Thermodynamics of Dissociation and Micellization of Sodium, Calcium, Aluminum, and Tin Stearates in Mixed Organic Solvents

Hüseyin Topallar*, Yüksel Bayrak, and Mehmet İşcan

Department of Chemistry, Faculty of Arts and Sciences, Trakya University, 22030 Edirne, Turkey

ABSTRACT: Sodium, calcium, aluminum, and tin stearates behave as weak electrolytes in dilute solutions (60% benzene + 40% methanol, vol/vol) below the critical micelle concentration, and conductance data can be explained on the basis of Ostwald's formula and the Debye-Hückel theory of weak electrolytes. Dissociation constants and thermodynamic parameters for dissociation and micellization of these soaps were also evaluated. Micellization was spontaneous and predominant over the dissociation process.

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KEY WORDS: Aluminum and tin stearate, calcium, conductance, critical micelle concentration, dissociation, micellization, sodium, thermodynamics.

Specific and equivalent conductivities of sodium and potassium soaps in alcohols, toluene, and pyridine have been determined by Bhatnagar and Prasad (1). Patrick *et al.* (2) pointed out that sodium oleate in alcohols behaves as a simple electrolyte. Several workers (3,4) have investigated soap solutions that bridge the transition from aqueous to nonaqueous solutions.

Critical micelle concentrations (CMC) of aqueous solutions of magnesium soaps were determined by Varma and Kumar (5). Varma and Dayal (6) studied the conductance behavior of aqueous solutions of barium, strontium, and nickel soaps.

Mehrotra and Upadhyaya (7) studied the thermodynamics of dissociation and micellization of praseodymium and neodymium linoleates in mixed organic solvents to determine physicochemical properties and structure.

In this work, we focused on conductance and micellar behavior of sodium, calcium, aluminum, and tin (stannic) stearate soaps in a mixture of 60% benzene and 40% methanol (vol/vol) at different temperatures.

EXPERIMENTAL PROCEDURES

Sodium hydroxide (NaOH), calcium sulfate dihydrate ($CaSO_4 \cdot 2H_2O$), aluminum sulfate-18-hydrate [$Al_2(SO_4)_3 \cdot 18H_2O$], tin (IV) chloride ($SnCl_4$), and stearic acid ($C_{17}H_{35}COOH$) were supplied by Merck (Darmstadt, Germany). The melting range of the stearic acid was 68–70°C, and its acid number was 196.

Sodium stearate was obtained from the reaction of NaOH with stearic acid. Ca^{2+}, Al^{3+}, and Sn^{4+} stearates were prepared by direct metathesis of Na^+ stearate with the stoichiometrically required amounts of $CaSO_4 \cdot 2H_2O$, $Al_2(SO_4)_3 \cdot 18H_2O$, and $SnCl_4$ in a water–alcohol medium (1:1, vol/vol). The precipitated soaps were washed with water and acetone to remove excess metal ion and unreacted stearic acid.

Soap solutions were prepared by dissolving a measured amount of soap in a mixture of 60% benzene and 40% methanol (vol/vol) and were kept for 2 h in a thermostatted water bath at the desired temperature.

Conductance of the soap solutions was measured with an Orion digital conductivity meter, Model 126 (Orion Research Inc., Boston, MA), and a dipping-type conductivity cell (cell constant 1.01) with platinized electrodes. The reproducibility of the measurements was ±0.1%.

RESULTS AND DISCUSSION

Specific conductance K of Na^+, Ca^{2+}, Al^{3+}, and Sn^{4+} stearate soap solutions in 60% benzene and 40% methanol (vol/vol) increases with increases in soap concentration and temperature. Plots of specific conductance K vs. soap concentration C (Fig. 1) are characterized by the intersections of two straight lines at concentrations that correspond to the CMC (Table 1).

The values of molar conductance Λ of the dilute soap solutions decrease with increasing soap concentration. The de-

TABLE 1
Critical Micellar Concentrations (CMC) of Na^+, Ca^{2+}, Al^{3+}, and Sn^{4+} Stearates in 60% Benzene and 40% Methanol (vol/vol)

	CMC × 10^3 (mol L^{-1})			
Soap	25°C	35°C	45°C	55°C
Sodium stearate	6.1	6.2	6.4	6.5
Calcium stearate	5.3	5.5	5.6	5.8
Aluminum stearate	4.9	4.9	5.1	5.2
Tin stearate	4.2	4.4	4.5	4.6

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*To whom correspondence should be addressed.

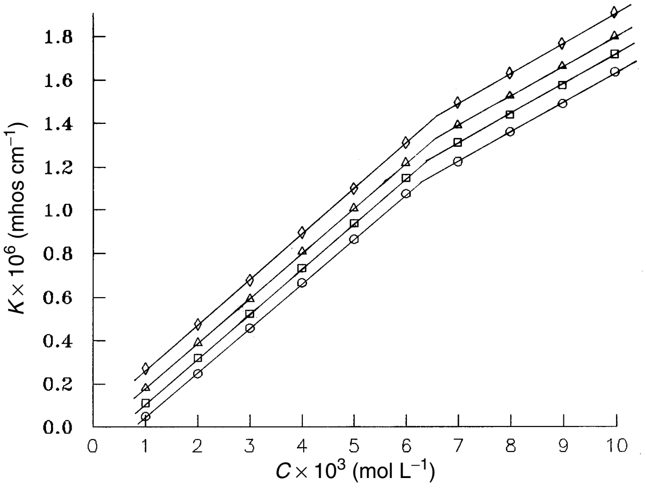

FIG. 1. Specific conductance (*K*) vs. concentration (*C*) plots of sodium stearate in 60% benzene and 40% methanol (vol/vol): ○, 25°C; □, 35°C; △, 45°C; and ◇, 55°C.

crease in molar conductance may be due to the combined effects of ionic atmosphere, solvation of ions and decrease of mobility, and ionization with formation of micelles.

However, CMC values cannot be obtained from plots of molar conductance vs. square root of soap concentration because the plots are concave upward with increasing slopes, indicating that metallic soaps behave as weak electrolytes in dilute solutions (6). Because Na^+, Ca^{2+}, Al^{3+}, and Sn^{4+} stearates behave as weak electrolytes in dilute solution, an expression for the dissociation of these soaps may be developed in Ostwald's manner and explained on the basis of the Debye-Hückel theory (7).

The dissociation of Na^+, Ca^{2+}, Al^{3+}, and Sn^{4+} soaps occurs as follows:

$$\underset{C(1-\alpha)}{M(C_{17}H_{35}COO)_n} \rightleftarrows \underset{C\alpha}{M(C_{17}H_{35}COO)^+_{n-1}} + \underset{C\alpha}{C_{17}H_{35}COO^-} \qquad [1]$$

where *C* is the concentration of soap (mol/L), α is the degree of dissociation, M is used for the cations Na^+, Ca^{2+}, Al^{3+}, and Sn^{4+}, and *n* is an integer with respect to charge of the metal. The dissociation constant K_d for the dissociation of soap can be represented as:

$$K_d = \frac{\left[M(C_{17}H_{35}COO)_{n-1}\right]\left[C_{17}H_{35}COO^-\right]}{\left[M(C_{17}H_{35}COO)_n\right]} = \frac{C\alpha \cdot C\alpha}{C(1-\alpha)} = \frac{(C\alpha)^2}{(1-\alpha)} \qquad [2]$$

The degree of dissociation α can be determined by the conductance ratio Λ/Λ_∞, where Λ is the molar conductance at finite concentration, and Λ_∞ is the molar conductance at infinite dilution. On substituting the value of α and rearranging, Equation 2 can be written as:

$$\Lambda C = \frac{K_d \Lambda_\infty^{\ 2}}{\Lambda} - K_d \Lambda_\infty \qquad [3]$$

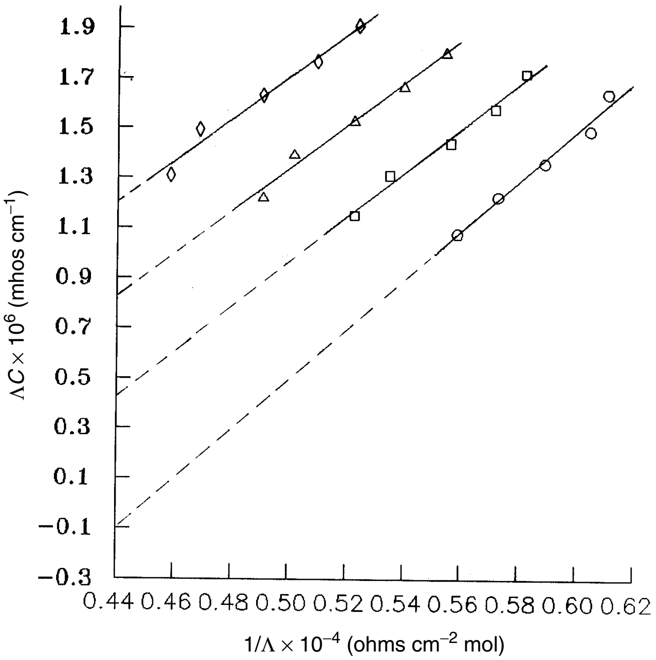

FIG. 2. Plots of Λ*C* vs. 1/Λ of sodium stearate in 60% benzene and 40% methanol (vol/vol): ○, 25°C; □, 35°C; △, 45°C and ◇, 55°C. Abbreviations: Λ, molar conductance; *C*, concentration.

TABLE 2
Dissociation Constants of Na^+, Ca^{2+}, Al^{3+}, and Sn^{4+} Stearates in 60% Benzene and 40% Methanol (vol/vol) at Different Temperatures

	Dissociation constant, K_d			
Soap	25°C	35°C	45°C	55°C
Sodium stearate	0.0201	0.0134	0.0101	0.0074
Calcium stearate	0.0094	0.0078	0.0038	0.0022
Aluminum stearate	0.0025	0.0013	0.0009	0.0005
Tin stearate	0.0019	0.0012	0.0008	0.0003

The values of limiting molar conductance Λ_∞ and dissociation constant K_d were calculated from the slope, $K_d \Lambda_\infty^{\ 2}$, and intercept, $-K_d \Lambda_\infty$ of the linear plots of Λ*C* vs. 1/Λ below the CMC (Fig. 2). The values of K_d are given in Table 2.

Data in Table 3 indicate that the values of molar conductance at infinite dilution, Λ_∞, increase while the dissociation constant decreases with increasing temperature. The values of limiting molar conductance and dissociation constant decrease with an increase in the charge of the cations. Values of degree of dissociation α at different soap concentrations and

TABLE 3
Molar Conductance of Na^+, Ca^{2+}, Al^{3+}, and Sn^{4+} Stearates in 60% Benzene and 40% Methanol (vol/vol) at Different Temperatures

	$\Lambda_\infty \times 10^{-4}$ (mhos cm^2 mol^{-1})			
Soap	25°C	35°C	45°C	55°C
Sodium stearate	2.22	2.56	2.91	3.37
Calcium stearate	1.55	1.87	2.35	3.03
Aluminum stearate	0.85	1.16	1.43	1.82
Tin stearate	0.52	0.65	0.84	1.33

temperatures have been determined by assuming α to be equal to the conductance ratio Λ/Λ_∞.

These data demonstrate that soaps act as weak electrolytes in dilute solutions. The degree of dissociation decreases rapidly in dilute solutions with an increase in soap concentration, whereas it decreases slowly above the CMC.

The heat of dissociation ΔH_d, for Na^+, Ca^{2+}, Ca^{2+}, Al^{3+}, and Sn^{4+} stearates has been determined by using the equation:

$$\frac{\partial(\log K_d)}{\partial T} = \frac{\Delta H_d}{RT^2} \qquad [4]$$

or

$$\log K_d = -\frac{\Delta H_d}{2.303RT} + c \qquad [5]$$

Values of heat of dissociation ΔH_d have been obtained from the slope of linear plots of log K_d vs. $1/T$ (Fig. 3) and are listed in Table 4. Negative values of heat of dissociation ΔH_d indicate that the dissociation process is exothermic.

Changes in free energy, ΔG_d, and entropy, ΔS_d, per mole for the dissociation process have been calculated from the relationships:

$$\Delta G_d = -R\,T \ln K_d \qquad [6]$$

$$\Delta S_d = \frac{(\Delta H_d - \Delta G_d)}{T} \qquad [7]$$

Calculated values of ΔG_d and ΔS_d are shown in Table 5.

In the process of micellization, when counter ions are bound to a micelle, the free energy of micellization ΔG_m (per mole of monomer), for the phase separation model (8) is given by the relationship:

$$\Delta G_m = 2\,R\,T \ln X_{CMC} \qquad [8]$$

where X_{CMC} is the CMC expressed in terms of mole fraction. X_{CMC} may be expressed by the relationship:

$$X_{CMC} = \frac{n_s}{n_s + n_o} \qquad [9]$$

where n_s and n_o are the numbers of moles of surfactants and solvent, respectively. Because the number of moles of free surfactant, n_s, is small compared to the number of moles of solvent, n_o, the relationship may be simplified:

$$X_{CMC} = \frac{n_s}{n_o} \qquad [10]$$

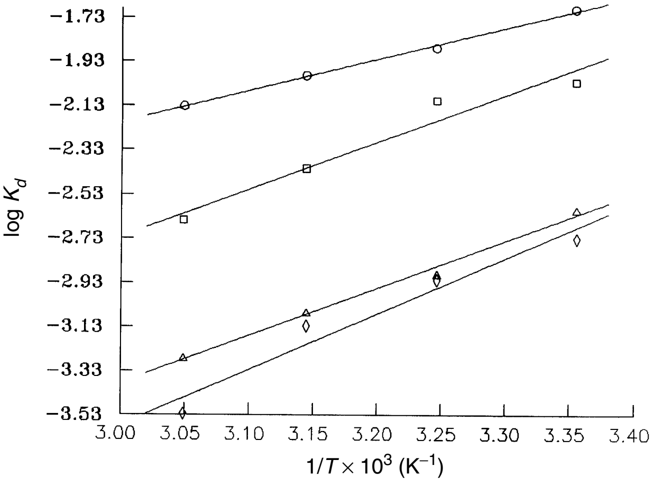

FIG. 3. Log K_d vs. $1/T$ in 60% benzene and 40% methanol (vol/vol); ○, Na^+ stearate; □, Ca^{2+} stearate; △, Al^{3+} stearate and ◇, Sn^{4+} stearate. Abbreviations: K_d, dissociation constant; T, temperature.

TABLE 4
Thermodynamic Parameters of Na^+, Ca^{2+}, Al^{3+}, and Sn^{4+} Stearates per Mole of Monomers in 60% Benzene and 40% Methanol (vol/vol)

Soap	Heat of dissociation ΔH_d (KJ mol^{-1})	Heat of micellization ΔH_m (kJ mol^{-1})
Sodium stearate	−26.9	3.9
Calcium stearate	−40.6	4.7
Aluminum stearate	−40.9	4.9
Tin stearate	−48.1	5.3

Table 6 lists values of X_{CMC} for the experimental soaps.

The enthalpy change of micellization per mole of monomer for the phase separation model (8,9), ΔH_m, is given by the relationship:

$$\frac{\partial(\ln X_{CMC})}{\partial T} = \frac{\Delta H_m}{2RT^2} \qquad [11]$$

or

$$\ln X_{CMC} = \frac{\Delta H_m}{2RT} + c \qquad [12]$$

Values of ΔH_m of Na^+, Ca^{2+}, Al^{3+}, and Sn^{4+} stearates were obtained from the slopes of linear plots of ln X_{CMC} vs. $1/T$ (Fig. 4) and are recorded in Table 4.

TABLE 5
Thermodynamic Parameters of Na^+, Ca^{2+}, Al^{3+}, and Sn^{4+} Stearates in 60% Benzene and 40% Methanol (vol/vol) for Dissociation at Various Temperatures

	ΔG_d (k J mol^{-1})^a				ΔS_d (k J mol^{-1}K^{-1})^a			
Soap	25°C	35°C	45°C	55°C	25°C	35°C	45°C	55°C
Sodium stearate	9.7	11.0	12.2	13.1	−0.123	−0.123	−0.123	−0.122
Calcium stearate	11.6	12.4	14.7	16.6	−0.175	−0.172	−0.174	−0.175
Aluminum stearate	14.9	17.1	18.7	20.5	−0.187	−0.188	−0.187	−0.187
Tin stearate	15.6	17.2	19.0	22.1	−0.214	−0.212	−0.211	−0.214

^{a}Abbreviations: ΔG_d, change in free energy for dissociation; ΔS_d, change in entropy for dissociation.

TABLE 6
Values of ln X_{CMC} of Na^+, Ca^{2+}, Al^{3+}, and Sn^{4+} Stearates in 60% Benzene and 40% Methanol (vol/vol) at Different Temperatures[a]

Soap	25°C	35°C	45°C	55°C
Sodium stearate	–7.91	–7.89	–7.87	–7.84
Calcium stearate	–8.05	–8.02	–7.99	–7.97
Aluminum stearate	–8.16	–8.13	–8.10	–8.07
Tin stearate	–8.28	–8.25	–8.21	–8.18

[a] Abbreviation: X_{CMC}, critical micellar concentration.

Careful scrutiny of the thermodynamic parameters reveals from the negative values of ΔG_m and positive values of ΔS_m for the micellization process (Table 7) and positive values of ΔG_d and negative values of ΔS_d for the dissociation process (Table 5), that micellization is favored over dissociation, and micellization is a spontaneous occurrence but dissociation is nonspontaneous.

CMC data in Table 6 show that an increase in temperature results in an increase of CMC because micellization is assumed to occur when the energy released as a result of aggregation of the hydrocarbon chains of the monomer is sufficient to overcome the electrical repulsion between the ionic head groups and to balance the decrease in entropy that accompanies aggregation. Therefore, an increase in temperature would have been expected to increase the CMC because the kinetic energy of the monomers would have been raised.

Thermodynamics of dissociation and micellization can be satisfactorily explained in light of the phase separation model. The data also indicate that micellization is predominant over dissociation, and that Na^+, Ca^{2+}, Al^{3+}, and Sn^{4+} stearates behave as weak electrolytes in a mixture of 60% benzene and 40% methanol (vol/vol).

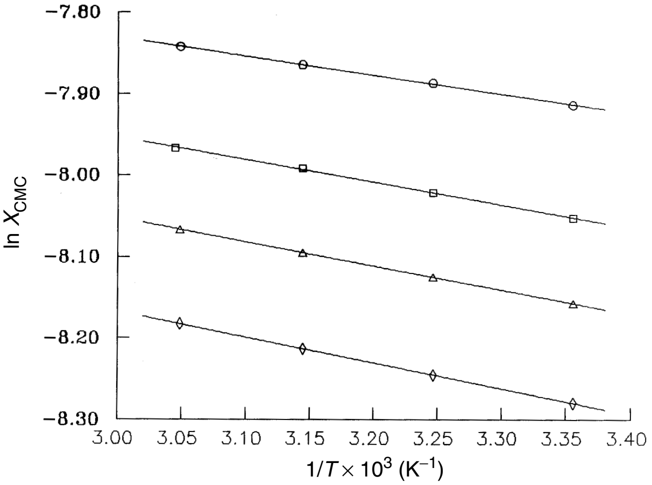

FIG. 4. Plot of ln X_{CMC} vs. $1/T$ in 60% benzene and 40% methanol (vol/vol): ○, Na^+ stearate; □, Ca^{2+} stearate; △, Al^{3+} stearate and ◇, Sn^{4+} stearate. Abbreviation: X_{CMC}, critical micellar concentration (mole fraction).

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TABLE 7
Thermodynamic Parameters of Na^+, Ca^{2+}, Al^{3+}, and Sn^{4+} Stearates in 60% Benzene and 40% Methanol (vol/vol) for Micellization at Various Temperatures

	ΔG_m (k J mol^{-1})				ΔS_m (k J $mol^{-1}K^{-1}$)			
Soap	25°C	35°C	45°C	55°C	25°C	35°C	45°C	55°C
Sodium stearate	–39.2	–40.4	–41.6	–42.8	0.145	0.144	0.143	0.142
Calcium stearate	–39.9	–41.1	–42.3	–43.6	0.150	0.149	0.148	0.145
Aluminum stearate	–40.4	–41.6	–42.8	–44.0	0.152	0.151	0.150	0.149
Tin stearate	–41.0	–42.2	–43.4	–44.6	0.155	0.154	0.153	0.152

[a] Abbreviations: ΔG_m, change in free energy for micellization; ΔS_m, change in entropy for micellization.