

Effect of Alkanols on the Micellar Behavior of Chromium Laurate

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The critical micelle concentration, CMC, degree of dissociation, and dissociation constant of chromium laurate in alcohols (methanol, ethanol, propanol-1, butanol-1 and pentanol-1) were determined using conductometric measurements. The results show that chromium laurate behaves as simple electrolyte in dilute solutions below the CMC, and the conductance results can be explained according to Ostwald's formula and Debye-Huckel's theory of electrolytes.

Keywords: Alkanol, chromium laurate, conductance, critical micelle concentration, dissociation, micellar behavior.

Introduction

In recent years, heavy-metal soaps have found extensive application in industry. However, study of these soaps has been limited, with the result that only few references¹⁻¹⁸ are available in this field. The application of metal soaps largely depends on their physical state, thermal stability, chemical reactivity, and solubility in polar and nonpolar solvents.

Several researchers¹⁹⁻²³ 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 an organic base.

Certain compounds in solution yield lyophilic colloidal systems as a result of spontaneous association of their molecules, forming colloidal particles. If one plots a physicochemical property such as the specific conductance, osmotic pressure, turbidity and surface tension of a solution of a soap versus the solute's stoichiometric concentration, one finds that at a certain concentration (called the critical micelle concentration, CMC) the solution shows a sharp change. Above the CMC a substantial portion of the solute ions are aggregated and form units of colloidal size (called micelles).

The molar conductance Λ of an electrolyte in solution is defined as

$$\Lambda = \frac{K}{C} \quad (1)$$

where K is the specific conductance and C is the electrolyte's stoichiometric molar concentration.

The degree of dissociation is usually called the ratio of the number of dissociated molecules to the total molecule number or the conductance ratio, Λ/Λ_∞ , where Λ is the molar conductance at finite concentration, and Λ_∞ is the limiting molar conductance at infinite dilution.

The dissociation constant is called the ratio of the molar concentrations of the dissociate ions (products) to the reactants. This constant may also be called the equilibrium constant in an equilibrium state. For example, a reaction may be written:



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

where C is the concentration in mol L^{-1} and α is the degree of dissociation. The dissociation constant K_d is

$$K_d = \frac{[Products]}{[Reactants]} = \frac{[A^+][B^-]}{[AB]} = \frac{C\alpha C\alpha}{C(1 - \alpha)} = \frac{C\alpha^2}{1 - \alpha} \quad (2)$$

In the Debye-Hückel theory, one assumes that the solution is very dilute and the activity coefficient is equal to one ($\gamma = 1$). Thus, $a = \gamma C$ and $a = C$ (a is the activity and C is the concentration). At high dilution, the main deviation from ideal dilute behavior comes from the long-range Coulomb's law attractions and repulsions between the ions. All deviation from ideal dilute behavior is due to interionic Coulombic forces²⁴.

This study deals with the determination of the critical micelle concentration (CMC), degree of dissociation (α) and dissociation constant (K_d) of solutions of chromium laurate in alkanols (methanol, ethanol, propanol-1, butanol-1 and pentanol-1).

Experimental

The potassium hydroxide, KOH, chrome alum, $K_2SO_4 \cdot Cr_2(SO_4)_3 \cdot 24H_2O$, and lauric acid, $C_{11}H_{23}COOH$, used in this study were supplied by Merck.

First, potassium soaps were obtained from the reaction between KOH and lauric acid and then chromium laurate was prepared by reacting potassium soap with the stoichiometrically required amount of chrome alum in a water-alcohol medium (1:1). The precipitated soap was washed with water and acetone to remove the excess of metal ions and unreacted lauric acid and then dried²⁵.

The conductance of the solutions of chromium laurate in alkanols (methanol, ethanol, propanol-1, butanol-1 and pentanol-1) was measured at 40°C 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. The reproducibility of the measurements was $\pm 0.1\%$.

Results and Discussions

The specific conductance, $K(K = \Lambda C)$, of the solutions of chromium laurate in organic solvents (i.e., methanol, ethanol, propanol-1, butanol-1 and pentanol-1) increased with increasing soap concentration (Figures 1-3). The increase in specific conductance with the increase in soap concentration may be due to the dissociation of chromium laurate into simple metal cations, Cr^{3+} , and fatty acid anions, $C_{11}H_{23}COO^-$, in dilute solutions as well as the formation of micelles at higher concentrations.

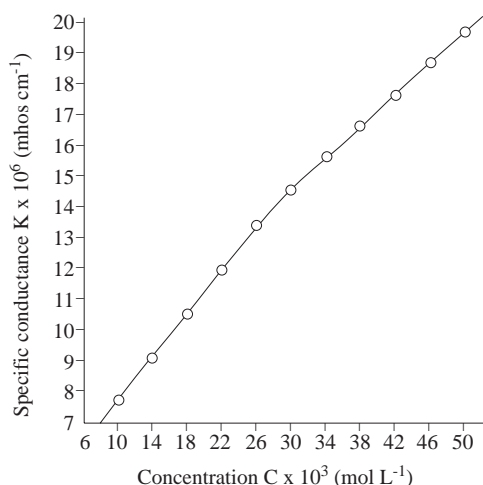


Figure 1. Specific conductance, K (mhos cm^{-1}), vs. concentration, C (mol L^{-1}), for chromium laurate in methanol at 40°C .

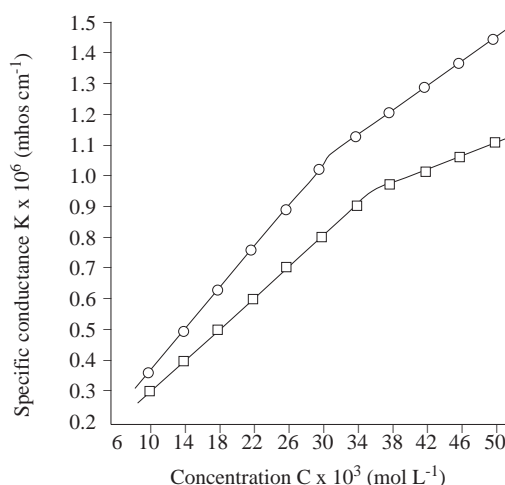


Figure 2. Specific conductance, K (mhos cm^{-1}), vs. concentration, C (mol L^{-1}), for chromium laurate in \circ : ethanol and \square : propanol-1 at 40°C .

The plots of specific conductance, K , vs. chromium laurate concentration, C , (Figures 1-3) for solutions in methanol (Figure 1), ethanol and propanol-1 (Figure 2), and butanol-1 (Figure 3) are characterized by an intersection of two straight lines at a definite chromium laurate concentration, 0.0271, 0.0322, 0.0356 and 0.0391 mol L^{-1} , respectively, corresponding to the CMC of the chromium laurate in these solvents (Table 1).

Table 1. The values of CMC, limiting molar conductance, Λ_∞ and dissociation constant, K_d , of chromium laurate in alkanols at 40°C .

Solvent	CMC (mol L^{-1})	Λ_∞	$K_d \times 10^4$
Methanol	0.0271	1.2750	2.2683
Ethanol	0.0322	0.0485	7.1433
Propanol-1	0.0356	0.0356	8.2450
Butanol-1	0.0391	0.0054	11.0610
Pentanol-1	-	0.0029	20.9503

The specific conductance of chromium-laurate solutions in pentanol-1 increased linearly with increasing chromium-laurate concentration. The CMC values show that micelle formation occurred more easily in methanol than in other, higher alcohols, showing the following trend:

$$\text{Methanol} > \text{Ethanol} > \text{Propanol-1} > \text{Butanol-1} > \text{Pentanol-1}$$

This trend was determined according to the level of micelle formation signified by the CMC values. This ability is greater in methanol than in other alcohols. As can be seen in Table 1, the CMC values of chromium laurate solution in methanol, ethanol, propanol-1 and butanol-1 increased with the increasing number of the carbon atom. Since dissociation replaces micelle formation and the value of the dissociation constant was high a CMC value was not obtained for pentanol-1, but perhaps can be obtained at a concentration higher than $50 \times 10^{-3} \text{ mol L}^{-1}$.

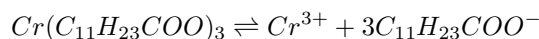
The molar conductance, Λ , of the dilute solutions of chromium laurate in methanol, ethanol, propanol-1, butanol-1 and pentanol-1 decreased with an increase in soap concentration (Table 2). The decrease seems

to be due to the tendency of the soap to form aggregates at higher soap concentrations. It is suggested that the mobility of the soap decreased with an increase in the size of the molecules, and, hence, the molar conductance decreased as the concentration increased.

Table 2. Specific conductance, K (mhos cm^{-1}), and molar conductance, Λ (mhos $\text{cm}^2 \text{mol}^{-1}$), of chromium laurate in alkanols at 40°C .

$C \times 10^3$ (M)	Solvents									
	Methanol		Ethanol		Propanol-1		Butanol-1		Pentanol-1	
	$K \times 10^6$	$\Lambda \times 10^2$	$K \times 10^6$	$\Lambda \times 10^2$	$K \times 10^6$	$\Lambda \times 10^2$	$K \times 10^6$	$\Lambda \times 10^2$	$K \times 10^6$	$\Lambda \times 10^2$
10	7.70	77.00	0.36	3.60	0.30	3.00	0.050	0.500	0.025	0.250
14	9.05	64.64	0.49	3.50	0.40	2.85	0.068	0.486	0.034	0.240
18	10.50	58.33	0.62	3.44	0.50	2.77	0.086	0.478	0.042	0.233
22	11.95	54.32	0.75	3.41	0.60	2.72	0.104	0.472	0.050	0.229
26	13.26	51.02	0.88	3.39	0.70	2.69	0.122	0.469	0.059	0.227
30	14.55	48.50	1.01	3.37	0.80	2.67	0.140	0.466	0.067	0.225
34	15.61	45.91	1.13	3.31	0.90	2.65	0.157	0.463	0.076	0.223
38	16.64	43.79	1.22	3.21	0.99	2.59	0.175	0.462	0.084	0.222
42	17.66	42.05	1.31	3.12	1.06	2.51	0.191	0.455	0.093	0.221
46	18.68	40.61	1.41	3.05	1.13	2.46	0.206	0.448	0.101	0.220
50	19.70	39.40	1.50	3.00	1.21	2.41	0.221	0.442	0.110	0.219

Since chromium laurate behaves as a simple electrolyte in dilute solutions an expression for the dissociation of chromium laurate can be developed using Ostwald's method. If C is the concentration in mol L^{-1} and α is the degree of dissociation of chromium laurate, the equivalent concentrations of different species can be represented as:



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

The dissociation constant, K_d , can be expressed as shown below in Eq. 1:

$$K_d = \frac{[Cr^{3+}][C_{11}H_{23}COO^-]^3}{[Cr(C_{11}H_{23}COO)_3]} = \frac{C\alpha(3C\alpha)^3}{C(1 - \alpha)} = \frac{27C^3\alpha^4}{(1 - \alpha)}. \quad (3)$$

The ionic concentrations in dilute solutions are low, and so the interionic effects may be considered negligible. Therefore, the dilute soap solutions do not deviate appreciably from ideal behavior and the activities of the 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 the molar conductance at finite concentration, and Λ_∞ is the limiting molar conductance at infinite dilution. On substituting the value of α , and rearranging Eq. 1, we obtain:

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

The values of K_d and Λ_∞ (Table 1) were obtained from the slope $[(K_d \Lambda_\infty^4)/27]$ and intercept $[-(K_d \Lambda_\infty^3)/27]$ of the linear parts of the plots of $\Lambda^3 C^3$ vs. $1/\Lambda$ below the CMC (Table 3 and Figures 4-8). There is no doubt that the soap (chromium laurate) is in micellar and other aggregate forms at and above the CMC and possess different conductivities in these forms. However, the plots of $\Lambda^3 C^3$ vs. $1/\Lambda$ are linear below the CMC and the slope and intercept of the linear portion were used to evaluate Λ_∞ and K_d .

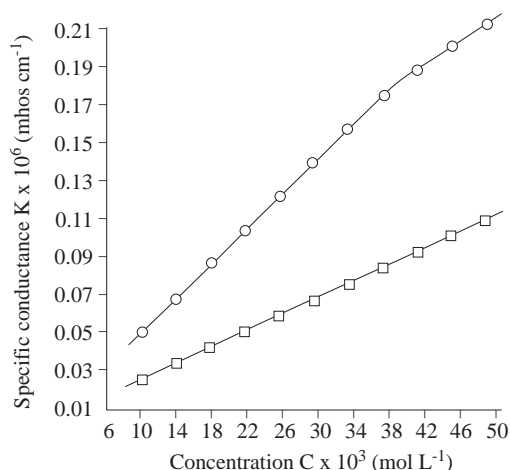


Figure 3. Specific conductance, K (mhos cm^{-1}), vs. concentration, C (mol L^{-1}), for chromium laurate in: butanol-1 and \square : pentanol-1 at 40°C .

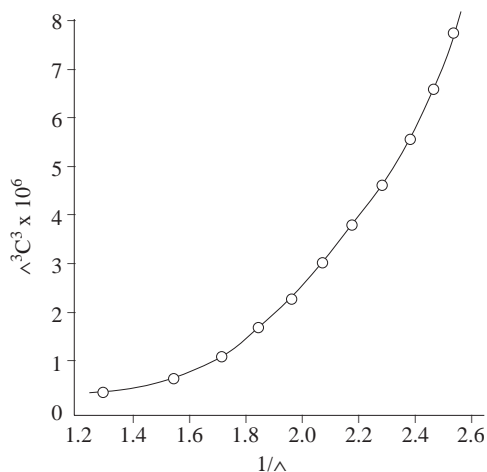


Figure 4. $\Lambda^3 C^3$ vs. $1/\Lambda$ for chromium laurate in methanol at 40°C .

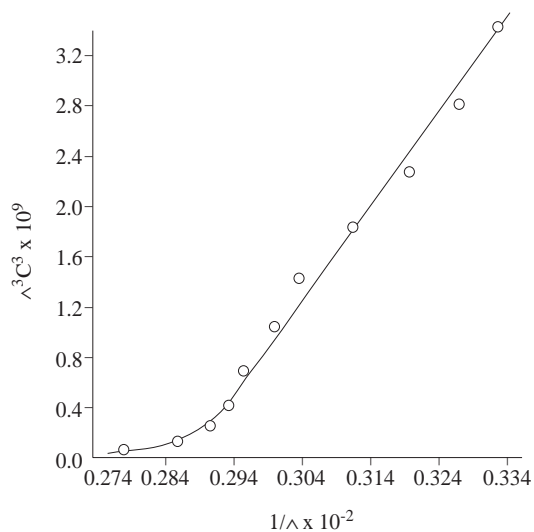


Figure 5. $\Lambda^3 C^3$ vs. $1/\Lambda$ for chromium laurate in ethanol at 40°C .

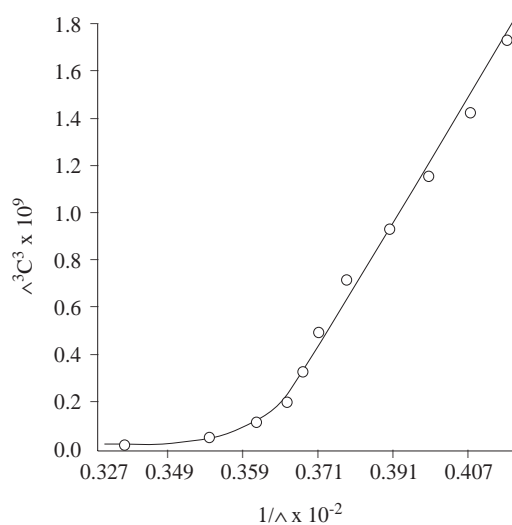


Figure 6. $\Lambda^3 C^3$ vs. $1/\Lambda$ for chromium laurate in propanol-1 at 40°C .

The soap is in monomeric form below the CMC, and the value of C was taken to be equal to the total concentration of the surfactant. The plots of $\Lambda^3 C^3$ vs. $1/\Lambda$ above the CMC were not used to evaluate any parameter. As can be seen in Table 1, the values of limiting molar conductance, Λ_∞ , decreased in the alkanol series. The values of the dissociation constant, K_d , increased in the alkanol series. The results indicate that chromium laurate behaves as a simple electrolyte in dilute solutions below the CMC, and the conductance results may be explained according to Ostwald's formula and Debye-Hckel's theory²⁴ of electrolytes.

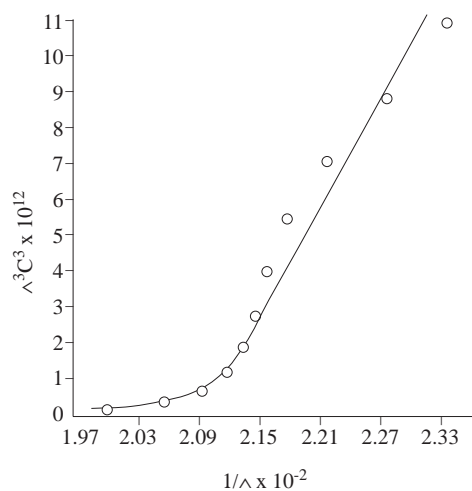


Figure 7. $\Lambda^3 C^3$ vs. $1/\Lambda$ for chromium laurate in butanol-1 at 40°C.

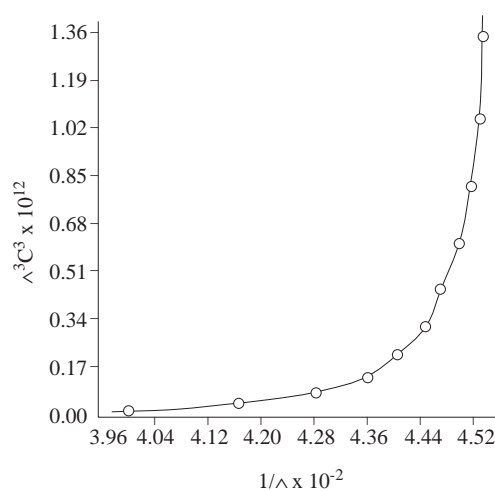


Figure 8. $\Lambda^3 C^3$ vs. $1/\Lambda$ for chromium laurate in pentanol-1 at 40°C.

Table 3. The values of $1/\Lambda$ and $\Lambda^3 C^3$ of chromium laurate in alkanols at 40°C.

Methanol		Ethanol		Propanol-1		Butanol-1		Pentanol-1	
$1/\Lambda$	$\Lambda^3 C^3 \times 10^6$	$1/\Lambda \times 10^{-2}$	$\Lambda^3 C^3 \times 10^9$	$1/\Lambda \times 10^{-2}$	$\Lambda^3 C^3 \times 10^9$	$1/\Lambda \times 10^{-2}$	$\Lambda^3 C^3 \times 10^{12}$	$1/\Lambda \times 10^{-2}$	$\Lambda^3 C^3 \times 10^{12}$
1.299	0.457	0.278	0.047	0.333	0.027	2.000	0.125	4.000	0.016
1.547	0.741	0.286	0.118	0.352	0.063	2.056	0.316	4.167	0.038
1.714	1.158	0.290	0.238	0.362	0.124	2.093	0.636	4.286	0.074
1.841	1.705	0.293	0.422	0.368	0.214	2.119	1.118	4.365	0.128
1.960	2.311	0.296	0.682	0.371	0.343	2.135	1.807	4.412	0.204
2.071	3.040	0.297	1.0303	0.375	0.512	2.147	2.726	4.454	0.306
2.178	3.804	0.302	1.424	0.377	0.731	2.160	3.900	4.480	0.437
2.284	4.607	0.312	1.816	0.386	0.956	2.167	5.396	4.508	0.599
2.378	5.508	0.321	2.248	0.398	1.174	2.222	6.968	4.526	0.799
2.463	6.518	0.327	2.774	0.407	1.443	2.285	8.742	4.541	1.040
2.538	7.645	0.333	3.375	0.415	1.750	2.343	10.794	4.546	1.331

Conclusion

The values of the CMC and dissociation constant, K_d , for a soap solution increase in the alkanol series as the number of the carbon atom increases. The increments of the values of the CMC and K_d show that the dissociation process increasingly replaces the micellization process (aggregation of the solute ions). The micelle formation of chromium laurate solutions occurs more easily in methanol than in ethanol, propanol-1, butanol-1 and pentanol-1. A CMC value was not obtained for pentanol-1. Since the value of the dissociation constant was high, it is understood that the chromium-laurate molecules dissociate and that there are more chromium and laurate ions in pentanol-1 than in the other alcohols.

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