Surface and Thermodynamic Properties of Octyl, Dodecyl, and Cetyl Sulfoacetates

E. A. M. Gad, M. M. A. El-Sukkary, and E. M. S. Azzam

Egyptian Petroleum Research Institute, Nasr City, Cairo, Egypt

Summary. Three anionic surfactants (Na-octysulfoacetate (A_8), Na-dodecylsulfoacetate (A_{12}), and Na-cetylsulfoacetate (A_{16}) were prepared from alkyl bromoacetate. Several studies were carried out with aqueous surfactant solutions including surface tension, and electrical conductivity measurements. Surface properties, in particular, critical micelle concentration (CMC), effectiveness (Π_{CMC}), efficiency (P_{c20}), maximum surface excess (Γ_{max}), and minimum surface area (A_{min}) were investigated at different concentrations at 20, 35 and 50°C, respectively. Free energies, enthalpies, entropies of micellization, and adsorption of the surfactants in the aqueous solution were studied.

Keywords. *Gibb*'s equation; Alkyl bromoacetate; Critical micelle concentration; Micellization; Adsorption; Thermodynamic parameters.

Thermodynamik und Oberflächeneigenschaften von Octyl-, Dodecyl- und Cetylsulfoacetaten

Zusammenfassung. Drei anionische Tenside (Na-Octylsulfoacetat (A_8), Na-Dodecylsulfoacetat (A_{12}) und Na-Cetylsulfoacetat (A_{16})) wurden aus Bromessigsäurealkylestern hergestellt. An wäßrigen Lösungen der Tenside wurden deren Oberflächenspannung und elektrische Leitfähigkeit gemessen. Oberflächeneigenschaften, insbesondere kritische Micellenkonzentration (MCC), Effektivität (Π_{CMC}), Effizienz (P_{c20}) maximaler Oberflächenüberschuß (Γ_{max}) und minimale Oberfläche (A_{min}) wurden bei verschiedenen Konzentrationen und bei Temperaturen von 20, 35 und 50°C untersucht. Die freien Energien, Enthalpien, Entropien und die Adsorption der Tenside in wäßriger Lösung wurden bestimmt.

Introduction

In a previous investigation, the structural effects of *N*-acyl sarcosinates on surface and thermodynamic properties of their solutions have been discussed [1]. Several investigations have covered these properties in relation to the structure of the various types of surfactants [2–8]. The surface activity of Na-alkyl sulfoacetate stems from the hydrophobic character of a higher alcohol attached to sulfoacetic acid *via* an ester linkage and the hydrophilic character of sulfonic group itself [9]. In this study, the structural effect of Na-alkylsulfoacetates on the surface and thermodynamic properties of their solutions using the methodology of *Rosen et al.* [6, 7] is investigated.

Results and Discussion

Critical micelle concentration (CMC)

Values of the surface tension γ at 20, 25, and 50°C obtained for various concentrations of aqueous solutions of the anionic surfactants are shown in Table 1 and graphically in Fig. 1. From the intersection points in the γ vs. log c curves, the critical micelle concentration (CMC) was determined at each temperature. The CMC values (Table 1) show an increasing trend with increasing temperature due to disruption of the structured water surrounding the hydrophobic group. This effect disfavors micellization.

For a homologous series of surfactants, the CMC value may also be expressed by the well-known empirical equation given by Klevens and Corrin [10]:

Table 1. Critical micelle concentration (CMC), effectiveness (Π_{CMC}, efficiency (PC_{20}), maximum surface excess (Γ_{max}), and minimum area (A_{min}) of the anionic surfactants

| Surfactant	T (°C)	CMC (mol·1)	Π_{CMC} (dyne·cm^{-1})	(PC_{20}) ($-\log(\text{mol}/1)$)	$\Gamma_{max} \times 10^{10}$ (mol·cm^{-2})	A_{min} (nm^2)
Sodium	20	1.9×10^{-3}	24.60	3.30	7.196	0.229
Octylsulfoacetate	35	3.8×10^{-3}	22.87	2.88	6.689	0.246
(A_8)	50	5×10^{-3}	22.10	2.60	5.990	0.276
Sodium	20	5.5×10^{-4}	25.75	3.88	5.604	0.294
dodecylsulfoacetate	35	9×10^{-4}	25.00	3.60	5.170	0.319
(A_{12})	50	1.5×10^{-4}	22.00	3.22	4.700	0.350
Sodium	20	1×10^{-4}	22.20	4.22	4.686	0.352
cetylsulfoacetate	35	2.5×10^{-4}	22.00	4.00	4.330	0.380
(A_{16})	50	4×10^{-4}	20.00	3.52	3.370	0.489
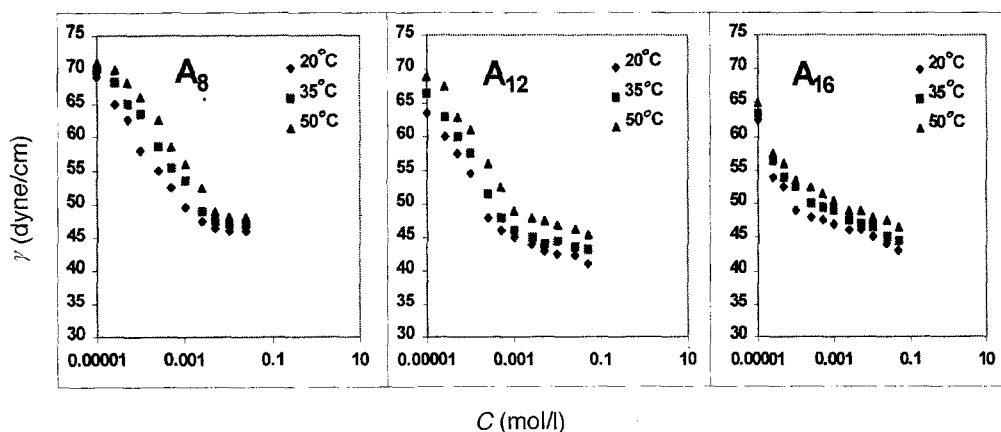
Fig. 1. Variation of surface tension (γ) with concentration of sodium alkyl sulfoacetate solution at 20, 35, and 50°C
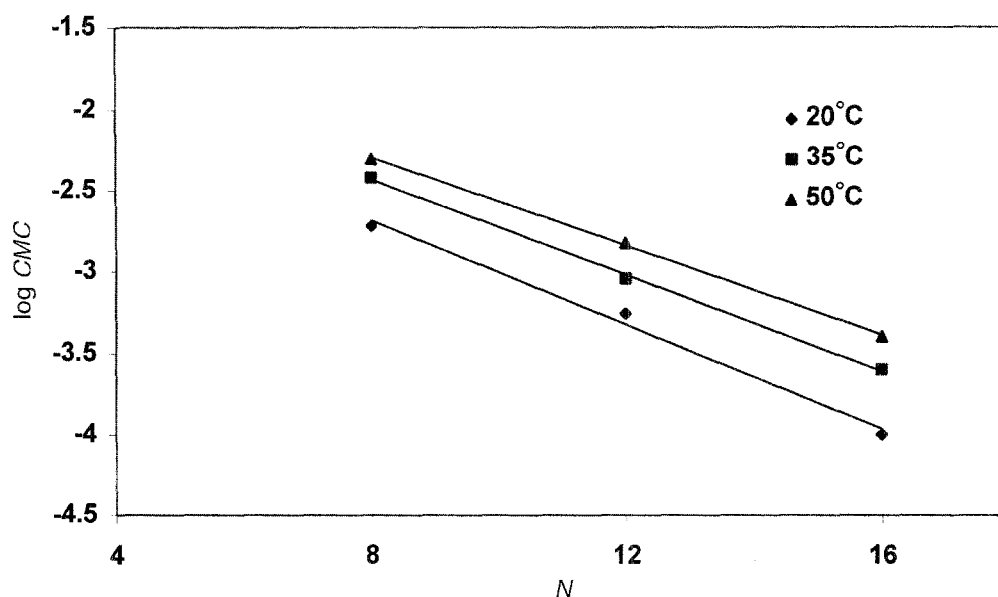
Fig. 2. Variation of log CMC with number of carbon atoms

$\log CMC = A - BN$ N is the number of carbon atoms in the hydrocarbon and A and B are constants representing temperature and homologous series. In the present study it was observed that CMC values decrease with increasing number of methylene groups in the hydrophobic moiety (Fig. 2), obeying a linear relationship as shown in the following equations:

$$20°C : \log CMC = -1.1956 - 0.1371N$$
$$35°C : \log CMC = -1.2499 - 0.1477N$$
$$50°C : \log CMC = -1.4088 - 0.1598N$$

Electrical conductivity

When the equivalent conductances of the anionic surfactants are plotted against the square root of the concentration (Fig. 3), the curves slope sharply downward in diluted solution. A break in the slope of the curve apparently coincides with the point at which ionic micelles begin to form rapidly. In this series, it was seen that when the temperature is increased, the slope in the pre-critical range becomes steeper and the critical point itself occurs at almost the same concentration. The temperature is therefore not an important factor in determining the critical micelle concentration. This result agrees with the previously reported ones [1].
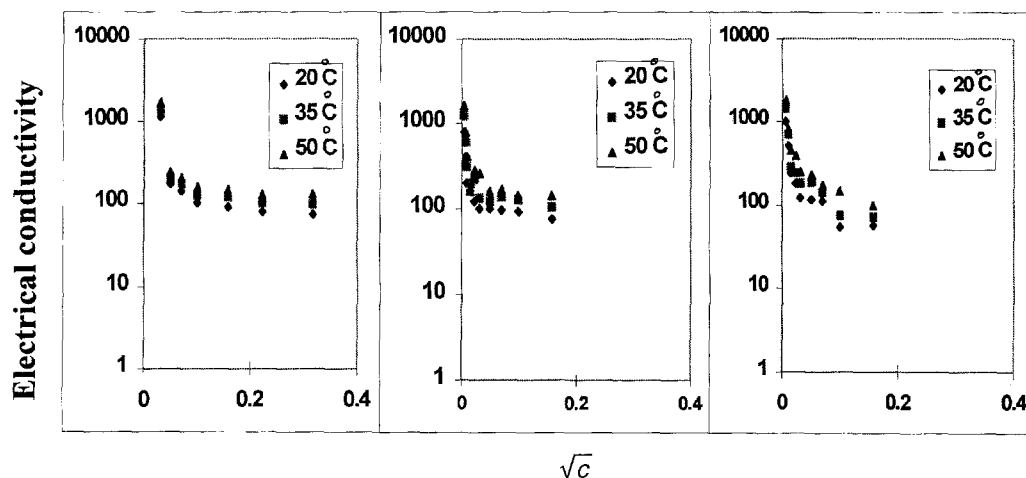
Fig. 3. Variation of electrical conductivity with the square root of the concentration of the anionic surfactants at different temperatures

Effectiveness (Π_{CMC})

The surface tension values (γ) at *CMC* were used to calculate values of the surface pressure (effectiveness) from $\Pi_{CMC} = \gamma_o - \gamma$ where γ_o is the surface tension measured for pure water at the appropriate temperature and γ is the surface tension at critical micelle concentration. Values of Π_{CMC} at 20, 35, and 50°C are given in Table 1. Obviously, sodium dodecylsulfoacetate (A_{12}) achieves the maximum reduction of the surface tension at *CMC*.

Efficiency ($^PC_{20}$)

($^PC_{20}$) is determined by the concentration of surfactant capable to suppress the surface tension by 20 dyne/cm. The values of efficiency of the surfactants are shown in Table 1. It could be observed that the efficiency increases with lengthening of the hydrophobic moiety. As the temperature increases, the values of ($^PC_{20}$) decreases.

Surface excess (Γ_{max})

According to $\Gamma = 1/RT \, (d\gamma/d\ln c)_T$ (*Gibb*'s equation; Γ: surface excess, $d\gamma$: surface pressure, c: concentration of the surfactant, T: absolute temperature, R: gas constant), a substance that lowers the surface energy is present in excess at or near the surface, *i.e.* when the surface tension decreases with increasing activity of surfactant, Γ is positive. Fig. 4 represents the variation of the surface pressure with the logarithm of the concentration of the surfactants A_8, A_{12}, A_{16} at different temperatures. Taking Γ as the slope of the plots in Fig. 4, it can be seen that it is approximately the same for each surfactant at various temperatures except for A_{16} at 35°C. As we go up the homologous series of the surfactants, this value is reached at a progressively lower concentration. The maximum surface excess of the
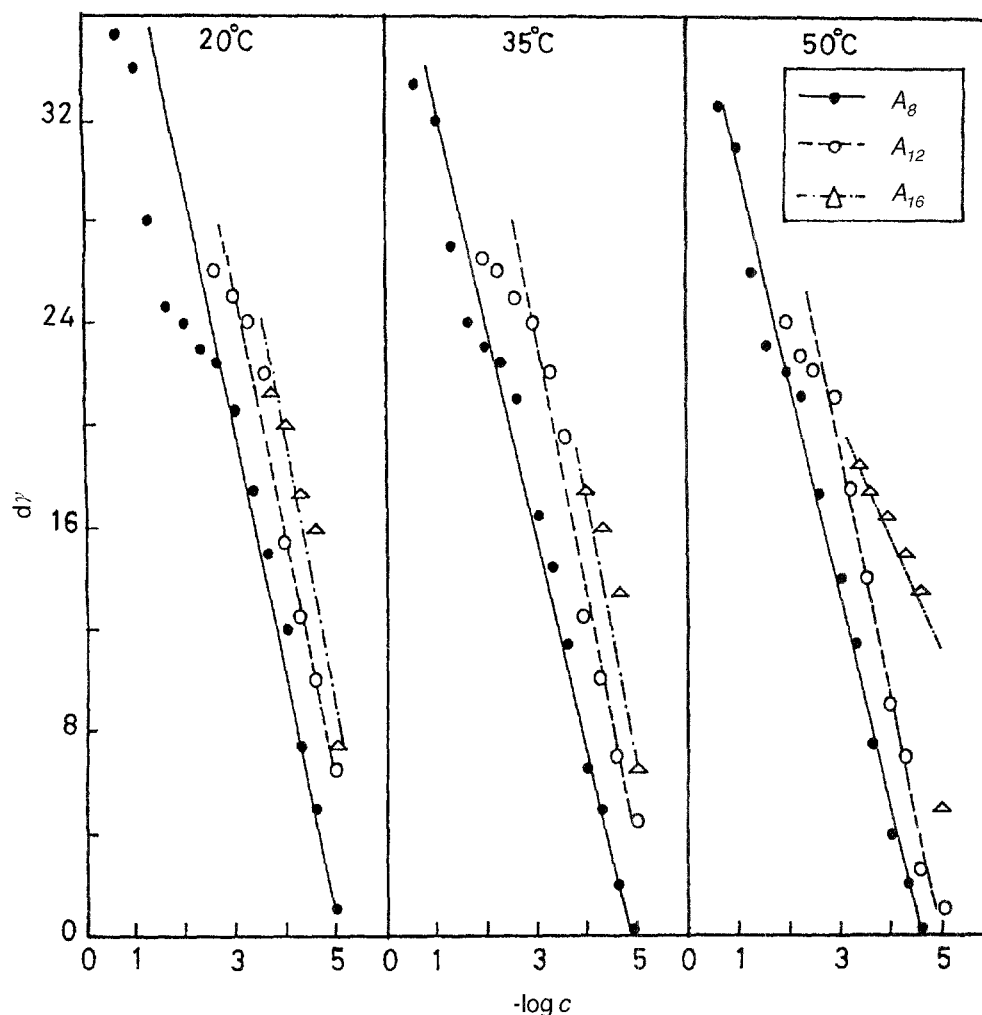
Fig. 4. Variation of surface pressure $(d\gamma)$ with $\log c$ at 20, 35, and 50°C

surfactants was calculated from *Gibb*'s adsorption equation at *CMC*. The values of Γ_{max} are represented in Table 1. Increasing the hydrophobic character of the anionic surfactants shifts Γ_{max} to lower concentrations. For all instances, Γ_{max} decreases as the temperature increases.

Minimum surface area (A_{min})

The average area occupied by each adsorbed molecule is given by $A_{min} = 1/\Gamma_{max} \cdot N \cdot \Gamma_{max}$ is the maximum surface excess, and N is *Avogadro*'s number. The minimum area per molecule at the aqueous solution/air interface for anionic surfactants (Table 1) increases with increasing length of hydrophobic moiety. The minimum area per molecule also increases with increasing temperature, as would be expected from the increased thermal agitation of the molecules in the interface film. Analysis of the data in Table 1 indicates that the surface pressure Π_{CMC} of anionic surfactants decreases with increasing surface area of the surfactant molecule.

Interfacial tension and emulsion stability

Correlation between the chemical structure of surface active agents and their emulsifying power are critical by the fact that both phases, oil and water, are of variable composition. Analysis of the date of interfacial tension and emulsion stability (Fig. 5) indicate that variations of both interfacial tension and emulsion stability are independent of the number of carbon atoms in the alkyl chain of the surfactants. More stable emulsions were found for surfactants with a higher ability to depress interfacial tension (A_{12}).

Thermodynamic parameters

Table 2 shows standard free energies, enthalpies and entropies of micellization for the surfactants. The values were calculated at three different temperatures (20, 35, and 50°C) according to *Rosen et al.* [6, 7]. Obviously, the standard free energies of micellization for the sodium alkyl sulfoacetate homologues are always negative, indicating that the micellization is a spontaneous process. The free energy change $\Delta G(CH_2)$ involved in the transfer of a methylene group from an aqueous environment to the interior of the micelle is negative, thus favouring micellization. This accounts for the fact that *CMC* decreases with increasing length of the hydrophobic group, *i.e.* introduction of additional methylene groups induces
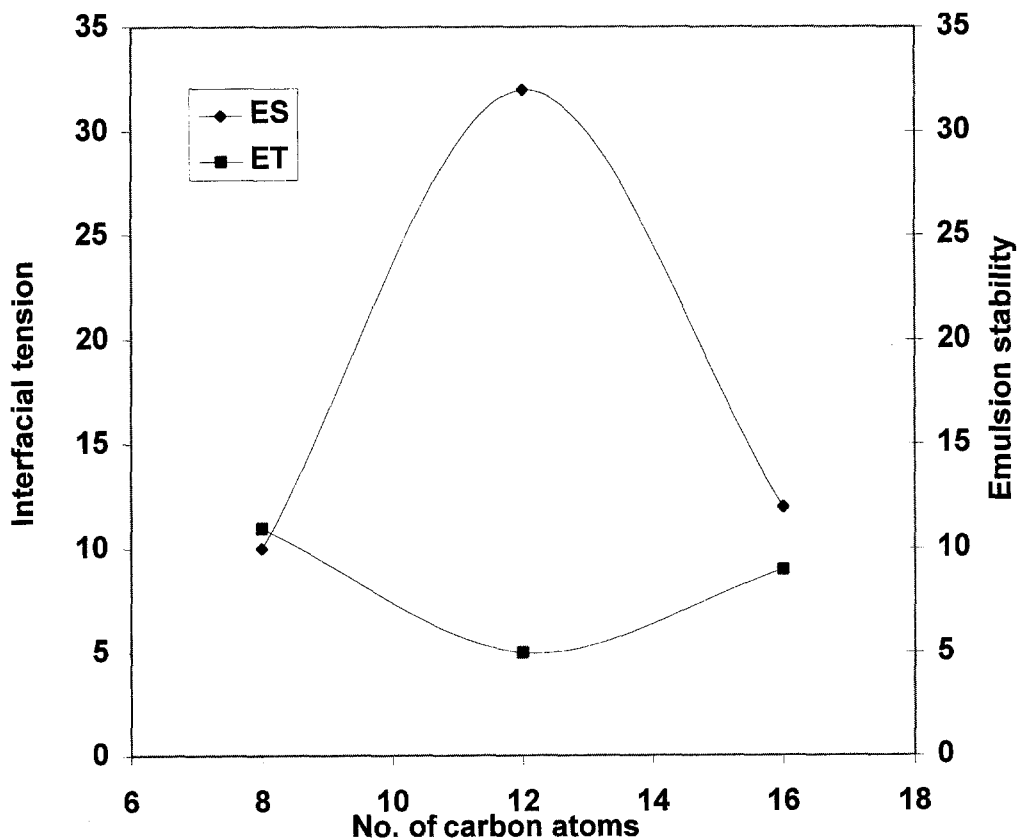

Fig. 5. Variation of interfacial tension and emulsion stability with number of carbon atoms

Table 2. Thermodynamic parameters of micellization and adsorption

Surfactant	T (°C)	ΔG^{o}_{mic} (kJ·mol⁻¹)	ΔS^{o}_{mic} (kJ·mol⁻¹·K⁻¹)	ΔH^{o}_{mic} (kJ·mol⁻¹)	ΔG^{o}_{ad} (kJ·mol⁻¹)	ΔS^{o}_{a} (kJ·mol⁻¹·K⁻¹)	ΔH^{o}_{a} (kJ·mol⁻¹)
Sodium octylsulfoacetate (A_8)	20	-30.48	-	-	-33.87	-	-
	35	-28.50	0.131	11.96	-31.89	0.132	9.00
	50	-28.41	0.069	-6.16	-32.07	0.060	-12.72
Sodium dodecylsulfoacetate (A_{12})	20	-36.53	-	-	-41.09	-	-
	35	-35.81	0.047	-21.33	-40.61	0.032	-30.76
	50	-34.88	0.055	-17.12	-39.52	0.052	-22.73
Sodium cetylsulfoacetate (A_{16})	20	-44.82	-	-	49.52	-	-
	35	-42.40	0.161	7.18	-47.45	0.138	-4.90
	50	-41.97	0.095	-11.28	-47.86	0.055	-30.09

micellization. As the temperature increases, ΔG°_{mic} becomes less negative. This may be due to steric inhibition of micellization.

ΔH°_{mic} is sometimes negative and sometimes positive; therefore, the micellization process is governed primarily by the entropy gain associated with it, and the driving force for the process is the tendency of the hydrophobic group of the surfactant to migrate from the solvent environment to the interior of the micelle. The positive values of the entropies are due to the increased freedom of the hydrophobic chain in the nonpolar interior of the micelles compared to the aqueous environment.

According to the data in Table 2, ΔS°_{mic} of A_8, A_{12}, and A_{16} is often slightly higher than ΔS°_{ad}. This indicates that there is less restriction to the motion of the surfactant molecule in the essentially water free environment of the micelle than in the aqueous phase.

Experimental

Alkyl bromoacetates were prepared from 0.3 mol of bromoacetic acid and 0.3 mol of octyl, dodecyl, and cetyl alcohol, respectively. Three ml of concentrated hydrochloric acid in 200 ml of toluene were added and the reaction mixture was heated and stirred at reflux temperature for 4 h with azeotropic removal of water.

A mixture of 0.3 mol of the alkyl-bromoacetate and 0.5 mol of sodium sulfite in 200 ml of water was stirred and refluxed for 1 h. After cooling, a yellowish white emulsion was obtained. Water was removed under reduced pressure.

The crude material was purified by three recrystallizations from methyl alcohol followed by extraction with petroleum ether for 100 h. The product was dried at room temperature under reduced pressure to give the purified sodium alkyl sulfoacetates as a white flaky powder. The compounds decompose above 170°C; their purity was confirmed by elementary analysis, IR, and ^{1}H NMR spectroscopy.

Surface and interfacial tension were measured using a Du Nouy Tensiometer (Kruss Type 8451, Germany) for various concentrations of the surfactants (from 1×10^{-5} to 2×10^{-1} mol/l) and at different temperatures (20, 35, and 50°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 Instruments S.A., Barcelona, Spain) was used to measure the conductivity of the various surfactant solutions. Their concentrations were similar to those used for the surface tension measurements.

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