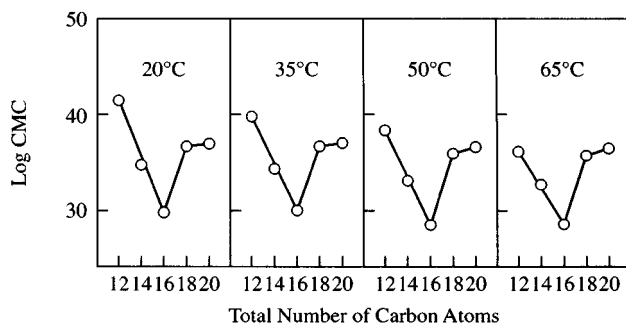


FIG. 2. Variation of log critical micelle concentration (CMC) against total number of carbon atoms in the alkyl chain of sodium *N*-acyl sarcosinate products at 20, 35, 50 and 65°C.

TABLE 1
Critical Micelle Concentration (CMC), Maximum Surface Excess (Γ_{\max}), Minimum Area (A_{\min}), Efficiency (P_{C20}), and Effectiveness (Π_{CMC}) of the Synthesized Sodium *N*-Acyl Sarcosinates, $RCON-(CH_2)_3CH_2-COONa$, *a-e*

Compound	Temp. (°C)	CMC	$\Gamma_{\max} \times 10^{10}$ (mol · cm ⁻²)	A_{\min} (nm ²)	P_{C20}	Π_{CMC} (dyne · cm ⁻¹)
I_a	20	1.5×10^{-2}	1.34	123	3.30	41
	35	1×10^{-2}	1.32	124.9	2.55	42
	50	1×10^{-3}	1.29	127.8	3.74	43.25
	65	4×10^{-3}	1.1518	133.1	3.92	45
I_b	20	3×10^{-3}	1.309	126	3.74	32
	35	2.5×10^{-3}	1.256	131	3.6	33
	50	2×10^{-3}	1.214	135.8	4.15	35.75
	65	1.8×10^{-3}	1.16	142.2	4	37.25
I_c	20	9×10^{-4}	1.261	130.8	3.95	33.5
	35	8×10^{-4}	1.245	132.49	4.22	35
	50	7×10^{-4}	1.20	137.4	4.42	36.75
	65	6.5×10^{-4}	1.1526	143	4.6	38.75
I_d	20	5×10^{-3}	1.233	133.7	3	29.75
	35	4.5×10^{-3}	1.205	136.86	3.18	32
	50	4×10^{-3}	1.2022	137.2	3.39	34
	65	3.8×10^{-3}	1.1789	139.9	3.65	36.75
I_e	20	5×10^{-3}	1.23	134.11	3.3	34.75
	35	5×10^{-3}	1.226	134.46	3.39	36.75
	50	4.5×10^{-3}	1.206	136.78	3.49	36.25
	65	4×10^{-3}	1.16	142.2	3.58	36.5

Effectiveness Π_{CMC} . Above the CMC, the surface tension γ did not change much with the concentration; accordingly, γ at the CMC was used to calculate the value of the surface pressure (effectiveness) $\Pi_{CMC} = \gamma_0 - \gamma$, where γ_0 is the surface tension for pure water at the appropriate temperature and γ is the surface tension at the CMC. The most effect surfactant is one that gives the greater lowering in surface tension for a critical micelle concentration (cmc). According to the

results shown in Table 1, Na-*N*-lauroyl sarcosinate, **I_a**, was the most effective, and the effectiveness increases with increasing temperature for all prepared sarcosinates.

Efficiency P_{C20} . Efficiency, P_{C20} is determined by the concentration (mol/L) that is capable to suppress the surface tension of the solvent by 20 dyne/cm. Therefore, the most effective surfactant is the one that gives a surface pressure of 52 dyne/cm at the lowest concentration. The efficiency values of the synthesized surfactants are given in Table 1 and shown graphically in Figure 4. The efficiency of adsorption P_{C20} increases linearly with increasing the number of carbon atoms in a straight chain of the hydrophobic group up to 16. This reflects the negative free energy of adsorption of the prepared surfactants at the aqueous solution/air interface (Table 2). However, beyond 16 carbon atoms, the efficiency of adsorption appears to decrease for Na-*N*-stearoyl sarcosinate, **I_d**, but a little increase in efficiency of adsorption was observed for Na-*N*-oleoyl sarcosinate. This indicates that the existence of double bonds in the skeleton of the surface-active agent also affects the adsorption.

Surface excess Γ . According to the Gibb's equation $\Gamma = 1/RT(d\gamma/d \ln c)$, where Γ is called surface excess, $d\gamma$ is surface pressure and c is the concentration of the surfactant. A substance that lowers the surface energy is thus present in excess at or near the surface, i.e., when the surface tension decreases with increasing activity of a surfactant, Γ is positive. Figure 5 represents the variation of the surface pressure, $d\gamma$, with $\log c$ of sarcosinate surfactants at different temperatures. Taking Γ as the slope of the plots $d\gamma$ - $\log c$, a slope with approximately the same value is reached in every case, but as we go up the surfactant series, **I_{a-c}**, this value was reached at progressively lower concentrations. Γ was attained at relatively higher concentrations for **I_d** and **I_e**.

The maximum surface excess, Γ_{\max} , of the synthesized surfactants was calculated from Gibb's adsorption equation at

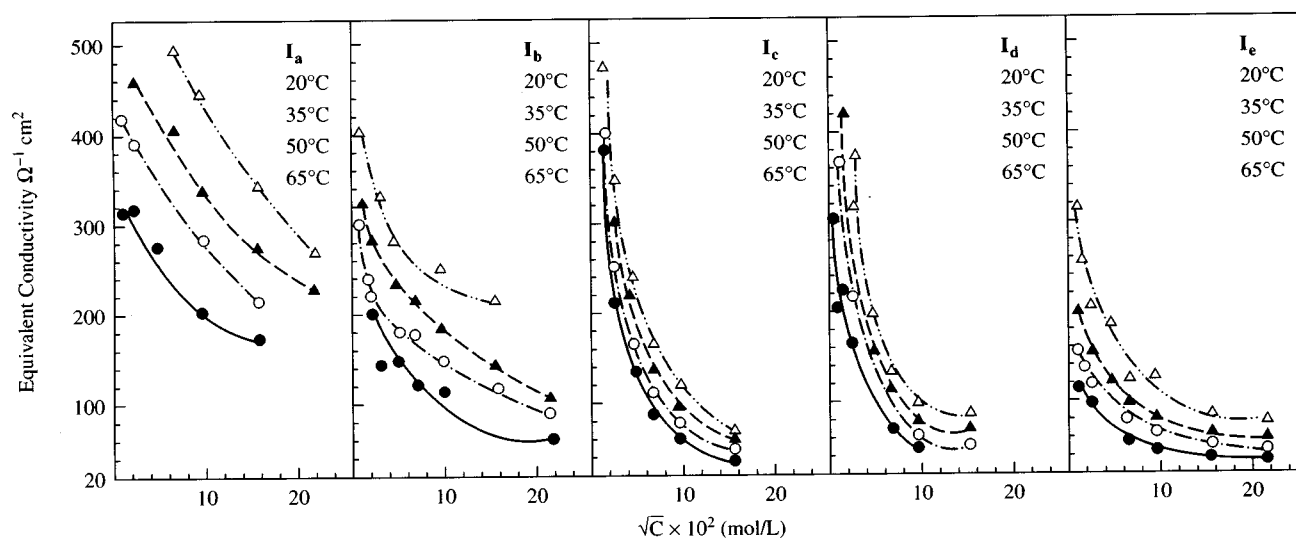


FIG. 3. Equivalent conductance vs. square root of concentration of Na-*N*-lauroyl sarcosinate, **I_a**; Na-*N*-myristoyl sarcosinate, **I_b**; Na-*N*-palmitoyl sarcosinate, **I_c**; Na-*N*-stearoyl sarcosinate, **I_d**; Na-oleoyl sarcosinate, **I_e**; at 20, 35, 50, and 65°C.

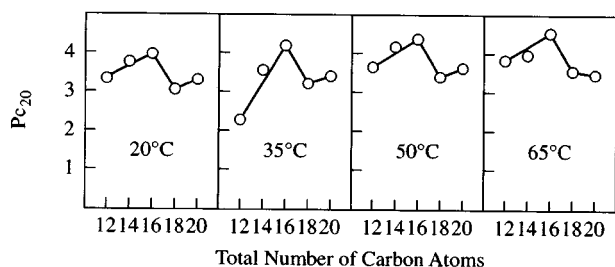


FIG. 4. Variation of efficiency ($P_{C_{20}}$) against total number of carbon atoms in the alkyl chain of sodium *N*-acyl sarcosinates at 20, 35, 50, and 65°C.

the CMC. The values of Γ_{\max} are given in Table 2. As the hydrophobic moiety of the denoted surfactants increases, Γ_{\max} is attained at a lower concentration. Increasing temperature from 20 up to 65°C causes a decrease in Γ_{\max} .

Minimum surface area A_{\min} . The minimum area per molecule at the aqueous solution/air interface increases with increasing length of the hydrophobic part. The minimum area per molecule also increases with temperature, as would be expected from the increased thermal agitation of the molecules in the interface film. Analysis of the data, shown in Table 1, indicated that the surface pressure Π of the prepared surfactants decreases with increasing surface area of the surfactant molecule.

Thermodynamic parameters. Table 2 lists standard free energy, $\Delta G^{\circ}_{\text{mic}}$; enthalpy, $\Delta H^{\circ}_{\text{mic}}$; and entropy, $\Delta S^{\circ}_{\text{mic}}$, of micellization for the synthesized surfactants **I_{a-e}**. $\Delta G^{\circ}_{\text{mic}}$ values were calculated at each of the four temperatures used (20, 35, 50, and 65°C), according to Rosen and colleagues (16). The

standard free energies of micellization for the sarcosinate surfactants are always negative values, indicating that micellization is a spontaneous process. At a constant temperature, $\Delta G^{\circ}_{\text{mic}}$ decreased as the chainlength of the hydrophobic moiety increases, indicating that thermodynamic favorability for micellization increases. Analysis of $\Delta G^{\circ}_{\text{mic}}$ indicates that the free energy change ΔG ($-\text{CH}_2$), involved in the transfer of a methylene unit of the hydrophobic group from an aqueous environment to the interior of the micelle, is negative and thus favors micellization. This accounts for the fact that the CMC decreases with an increase in the length of the hydrophobic group, up to 16 carbon atoms. For Na-*N*-stearoyl sarcosinate, **I_d**, which contains 18 carbon atoms in the hydrophobic part, $\Delta G^{\circ}_{\text{mic}}$ becomes less negative, i.e., the tendency of micellization under the stated conditions decreases. $\Delta G^{\circ}_{\text{mic}}$ for Na-*N*-oleoyl sarcosinate, **I_e**, indicates that the presence of the double bond in the skeleton of the hydrophobic part also affects the micellization process.

The results in Table 2 show that micellization of the prepared surfactants is thermodynamically controlled by the contributions of $\Delta H^{\circ}_{\text{mic}}$ and $\Delta S^{\circ}_{\text{mic}}$ coming from the hydrocarbon-water interaction. An increase in temperature from 35 to 50°C seems to cause both $\Delta H^{\circ}_{\text{mic}}$ and $\Delta S^{\circ}_{\text{mic}}$ to become more positive, indicating that the amount of water that is structured by the hydrophobic chain increases. However, increasing temperature up to 65°C causes a dehydration process. The $\Delta S^{\circ}_{\text{mic}}$ values in Table 2 are all positive, indicating increased randomness in the system upon transformation of the surfactant molecules into micelles. The slight decrease in the positive $\Delta S^{\circ}_{\text{mic}}$ value with increasing number of methylene groups in the hydrophobic part is due to the relative cramped

TABLE 2
Thermodynamic Parameters of Micellization and Adsorption for Sodium *N*-Acyl Sarcosinates, **I_{a-e}**

Compound	Temp. (°C)	$\Delta G^{\circ}_{\text{mic}}$ (KJ · mol ⁻¹)	$\Delta H^{\circ}_{\text{mic}}$ (KJ · mol ⁻¹)	$\Delta S^{\circ}_{\text{mic}}$ (KJ · mol ⁻¹ K ⁻¹)	$\Delta G^{\circ}_{\text{ad}}$ (KJ · mol ⁻¹)	$\Delta H^{\circ}_{\text{ad}}$ (KJ · mol ⁻¹)	$\Delta S^{\circ}_{\text{ad}}$ (KJ · mol ⁻¹ K ⁻¹)
I_a	20	-20.5	—	—	-50.87	—	—
	35	-23.56	—	—	-55.15	—	—
	50	-26.62	—	—	-59.9	—	—
	65	-28.27	30.2414	0.1726	-64.66	21.35	0.2459
I_b	20	-28.27	—	—	-52.55	—	—
	35	-30.63	—	—	-56.66	—	—
	50	-33.33	—	—	-52.57	—	—
	65	-35.48	18.601	0.16	-267.38	43.823	0.329
I_c	20	-34.12	—	—	-60.5	—	—
	35	-36.48	—	—	-64.4	—	—
	50	-38.97	—	—	-69.38	—	—
	65	-41.97	11.869	0.157	-74.57	31.1226	0.3127
I_d	20	-25.77	—	—	-49.73	—	—
	35	27.63	—	—	54.01	—	—
	50	-29.62	—	—	-57.71	—	—
	65	-31.28	10.088	0.1224	-62.25	31.716	0.278
I_e	20	-25.77	—	—	-53.84	—	—
	35	-27.09	—	—	-56.85	—	—
	50	-28.98	—	—	-58.83	—	—
	65	-30.99	8.23904	0.11608	-62.60	3.23391	0.1948

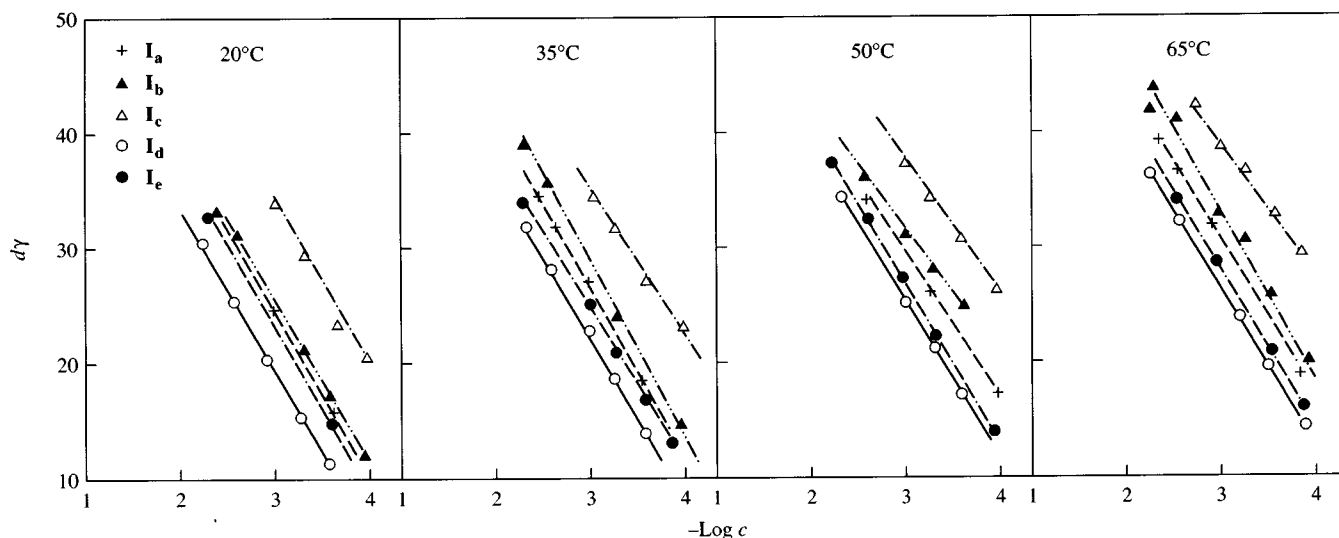


FIG. 5. Variation of surface pressure ($d\gamma$) against $-\log$ conc. of sodium *N*-acyl sarcosinates I_{a-e} at 20, 35, 65°C; +, I_a ; ▲, I_b ; △, I_c ; ○, I_d ; ●, I_e .

interior beneath the convex surface of the micelles. According to the data in Table 2, ΔS°_{ad} values of the prepared surfactants I_{a-e} are all positive and slightly greater than the ΔS°_{mic} values of the same compounds, which may reflect on the greater freedom of motion of the hydrocarbon chain at the planar air/aqueous solution interface than in the interior of the micelles.

The linearity in the \log CMC- C_n relationship is limited to sarcosinates that contain 12, 14, and 16 carbon atoms. As the temperature increases, the CMC values measured by surface tension are not parallel with the critical ranges measured by the electrical conductivity method. Thermodynamic parameters indicate that the sarcosinate molecules prefer adsorption at the liquid/air interface more than micellization in the bulk of their solution.

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