

Thermodynamics of the Dissociation of Chromium Soap Solutions in Benzene-Dimethyl Formamide

Hüseyin TOPALLAR, Yüksel BAYRAK

*Department of Chemistry, Faculty of Sciences and Letters,
Trakya University, 22030, Edirne-TURKEY*

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Critical micelle concentrations and dissociation constants for chromium soaps (myristate, palmitate and stearate) in a mixture of benzene and dimethyl formamide (7:3, vol/vol) were determined by means of conductivity measurements. These soaps behave as simple moderate electrolytes in dilute solutions. Critical micelle concentrations and dissociation constants decreased with increasing numbers of carbon atoms in the soap molecules. Thermodynamic parameters such as heat of dissociation, ΔH_d , change in free energy, ΔG_d , and entropy, ΔS_d , per mole for the dissociation process were also evaluated.

Key Words: chromium soaps, conductivity, critical micellar concentration, dissociation constant, thermodynamics.

Introduction

Metallic soaps are becoming increasingly important in technological uses as well as in academic studies. Application of metallic soaps largely depends on their physicochemical properties such as physical state, thermal stability, chemical reactivity and solubility in polar and non-polar solvents.

Several researchers¹⁻⁵ have prepared transition metallic soaps by treating the fatty acid with the requisite amount of metal oxide or hydroxide in the presence of organic solvent or organic base. Physicochemical studies of zinc dicaprylate were described by Mehrotra et al.⁶. The critical micellar concentration (CMC) of nickel, cobalt, manganese, iron, and yttrium soaps at different temperatures were determined conductometrically by Varma et al.^{7,8} and Mehrotra et al.^{9,10}.

Mehrotra et al.¹¹ also determined the density, viscosity, specific viscosity, fluidity, and conductivity of solutions of copper caprylate. In another study Mehrotra et al.¹² investigated the conductance and micellar behavior of praseodymium and neodymium linoleate soaps in a mixture of 60 % benzene and 40 % methanol at different temperatures.

The present paper deals with the evaluation of CMC values, dissociation constants, and the determination of thermodynamic parameters for chromium soaps (myristate, palmitate and stearate) in a mixture of benzene and dimethyl formamide (7:3, vol/vol) by conductivity measurements at different temperatures.

Experimental

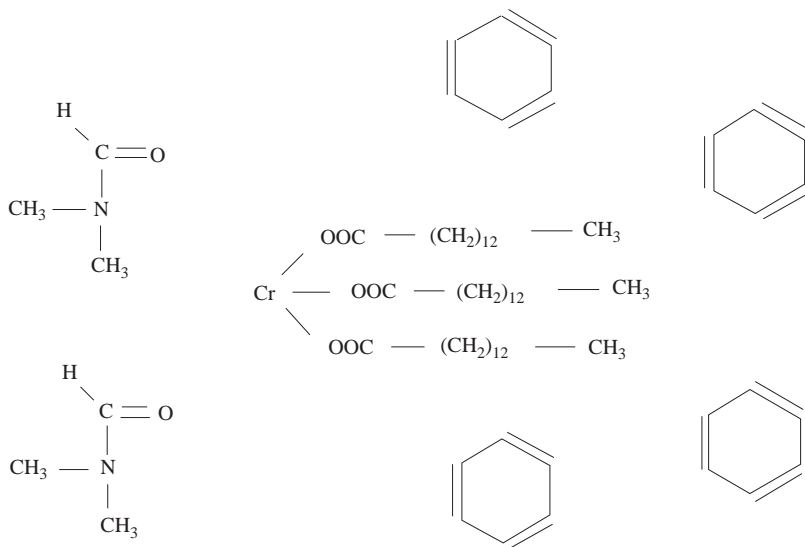
Potassium hydroxide, KOH, chrome alum, $K_2SO_4Cr_2(SO_4)_3 \cdot 24 H_2O$, myristic acid, $C_{13}H_{27}COOH$, palmitic acid, $C_{15}H_{31}COOH$, and stearic acid, $C_{17}H_{35}COOH$, used in this study were supplied by Merck.

Firstly the potassium soaps were obtained from the reaction between KOH and the fatty acids and then the chromium soaps were prepared by a reaction of potassium soap with the stoichiometrically required amount of chrome alum in a water-alcohol medium (1:1). The precipitated soaps were washed with water and acetone to remove the excess metal ions and unreacted fatty acids and were then dried.

The solutions of soaps were prepared by dissolving a known amount of soap in a benzene-dimethyl formamide mixture (7:3, vol/vol) and were kept for 2 hr in a thermostat at the desired constant temperature.

The reason for the choice of a benzene-dimethyl formamide (7:3, vol/vol) can be explained as follows. A chromium soap (myristate, palmitate and stearate) molecule consists of two parts as a nonpolar saturated hydrocarbon chain and a polar carboxylate end. The myristate, palmitate and stearate salts are very slightly soluble in pure benzene and dimethyl formamide¹³. Since benzene is a nonpolar solvent and dimethyl formamide is a polar solvent, the hydrocarbon chain has a tendency to dissolve in benzene and the carboxylate end in dimethyl formamide.

According to the effect of the solvent, the benzene and dimethyl formamide molecules may solvate a chromium soap molecule (for example chromium myristate) as shown in Scheme 1:



Scheme 1.

The hydrocarbon chain is longer and bulkier than the carboxylate end. However, the hydrocarbon chain requires more benzene to dissolve as 7 vol, and dimethyl formamide for the carboxylate end as 3 vol. As a result, the chromium soap molecule dissolves more in a benzene-dimethyl formamide mixture (7:3, vol/vol) than in the pure solvents¹⁴. For this reason, it seems that this solvent mixture was suitable for our experiments.

The conductance of the soap solutions was measured with an Orion digital conductivity meter, Model 126 (Orion Research Inc., Boston, USA), and a dipping type conductivity cell (cell constant 1.01) with platinized electrodes at different temperatures. The reproducibility of the measurements was $\pm 0.1\%$.

Table 1. Specific conductance, \mathbf{K} / (mhos cm^{-1}), and molar conductance, Λ / (mhos $\text{cm}^2 \text{mol}^{-1}$) of chromium soaps in a benzene-dimethyl formamide mixture (7:3, vol/vol) at 30°C.

$\mathbf{C} \times 10^3 /$ (mol L^{-1})	Myristate		Palmitate		Stearate	
	$\mathbf{K} \times 10^6$	Λ	$\mathbf{K} \times 10^6$	Λ	$\mathbf{K} \times 10^6$	Λ
2	1.95	0.975	1.44	0.720	1.19	0.595
3	2.27	0.757	1.67	0.557	1.39	0.463
4	2.60	0.650	1.89	0.473	1.58	0.395
5	2.92	0.584	2.11	0.422	1.78	0.356
6	3.24	0.540	2.35	0.392	2.01	0.335
7	3.59	0.513	2.65	0.379	2.26	0.323
8	3.96	0.495	2.94	0.368	2.51	0.314
9	4.32	0.480	3.25	0.361	2.75	0.306
10	4.68	0.468	3.54	0.354	3.00	0.300

Table 2. Critical micellar concentrations of chromium soaps in a benzene-dimethyl formamide mixture (7:3, vol/vol) at various temperatures.

Soap	$\text{CMC} \times 10^3 / (\text{mol L}^{-1})$			
	30°C	40°C	50°C	60°C
Chromium myristate	6.2	6.7	7.0	7.3
Chromium palmitate	5.8	6.2	6.5	6.8
Chromium stearate	5.4	5.8	6.1	6.4

Results and Discussion

Specific conductance, \mathbf{K} , of the solutions of chromium soaps (myristate, palmitate, and stearate) in a mixture of benzene and dimethyl formamide (7:3, vol/vol) increased with increasing soap concentration and decreasing numbers of carbon atoms in the soap (Table 1).

Molar conductance, Λ , of the chromium soap solutions in a benzene-dimethyl formamide (7:3, vol/vol) mixture decreased with increasing concentration and chainlength of the soap (Table 1). The decrease in molar conductance is attributed to the combined effects of ionic atmosphere, solvation of ions, and decrease of mobility and ionization with the formation of micelles.

The increase in specific conductance with soap concentration may have been due to dissociation of chromium soaps into simple chromium metal cations (Cr^{3+}) and fatty acid anions (RCOO^-), where R is $\text{C}_{13}\text{H}_{27}$, $\text{C}_{15}\text{H}_{31}$, and $\text{C}_{17}\text{H}_{35}$ for myristate, palmitate, and stearate, respectively, in dilute solutions and due to the formation of micelles at higher soap concentrations ($\text{C} > 0.005 \text{ M}$)

The decrease in specific conductance with increasing number of carbon atoms in the fatty acid chain of the soap molecules may have been due to the higher molecular weight and decreasing mobility of anions. Plots of specific conductance, \mathbf{K} , vs. soap concentration, \mathbf{C} , (Figures 1 and 2) are characterized by a break, corresponding to CMC (Table 2), which shows that micelle formation takes place at a definite soap concentration.

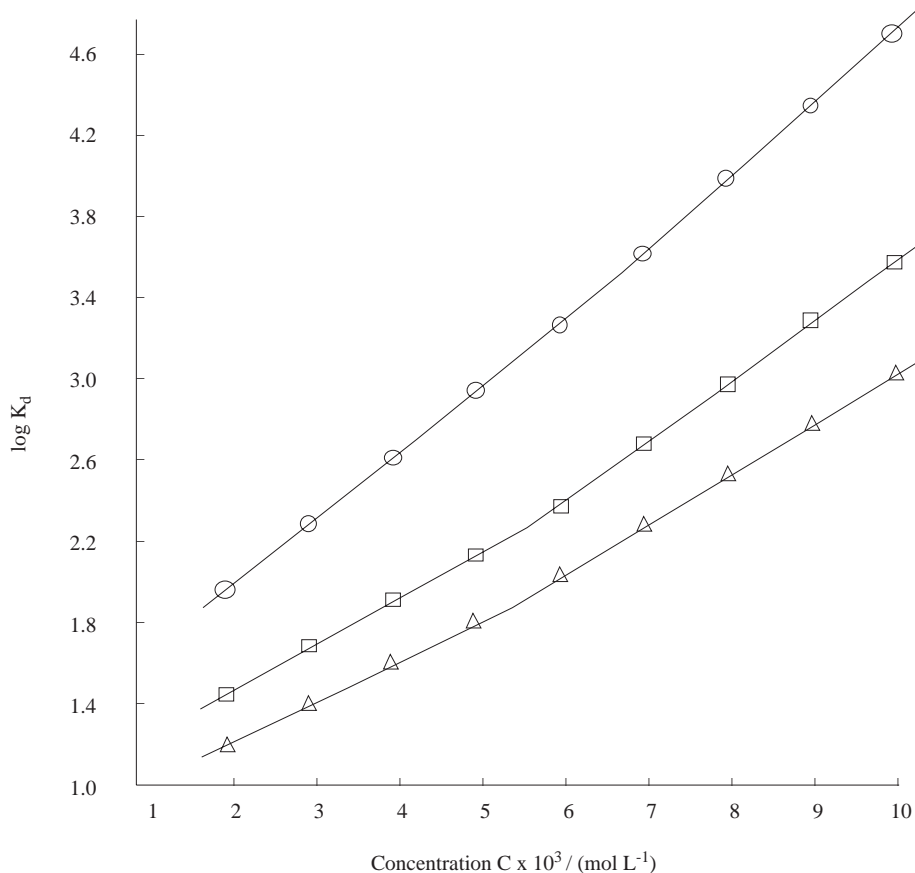
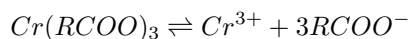


Figure 1. Specific conductance vs. soap concentration in a benzene-dimethyl formamide mixture (7:3, vol/vol) at 303 K. \circ : chromium myristate, \square : chromium palmitate and \triangle : chromium stearate.

Since the molar conductance of the solutions of chromium soaps does not vary linearly with the square root of soap concentration, the Debye-Hückel-Onsager equation¹⁵ is not applicable to these solutions. Molar conductance results show that chromium soaps behave as weak electrolytes in solution. Ionization of chromium soaps may be explained by Ostwald's formula.

If C is the concentration and α is the degree of dissociation of the chromium soap, molar concentration may be represented as follows:



$$C(1 - \alpha) \quad C\alpha \quad 3C\alpha$$

The dissociation constant, K_d , for this equilibrium may be expressed as follows:

$$K_d = \frac{[Cr^{3+}][RCOO^-]^3}{[Cr(RCOO)_3]} = \frac{27C^3\alpha^4}{(1 - \alpha)} \quad (1)$$

Since ionic concentrations are low and interionic effects are almost negligible in dilute solutions, the solutions of soaps do not deviate appreciably from ideal behavior, and the activities of ions can be taken as almost equal to the concentrations. The degree of dissociation, α , may be replaced by the conductance ratio,

Λ/Λ_∞ , where Λ is molar conductance at finite concentration and Λ_∞ is the limiting molar conductance at infinite dilution.

By substituting the value of α and rearranging, Equation 1 can be rewritten as follows:

$$\Lambda^3 C^3 = \frac{K_d \Lambda_\infty^4}{27\Lambda} - \frac{K_d \Lambda_\infty^3}{27} \quad (2)$$

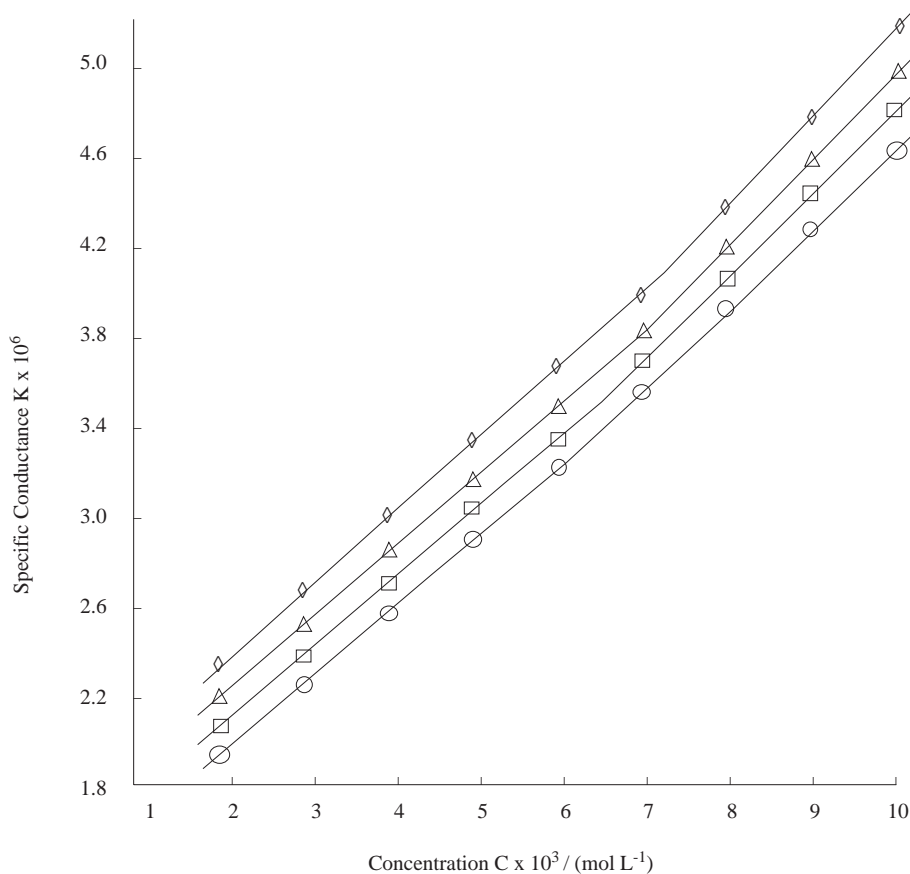


Figure 2. Specific conductance vs. concentration plots of chromium myristate in a benzene-dimethyl formamide mixture (7:3, vol/vol) at various temperatures. \circ : 30°C, \square : 40°C, \triangle : 50°C and \diamond : 60°C.

The values of K_d (Table 4) were calculated from the slope $[(K_d \Lambda_\infty^4)/27]$ and intercept $[-(K_d \Lambda_\infty^3)/27]$ of the linear portion of the plots of $\Lambda^3 C^3$ vs. $1/\Lambda$ below the CMC (Table 3 and Figure 3). It is seen that the values of K_d decreased with an increase in the numbers of carbon atoms in the soap molecules, i.e., with increasing chainlength of the soap.

However, the decrease in the values of dissociation constant with increasing temperature indicates the exothermic nature of the dissociation of chromium soaps (myristate, palmitate and stearate) in a benzene-dimethyl formamide mixture (7:3, vol/vol).

The heat of dissociation, ΔH_d , for chromium soaps (myristate, palmitate and stearate) is determined with the following equation¹²:

$$\frac{\partial(\log K_d)}{\partial T} = \frac{\Delta H_d}{RT^2} \quad (3)$$

or

$$\log K_d = -\frac{\Delta H_d}{2.303RT} + C \quad (4)$$

The values of heat of dissociation, ΔH_d , were obtained from the slope of the linear plots of $\log K_d$ vs. $1/T$ (Figure 4), and are shown in Table 5. The negative values of heat of dissociation, ΔH_d , indicate that the dissociation process for chromium soaps is exothermic in nature.

Table 3. The values of $\Lambda^3 C^3$ and $1/\Lambda$ for chromium soaps in a benzene-dimethyl formamide mixture (7:3, vol/vol) at 30°C.

Myristate		Palmitate		Stearate	
$\Lambda^3 C^3 \times 10^{16}$	$1/\Lambda$	$\Lambda^3 C^3 \times 10^{16}$	$1/\Lambda$	$\Lambda^3 C^3 \times 10^{16}$	$1/\Lambda$
0.0742	1.0256	0.0299	1.3889	0.0169	1.6807
0.1170	1.3210	0.0466	1.7953	0.0269	2.1598
0.1758	1.5385	0.0675	2.1142	0.0394	2.5317
0.2490	1.7123	0.0939	2.3697	0.0564	2.8090
0.3401	1.8519	0.1298	2.5510	0.0812	2.9851
0.4627	1.9493	0.1861	2.6385	0.1154	3.0960
0.6210	2.0202	0.2541	2.7174	0.1581	3.1847
0.8062	2.0833	0.3433	2.7700	0.2080	3.2680
1.0250	2.1368	0.4436	2.8249	0.2700	3.3333

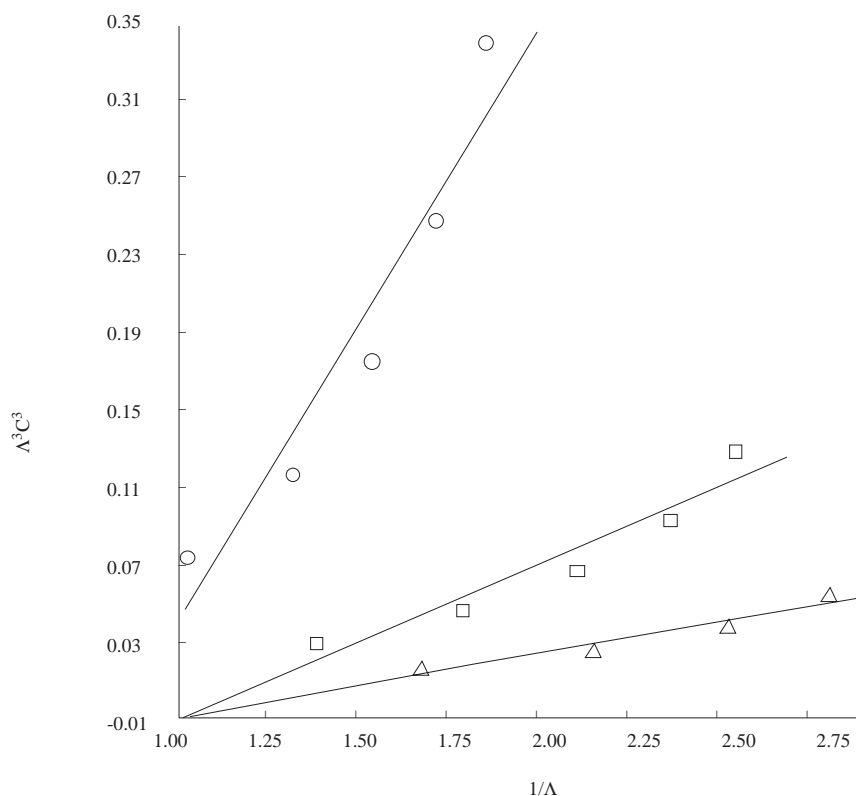


Figure 3. The plot of $\Lambda^3 C^3$ vs. $1/\Lambda$ of chromium soaps in a benzene-dimethyl formamide mixture (7:3, vol/vol) at 303 K. \circ : chromium myristate, \square : chromium palmitate and \triangle : chromium stearate.

Table 4. Dissociation constants, K_d (from the plot of $\Lambda^3 C^3$ vs. $1/\Lambda$), of chromium soaps in a benzene-dimethyl formamide mixture (7:3, vol/vol) at various temperatures.

Soap	$K_d \times 10^7$			
	30°C	40°C	50°C	60°C
Chromium myristate	4.9329	3.6949	2.6412	2.2329
Chromium palmitate	4.3275	2.4048	1.4971	1.0301
Chromium stearate	2.3440	1.5817	0.885	0.4931

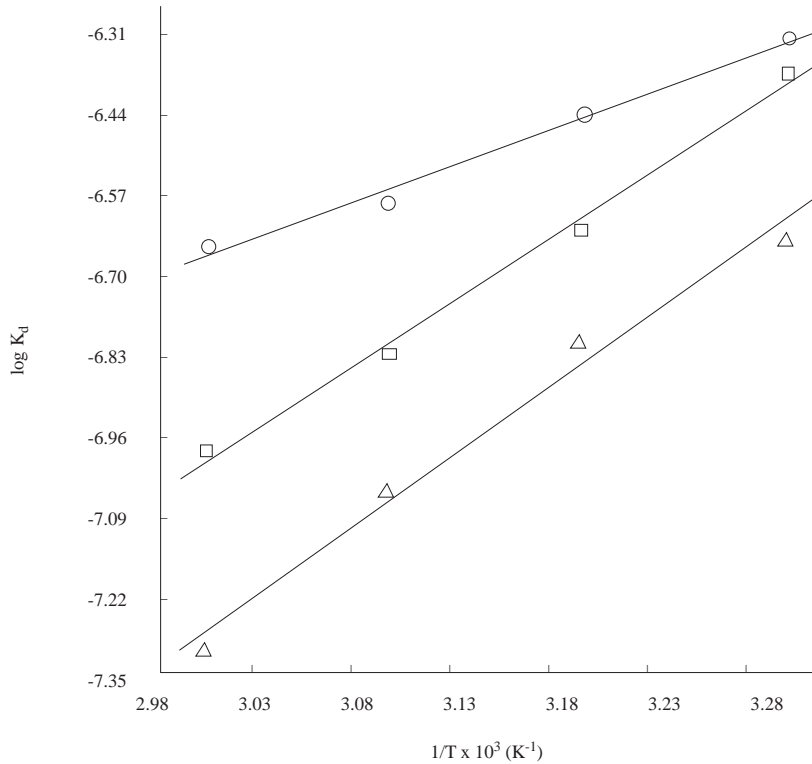


Figure 4. The $\log K_d$ vs. $1/\Lambda$ of chromium soaps in a benzene-dimethyl formamide mixture (7:3, vol/vol) at 303 K. \circ : chromium myristate, \square : chromium palmitate and \triangle : chromium stearate.

The values of change in free energy, ΔG_d , and entropy, ΔS_d per mole for the dissociation process are calculated by using the relationships¹²:

$$\Delta G_d = -RT \ln K_d \quad (5)$$

$$\Delta S_d = \frac{\Delta H_d - \Delta G_d}{T} \quad (6)$$

The calculated values of ΔG_d and ΔS_d are shown in Table 6. Careful scrutiny of the thermodynamic parameters indicates that the positive values of ΔG_d and negative values of ΔS_d for the dissociation process (Table 6) show that the dissociation process is a nonspontaneous occurrence physicochemically for chromium soaps (myristate, palmitate and stearate) in a benzene-formamide mixture (7:3, vol/vol).

Table 5. The values of heat of dissociation, ΔH_d , of chromium soaps in a benzene-dimethyl formamide mixture (7:3, vol/vol).

Soap	Heat of dissociation ΔH_d / kJ mol ⁻¹
Chromium myristate	-22.82
Chromium palmitate	-40.20
Chromium stearate	-44.00

Table 6. The values of change in free energy, ΔG_d , and entropy, ΔS_d , per mole for the dissociation process of chromium soaps in a benzene-dimethyl formamide mixture (7:3, vol/vol) at various temperatures.

Soap	ΔG_d / kJ mol ⁻¹				$\Delta S_d \times 10^2$ / K ⁻¹ mol ⁻¹			
	30°C	40°C	50°C	60°C	30°C	40°C	50°C	60°C
Chromium myristate	36.59	38.55	40.68	42.50	-19.61	-19.61	-19.66	-19.59
Chromium palmitate	36.92	39.66	42.20	44.55	-25.45	-25.51	-25.51	-25.45
Chromium stearate	38.46	40.75	43.61	46.58	-27.22	-27.08	-27.12	-27.20

However, as can be seen in Table 6, the values of change in free energy, ΔG_d , increased with increasing temperature whereas the values of entropy, ΔS_d , decreased. Since the solute ions are aggregated to form the colloidal particles as micelles near the CMC value and after the CMC the micellization process is replaced the dissociation process, the negative changes of entropy may be obtained below the CMC value.

According to our previous work¹⁶, the parameters for the thermodynamics of dissociation and micellization of sodium, calcium, aluminum and tin stearates in mixed organic solvents indicates that the negative values of ΔG_m and positive values of ΔS_m for the micellization process and positive values of ΔG_d and negative values of ΔS_d for the dissociation process show that the micellization process is favored over the dissociation process and the micellization is a spontaneous occurrence but the dissociation is nonspontaneous.

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