Conductometric and Spectrophotometric Studies on Chromium Soap Solutions in Benzene–Dimethyl Formamide

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ABSTRACT: Critical micelle concentrations, degrees of dissociation, and dissociation constants of chromium soaps (laurate, myristate, palmitate, and stearate) in a mixture of benzene and dimethyl formamide (7:3, vol/vol) were determined from conductivity measurements. The soaps behave as simple moderate electrolytes in dilute solutions. Critical micelle concentration, limiting molar conductance and dissociation constants decreased with increasing numbers of carbon atoms in the soap molecules. Spectrophotometric results show that metal-to-oxygen bonds in chromium soaps are not purely ionic but have some covalent character.

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KEY WORDS: Chromium soaps, conductivity, critical micelle concentration, dissociation constant, spectrophotometry.

Metallic soaps are becoming increasingly important in technological uses as well as in academic studies. Application of metal soaps largely depends on their physical state, thermal stability, chemical reactivity, and solubility in polar and nonpolar solvents. Several researchers (1–5) have prepared transition metal 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 explored by Mehrotra *et al.* (6). Critical micelle concentration (CMC) of nickel, cobalt, manganese, iron, and yttrium soaps at different temperatures was 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.

The present paper deals with evaluation of CMC values, degrees of dissociation, dissociation constants, and spectrophotometric parameters of chromium soaps (laurate, myristate, palmitate, and stearate) in a mixture of benzene and dimethyl formamide (7:3, vol/vol) by conductivity and spectrophotometric measurements.

EXPERIMENTAL PROCEDURES

Analar-grade chemicals (BDH, Bombay, India) were used. Chromium soaps (laurate, myristate, palmitate, and stearate) were prepared from the corresponding potassium soap with a slight excess of a solution of chrome alum under constant stirring. The precipitated soaps were washed with distilled water, methanol, and acetone to remove excess metal ions, potassium soap, and unreacted fatty acids. Purity of the soaps was checked by infrared (IR) absorption spectra, elemental analysis, and determination of the melting points (laurate, 59°C; myristate, 61°C; palmitate, 66°C; and stearate, 69°C). Solutions at different concentrations of soaps were prepared in a benzene–dimethyl formamide mixture (7:3, vol/vol).

A Toshniwal digital conductivity meter (model CL.01.10; Toshniwal Pvt., Ltd., Bombay, India) and a dipping conductivity cell with platinized electrodes were used for measuring conductance of the solutions at a constant temperature of 313 K. The accuracy of results was ±0.5%. Spectrophotometric measurements were carried out in the region of 350–940 nm with a digital Toshniwal visible spectrophotometer (model CL.10A3) with a wavelength reproducibility of ±5 nm.

RESULTS AND DISCUSSION

Specific conductance, k. Specific conductance, *k*, of the solutions of chromium soaps (laurate, myristate, palmitate, and stearate) in a mixture of benzene and dimethyl formamide (7:3, vol/vol) increases with increasing soap concentration and decreasing numbers of carbon atoms in the soap (Table 1). Increase in specific conductance with soap concentration may be due to dissociation of chromium soaps into simple chromium metal cations (Cr^{3+}) and fatty acid anions ($RCOO^-$), where R is $C_{11}H_{23}$, $C_{13}H_{27}$, $C_{15}H_{31}$, and $C_{17}H_{35}$ for laurate, myristate, palmitate, and stearate, respectively, in dilute solutions and due to formation of micelles at higher soap concentrations (>0.005 M). The decrease in specific conductance with increasing number of carbon atoms in the fatty acid chain of the soap molecules may be due to the higher molecular weight and decreasing mobility of anions. Plots of specific conductance *k* vs. soap concentration *C* (Fig. 1) are characterized by a break, corresponding to CMC (Table 2), which shows that micelle formation takes place at a definite soap concentration. The change in the slope of the two lines is small, however, particularly for laurate, indicating that the conductivity method is not accurate for determining CMC in nonaqueous solvents.

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TABLE 1
Specific Conductance, *k* (mhos cm^{-1}), and Molar Conductance, μ (mhos cm^{2}mol^{-1}), of Chromium Soaps

Concentration $C \times 10^3$ (mol L^{-1})	Laurate		Myristate		Palmitate		Stearate	
	$k \times 10^6$	μ	$k \times 10^6$	μ	$k \times 10^6$	μ	$k \times 10^6$	μ
2.3	2.49	1.083	2.13	0.926	1.63	0.709	1.35	0.587
2.5	2.62	1.048	2.21	0.884	1.70	0.680	1.40	0.560
2.8	2.78	0.993	2.31	0.825	1.76	0.629	1.45	0.518
3.1	2.94	0.948	2.40	0.774	1.83	0.590	1.59	0.513
3.6	3.23	0.897	2.56	0.711	1.93	0.536	1.65	0.458
3.8	3.40	0.895	2.64	0.695	1.99	0.524	1.68	0.442
4.2	3.54	0.843	2.68	0.638	2.05	0.488	1.72	0.409
4.5	3.77	0.838	2.89	0.642	2.10	0.467	1.80	0.400
5.0	4.04	0.808	3.05	0.610	2.24	0.448	1.86	0.372
5.5	4.16	0.756	3.20	0.582	2.37	0.431	2.01	0.365
6.2	4.59	0.740	3.44	0.555	2.52	0.406	2.15	0.347
6.7	4.70	0.701	3.53	0.527	2.65	0.396	2.26	0.337
7.1	5.06	0.713	3.72	0.524	2.79	0.393	2.39	0.337
7.7	5.25	0.682	3.93	0.510	2.94	0.382	2.57	0.334
8.3	5.70	0.687	4.18	0.504	3.15	0.379	2.69	0.324
9.1	6.17	0.678	4.44	0.488	3.41	0.375	2.94	0.323
10.0	6.72	0.672	4.79	0.479	3.71	0.371	3.25	0.325

Molar conductance, μ. Molar conductance, μ, of the chromium soap solutions in a benzene–dimethyl formamide (7:3, vol/vol) mixture decreases with increasing concentration and chainlength of the soap (Table 1). 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. Molar conductance μ of solutions of chromium soaps does not vary linearly with the square root of soap concentration, indicating that the Debye–Hückel–Onsager equation is not applicable to these solutions. Molar conductance results show that chromium soaps do not behave as strong electrolytes in solution. Ionization of chromium soaps may be explained in Ostwald's manner. If C is the concentration and α is the degree of dissociation of the chromium soap, molar concentration may be represented as follows:

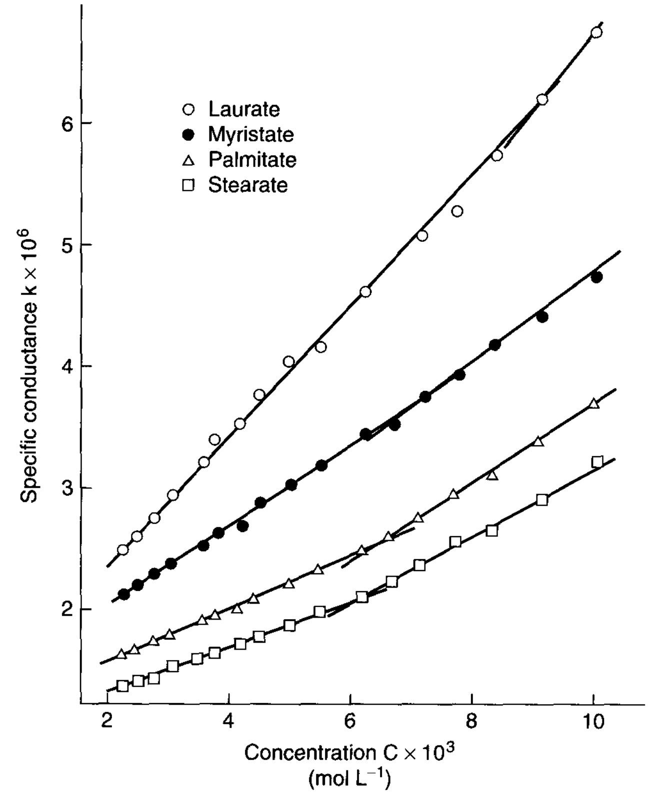

FIG. 1. Specific conductance vs. soap concentration for chromium laurate, myristate, palmitate, and stearate in benzene–dimethyl formamide at 313 K.

$$(R\mathrm{COO})_3\mathrm{Cr} \rightarrow \mathrm{Cr}^{3+} + 3R\mathrm{COO}^-$$

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

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

$$K = \frac{[\mathrm{Cr}^{3+}][R\mathrm{COO}^-]^3}{[(R\mathrm{COO})_3\mathrm{Cr}]} = \frac{27C^3 \bullet \alpha^4}{(1-\alpha)} \qquad [1]$$

Because 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

TABLE 2
CMC, Limiting Molar Conductance μ_0, and Dissociation Constant *K* (from the plot of μ^3C^3 vs. $1/\mu$) of Chromium Soaps[a]

Soap	CMC × 10^3 (mol L^{-1})	μ_0	$K \times 10^7$
Laurate	9.0	1.59	2.284
Myristate	6.7	1.29	2.085
Palmitate	6.2	1.15	1.154
Stearate	5.8	1.02	1.018

[a] CMC, critical micelle concentration.

activities of ions can be taken as almost equal to the concentrations. The degree of dissociation, α, may be replaced by the conductance ratio, μ/μ_0, where μ is molar conductance at finite concentration and μ_0 is the limiting molar conductance at infinite dilution. By substituting the value and rearranging, Equation 1 can be rewritten as follows:

$$\mu^3C^3 = \frac{K\mu_0^4}{27\mu} - \frac{K\mu_0^3}{27} \qquad [2]$$

The values of K and μ_0 (Table 2) were obtained from the slope $[(K\mu_0^4)/27]$ and intercept $[-(K\mu_0^3)/27]$ of the linear portion of the plots of μ^3C^3 vs. $1/\mu$. Values of μ_0 and K are found to decrease with an increase in the numbers of carbon atoms in the soap molecules (Table 2).

Values of the degree of dissociation α at different soap concentration have been evaluated by assuming that it is equal to μ/μ_0 and by using the value of μ_0 obtained from the plots of μ^3C^3 vs. $1/\mu$. The plots of degree of dissociation α vs. soap concentration C (Fig. 2) show that the degree of dissociation decreases rapidly in dilute solution but decreases slowly in relatively concentrated solutions. Values of degree of dissociation α (0.32–0.68), show that these soaps behave as simple moderate electrolytes in solution of benzene–dimethyl formamide mixture.

Values of dissociation constant K have been evaluated by using Equation 1 and assuming that the degree of dissociation is equal to molar conductance ratio μ/μ_0. The results show that values of K decrease with increasing chainlength of the soap (Fig. 3). K values show approximate constancy in dilute solution but exhibit a drift with increasing soap concentration, which shows that the soaps do not behave as weak electrolytes in solutions (Fig. 3). The drift in values of the dissociation constant with increasing soap concentration may be partly due to the fact that the degree of dissociation is not exactly equal to the conductance ratio μ/μ_0, but is mainly caused by the fact that the activity coefficients of the ions are not equal to unity. The deviations at higher soap concentrations may also be due to failure of the simple Debye–Hückel activity equation in concentrated solutions. It is therefore concluded that chromium soaps behave as simple moderate electrolytes in solution in a benzene and dimethyl formamide mixture.

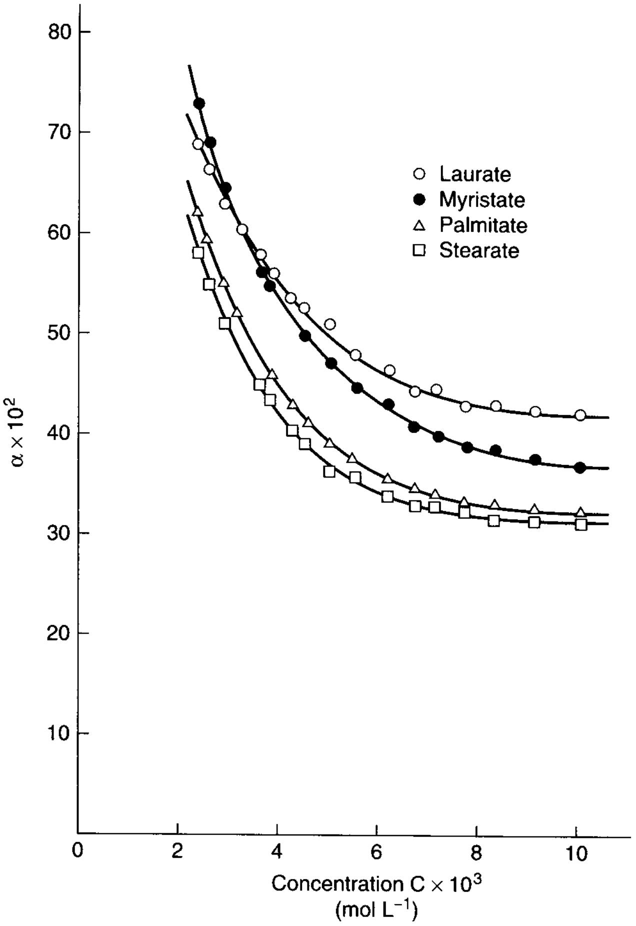

FIG. 2. Degree of dissociation vs. concentration for chromium laurate, myristate, palmitate, and stearate in benzene–dimethyl formamide.

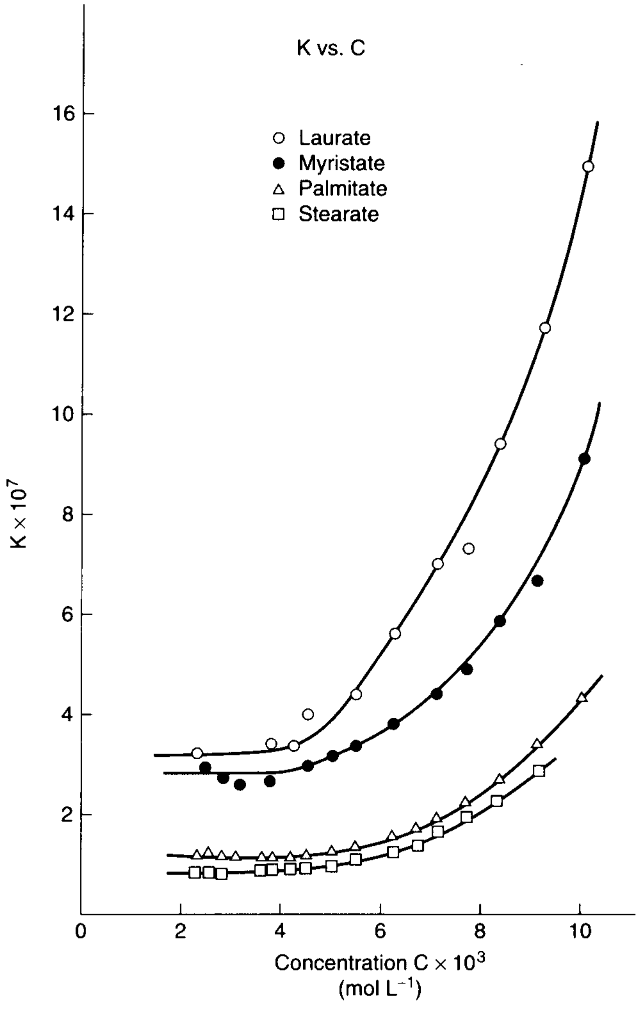

FIG. 3. Dissociation constant vs. concentration for chromium laurate, myristate, palmitate, and stearate in benzene–dimethyl formamide.

Spectrophotometry. Solutions of chromium soaps (laurate, myristate, palmitate, and stearate) in benzene–dimethyl formamide (7:3, vol/vol) mixture exhibit well-defined maxima at 575 nm (17,391 cm^{-1}). Absorption studies have also been carried out in aqueous solutions of chrome alum, and maxima were observed at 590 nm (16,949 cm^{-1}) and 420 nm (23,809 cm^{-1}). This shows that the behavior of chromium soaps in benzene–dimethyl formamide mixture is quite similar to aqueous solutions of chrome alum.

Cr(III) possesses a d^3 electronic configuration and permits the following three electronic transitions (12):

$$^4T_{2g}(F) \leftarrow {}^4A_{2g}(F) \qquad [3]$$

$$^4T_{1g}(F) \leftarrow {}^4A_{2g}(F) \qquad [4]$$

$$^4T_{1g}(P) \leftarrow {}^4A_{2g}(F) \qquad [5]$$

The electronic band observed at 17,391 cm^{-1} is assigned to the first transition (Equation 3), and the second transition (Equation 4) lies at 23,809 cm^{-1}. The third transition (Equation 5), which usually occurs at about 37,000 cm^{-1}, is beyond the range of our instruments.

The crystal field splitting energy parameter (12), Dq; the Racah (13) interelectronic repulsion parameter, B; the nephelauxetic ratio (14), β; the percentage covalency, δ; and the bonding parameter (15), $b^{1/2}$, have been evaluated by the following relationships:

$$\upsilon_1 = 10\,Dq \qquad [6]$$

$$\frac{Dq}{B} = 2.45 \qquad [7]$$

$$\beta = \frac{B}{B_0} \qquad [8]$$

$$\delta = \frac{(1-\beta)\times 100}{\beta} \qquad [9]$$

$$b^{1/2} = \left(\frac{1-\beta}{2}\right) \qquad [10]$$

where υ_1 is the wavenumber of the electronic band due to $[{}^4T_{2g}(F) \leftarrow {}^4A_{2g}(F)]$ and B_0 is the value of the interelectronic repulsion parameter for Cr(III) ion and equal to 1,030 cm^{-1}.

Values of β (0.69) for chromium soaps are less than unity, which suggests that metal-to-oxygen bonds in chromium soaps are not purely ionic but have some covalent character. Values of percentage covalency ($\delta = 45$) and bonding parameter ($b^{1/2} = 0.155$) also indicate that these soaps are partially covalent in character.

The plots of optical density vs. soap concentration (Fig. 4) are linear for dilute solutions (<0.008 M) with an intercept equal to zero, which proves the validity of the Beer–Lambert law for these solutions. It is evident that the spectrophotometric method can be used to estimate the chromium content at λ_{max} in dilute solutions of these soaps. Plots show deviations for concentrated solutions above the CMC value, however. The deviations may be partly due to micelle formation but are mainly due to the nonvalidity of the Beer–Lambert law at higher soap concentrations.

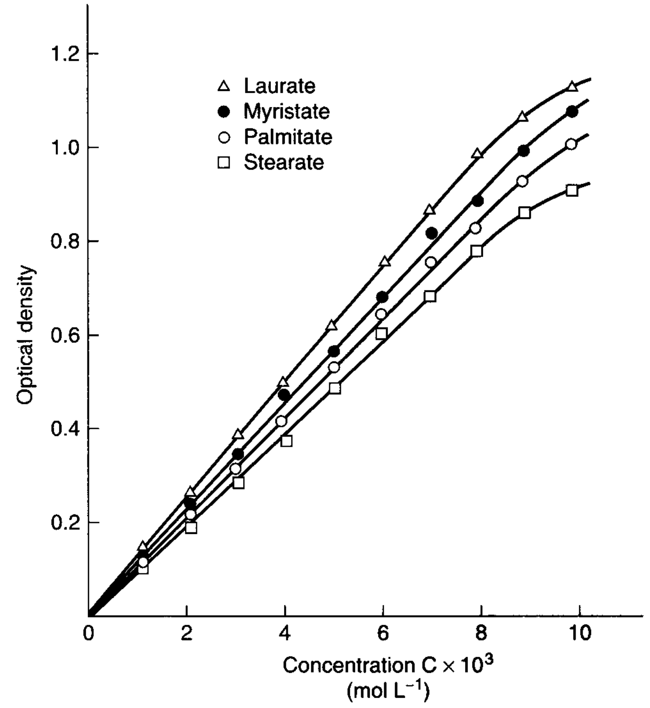

FIG. 4. Optical density vs. concentration for chromium laurate, myristate, palmitate, and stearate in benzene–dimethyl formamide.

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