



CONDUCTOMETRIC STUDIES OF DYSPROSIUM LAURATE AND MYRISTATE IN METHANOL

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ABSTRACT

Dysprosium laurate and myristate behave as a weak electrolytes in dilute solutions and CMC have been found to decrease with increasing chain length of fatty acid constituent of the soap molecules. The CMC, degree of dissociation and dissociation constant of dysprosium laurate and myristate in methanol have been determined by conductometric measurements.

Key words: Dysprosium soaps, Conductivity, Micellization, CMC value.

INTRODUCTION

The uses of metal soaps largely depend on their physical state, stability, chemical reactivity and solubility in polar and non-polar solvents. Several workers¹⁻¹⁴ have been used different methods and techniques for studying the preparation, properties and uses of metal soaps. The physico-chemical properties and structure of alkaline earth, and transition metal soaps have been thoroughly investigated, however the same is not true with regards to Lanthanide metal soaps. Here the title study has been undertaken to initiated with a view to determining the CMC of dysprosium laurate and myristate in methanol.

EXPERIMENTAL

Preparation of carboxylates

The chemicals used were of AR/GR grade. Dysprosium laurate and myristate, were prepared by direct metathesis of the corresponding potassium soap with slight excess of aqueous solutions of dysprosium nitrate at 50-55°C under vigorous stirring. The precipitated soaps were filtered off and washed with distilled water and acetone to remove the excess of metal ions and unreacted fatty acid. The soaps were purified by recrystallisation, dried in an air oven at 50-60°C and the final drying of the soap was carried out under reduced pressure. The purity of these soaps was checked by elemental analysis, IR spectra and by determination of their melting point.

Measurements

The conductance of the solutions was measured with a digital conductivity meter (Toshniwal Model CL 01, 01 10A) and a dipping type conductivity cell (cell constant 0.90 cm⁻¹) with platinized electrode.

RESULTS AND DISCUSSION

Specific conductance (k) and molar conductance

The specific conductance (k) of the solutions of dysprosium laurate and myristate in methanol increases with the increasing concentration (C) (Table 1-2) and this may be due to ionization of dysprosium laurate and myristate into simple metal cation M^{3+} and fatty acids anions $RCOO^-$ [where M is dysprosium and R is $C_{11}H_{23}$ and $C_{13}H_{37}$ for laurate and myristate respectively] in solutions and also due to the formation of micelles at higher soap concentration. The plots of k vs C (Fig. 1) are characterized by an intersection of two straight lines at a definite soap concentration which corresponds to the CMC of the soaps indicating the formation of ionic micelles at this concentration. The results show that the CMC decreases with increasing chain length of fatty acid (Table 3).

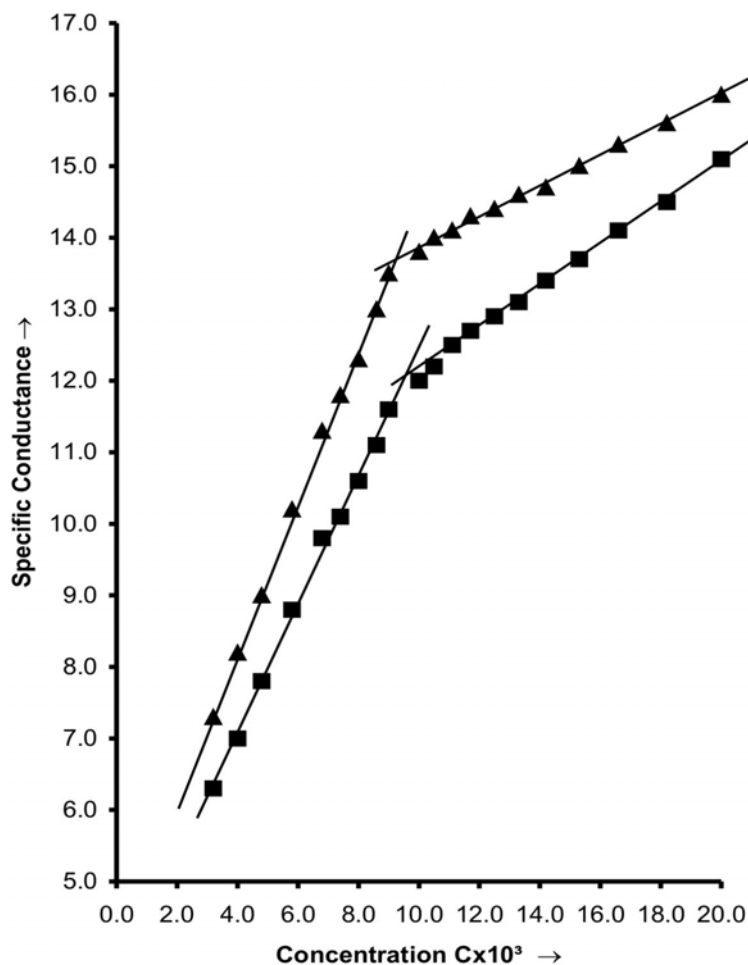


Fig. 1: Specific conductance vs. concentration for dysprosium soaps (\blacksquare) Laurate (\blacktriangle) Myristate

The molar conductance (μ) of the solutions of dysprosium laurate and myristate decreases with increasing concentration (Table 1-2). The decrease in molar conductance may be attributed to combined effects of ionic atmosphere, solvation of ions and decreases of mobility and ionization with the formation of micelles.

Table 1: Conductivity measurements of Dysprosium laurate in methanol at $30 \pm 0.05^\circ\text{C}$

S. No.	Concentration ($\text{C} \times 10^3$) mol L ⁻¹	Specific conductance ($\text{k} \times 10^3$) mhos cm ⁻¹	Molar conductance (μ) mhos cm ² mol ⁻¹	Degree of dissociation α	Dissociation constant ($\text{K} \times 10^6$)
1.	20.0	15.1	0.755	0.314	3.060
2.	18.2	14.5	0.797	0.333	3.001
3.	16.6	14.1	0.849	0.354	3.002
4.	15.3	13.7	0.895	0.373	3.022
5.	14.2	13.4	0.944	0.393	3.038
6.	13.3	13.1	0.985	0.410	3.042
7.	12.5	12.9	1.032	0.430	3.163
8.	11.7	12.7	1.086	0.452	3.329
9.	11.1	12.5	1.126	0.469	3.364
10.	10.5	12.2	1.162	0.484	3.324
11.	10.0	12.0	1.200	0.500	3.375
12.	9.0	11.6	1.288	0.537	3.535
13.	8.6	11.1	1.290	0.538	3.114
14.	8.0	10.6	1.325	0.552	2.865
15.	7.4	10.1	1.365	0.569	2.661
16.	6.8	9.8	1.441	0.600	2.755
17.	5.8	8.8	1.517	0.632	2.284
18.	4.8	7.8	1.625	0.677	1.942
19.	4.0	7.0	1.750	0.729	1.801
20.	3.2	6.3	1.969	0.820	2.222

Table 2: Conductivity measurements of Dysprosium myristate in methanol at $30 \pm 0.05^\circ\text{C}$

S. No.	Concentration ($\text{C} \times 10^3$) mol L ⁻¹	Specific conductance ($\text{k} \times 10^3$) mhos cm ⁻¹	Molar conductance (μ) mhos cm ² mol ⁻¹	Degree of dissociation α	Dissociation constant ($\text{K} \times 10^6$)
1.	20.0	16.0	0.800	0.267	1.498
2.	18.2	15.6	0.857	0.286	1.525
3.	16.6	15.3	0.922	0.307	1.583
4.	15.3	15.0	0.980	0.327	1.643
5.	14.2	14.7	1.035	0.345	1.672
6.	13.3	14.6	1.098	0.366	1.798
7.	12.5	14.4	1.160	0.387	1.930
8.	11.7	14.3	1.220	0.407	2.001
9.	11.1	14.1	1.270	0.423	2.049

Cont...

S. No.	Concentration ($C \times 10^3$) mol L ⁻¹	Specific conductance ($k \times 10^3$) mhos cm ⁻¹	Molar conductance (μ) mhos cm ² mol ⁻¹	Degree of dissociation α	Dissociation constant ($K \times 10^6$)
10	10.5	14.0	1.330	0.443	2.016
11.	10.0	13.8	1.380	0.460	2.239
12.	9.0	13.5	1.500	0.500	2.460
13.	8.6	13.0	1.512	0.504	2.234
14.	8.0	12.3	1.538	0.513	1.965
15.	7.4	11.8	1.595	0.532	1.873
16.	6.8	11.3	1.661	0.554	1.793
17.	5.8	10.2	1.759	0.586	1.501
18.	4.8	9.0	1.875	0.625	1.215
19.	4.0	8.2	2.050	0.683	1.186
20.	3.2	7.3	2.281	0.760	1.229

The plots of the molar conductance, μ against the square root of the concentration, $C^{1/2}$ (Fig. 2) is not linear which indicates that these soaps behaves as a weak electrolyte in these solutions.

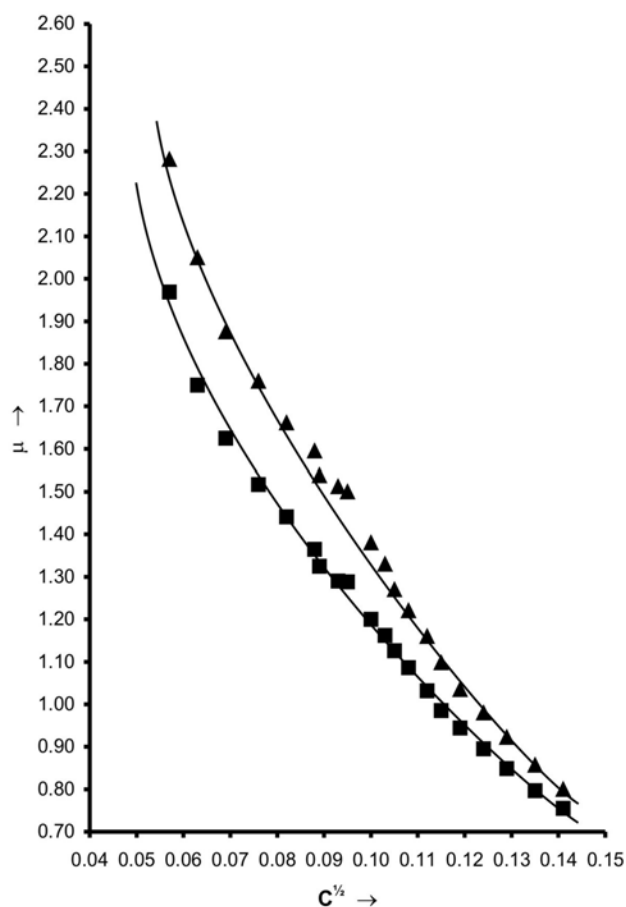
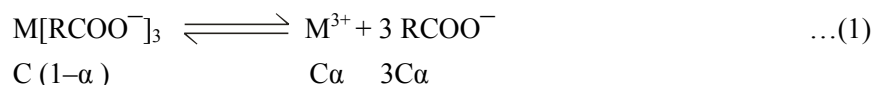


Fig. 2: Molar conductance μ vs. $C^{1/2}$ for Dysprosium Soaps (■) Laurate (▲) Myristate

The molar conductance (μ_0) cannot be obtained by the usual extrapolating method as the Debye-Huckel Onsanger's equation is not applicable to these soap solutions.

Assuming that these soaps are completely associated into M^{3+} and $RCOO^-$ ions. The dissociation of metal soap may be represented as :



where M is dysprosium and R is $C_{11}H_{23}$ and $C_{13}H_{27}$ for laurate and myristate respectively and α and C are the degree of dissociation and concentration.

The dissociation constant, K can be written as –

$$K = \frac{[M^{3+}][RCOO^-]^3}{[M(RCOO^-)_3]} \quad \dots(2)$$

$$\begin{aligned} &= \frac{C\alpha(3C\alpha)^3}{C(1-\alpha)} \\ &= \frac{27C^3\alpha^4}{1-\alpha} \end{aligned} \quad \dots(3)$$

Assuming that the dilute solutions do not deviate appreciably from ideal behaviour and the activities of ions can be taken as almost equal to concentration. Thus α may be defined by conductance ratio μ/μ_0 . Where μ is the molar conductance at a finite concentration that is attributed to the ions formed by the dissociation of metal soaps and μ_0 is the limiting molar conductance of these ions.

On substituting the value of α and rearranging, equation (3) can be written as :

$$\mu^3 C^3 = \frac{K\mu_0^4}{27\mu} - \frac{\mu_0^3 K}{27} \quad \dots(4)$$

The values of K and μ_0 have been obtained from the slope and intercept of the linear plots of $\mu^3 c^3$ vs $1/\mu$ below the CMC and are recorded in (Table 3). The results show that the values of limiting molar conductance increases while the dissociation constant decreases with increasing concentration.

Table 3: CMC and values of various constants for Dysprosium soaps at $30 \pm 0.05^\circ\text{C}$

Name of dysprosium soaps	CMC	μ_0	$K \times 10^6$
Laurate	0.0096	2.4	5.00
Myristate	0.0090	3.0	4.17

The values of degree of dissociation (α) and dissociation constant (K) have been calculated at different concentrations by using the values of μ_0 and equation (3). The plots of α vs C show that the dysprosium laurate and myristate behave as a weak electrolyte in these solutions. The values of dissociation constant remain almost constant in dilute solutions but show a drift at higher concentration which may be due to the failure of Debye-Huckel's activity equation at higher soap concentration.

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