

## Research Article

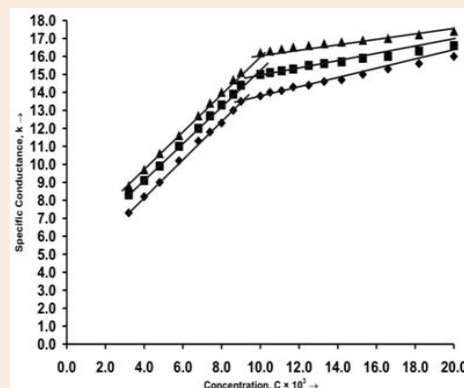
# Thermodynamics of Dissociation and Micellization of Carboxylates of Dysprosium in Organic Solvent

Sangeeta\* and M. K. Rawat

Department of Chemistry, Agra College, Agra 282002, India

## Abstract

Dysprosium myristate and palmitate behave as weak electrolytes in methanol below the Critical micelle concentration. The value of dissociation constant,  $K$  and degree of dissociation,  $\alpha$  obtained from Conductance data and it show that Dysprosium myristate and palmitate behave as weak electrolyte and it can be explained on the basis of Ostwald's formula and Debye Huckel theory of weak electrolytes. Thermodynamic parameters such as heat of dissociation  $\Delta H^0_D$ , change in free energy  $\Delta G^0_D$  and entropy  $\Delta S^0_D$  per mole for dissociation process have also been evaluated by using thermodynamic equations for the aggregation process, the standard free energy of micellization  $\Delta G^0_A$  has been explained on the basis of number of moles of free surfactants and  $n_s$  of moles of solvent  $n_o$ . The negative values of free energy of micellization  $\Delta G^0_A$  and positive values  $\Delta G^0_D$ , negative values of  $\Delta S^0_D$  for the dissociation indicate that the micellization process was spontaneous and predominant over the dissociation process.



## \*Correspondence

Author: Sangeeta

Email: singhs\_chem@yahoo.in

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## Introduction

The uses of metal carboxylates largely depend on their physical state, stability, chemical reactivity and solubility in polar and non-polar solvents. Mehmet et al [1] have used precipitation process for the preparation of calcium soap. Matsumoet et.al [2-3] were prepared potassium soaps by heating fats, oil, KOH and water. Conductometric investigation of nickel myristate in benzene – methanol mixture were performed by Mehrotra.[4]. Topallar et al. [5] investigated the conductance behaviour of chromium soaps in different solvents. The physico-chemical properties and structure of alkaline earth, and transition metal carboxylates have been thoroughly investigated. However, the same is not true with regards to Lanthanide metal carboxylates. The title study has been undertaken with a view to determining the CMC of Dysprosium myristate and palmitate in methanol at different temperatures with measuring conductivity and data were used to evaluate thermodynamics quantities  $\Delta H^0_D$ ,  $\Delta G^0_D$  and  $\Delta S^0_D$  to explain the dissociation and association process.

## Experimental

The chemicals used for the present investigation were of AR (Analytical Reagent) grade. Dysprosium myristate and palmitate were prepared by direct metathesis (metathesis is a displacement reaction in which the carbonate or some other salts of the metal with volatile acids such as acetone is treated with fatty acid with fused state[6]. The main advantage of this method is the possibility of getting directly anhydrous sample of metal soaps. Since attempt to remove the water of hydration from soaps isolated from an aqueous medium often yield hydrolysed products) of the corresponding potassium carboxylates with slight excess of aqueous solutions of Dysprosium Nitrate at 50-55°C

under vigorous stirring. The precipitated carboxylates were filtered off and washed with distilled water and Acetone (Acetone is a solvent which was used to pure the metal soaps as dysprosium carboxylates are insoluble in it and fatty acid is soluble) to remove excess metal ions and unreacted fatty acid. The carboxylates 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 carboxylates was checked by elemental analysis, IR spectra and by determination of their melting points.

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 0.90cm<sup>-1</sup>) with platinized electrode at different temperature (303.15, 313.15 and 323.15 K).

## Results and Discussion

### Specific conductance, k and molar conductance

The specific conductance, k of the solutions of Dysprosium myristate and palmitate in methanol increases with the increasing concentration, C and temperature and this may be due to ionization of Dysprosium myristate and palmitate into simple metal cation M<sup>3+</sup> and fatty acids Anions RCOO<sup>-</sup> [where M is Dysprosium and R is C<sub>13</sub>H<sub>27</sub>, and C<sub>15</sub>H<sub>31</sub> for myristate and palmitate respectively] in solutions and also due to the formation of micelles at higher concentration. The plots of k Vs C are characterized by an intersection of two straight lines at a definite concentration which corresponds to the CMC of the carboxylates indicating the formation of ionic micelles at this concentration. The results show that the CMC decreases with increasing chain length of fatty acid (table-1).

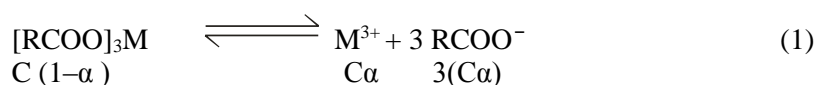
**Table 1** Critical Micelle Concentration, CMC (Mol L<sup>-1</sup>) and Values of  $\mu_0$  of Dysprosium carboxylates at different temperature (K)

S. No.	Temperature (K)	CMC x 10 <sup>3</sup>			$\mu_0$
		Dysprosium Myristate	Dysprosium Palmitate	Dysprosium Myristate	Dysprosium Palmitate
1.	303.15	8.6	7.6	3.00	3.80
2.	313.15	9.4	7.8	3.50	4.20
3.	323.15	10.0	8.2	3.80	4.40

The molar conductance,  $\mu$  of the solutions of Dysprosium myristate and palmitate decreases with increasing concentration and increases with increase in temperature. 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.

The plots of the molar conductance,  $\mu$  against the square root of the concentration, C<sup>1/2</sup> is not linear which indicates that these carboxylates behaves as a weak electrolytes in these solutions. The molar conductance,  $\mu_0$  cannot be obtained by the usual extrapolating method as the Debye-Huckel Onsanger's equation is not applicable to these carboxylates solutions. An expression for the dissociation of Dysprosium carboxylates may be obtained in Ostwald's manner.

Assuming that these carboxylates, are completely associated in to M<sup>3+</sup> and RCOO<sup>-</sup> ions. The dissociation of metal soap may be represented as :



where M is Dysprosium and R is C<sub>13</sub>H<sub>27</sub> and C<sub>15</sub>H<sub>31</sub> for myristate and palmitate, respectively and  $\alpha$  and C are the degree of dissociation and concentration.

The dissociation constant, K can be written as

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

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

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,  $\alpha$  may be defined by conductance ratio  $\mu/\mu_0$ . Where  $\mu$  is the molar conductance at a finite concentration that is attributed to the ions formed by the dissociation of metal carboxylates and  $\mu_0$  is the limiting molar conductance of these ions.

On substituting the value of  $\alpha$  and rearranging, equation  $\frac{27C^3\alpha^4}{1-\alpha}$  can be written as :

$$\mu^2 c^2 = \frac{K\mu_0^4}{27\mu} - \frac{\mu_0^3 K}{27} \quad (4)$$

The values of K and  $\mu_0$  have been obtained from the slope and intercept of the linear plots of  $\mu^2 c^2$  vs  $1/\mu$  below the CMC.

The results show that the values of limiting molar conductance increases while the dissociation constant decreases with increasing temperature.

The decrease in the dissociation constant with increasing temperature indicates the exothermic nature of the dissociation of Dysprosium carboxylates in methanol.

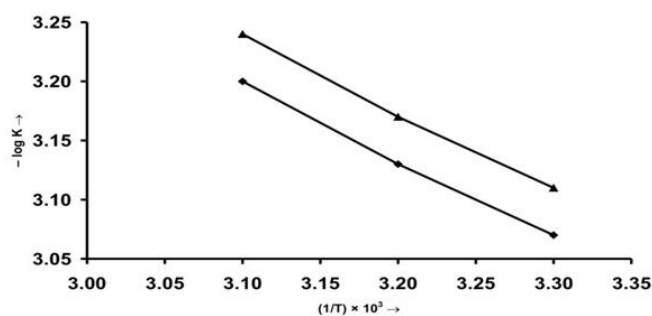
The degree of dissociation,  $\alpha$  and dissociation constant, K have been calculated at different concentrations by using the values of  $\mu_0$  and  $\frac{27C^3\alpha^4}{1-\alpha}$ . The plots of  $\alpha$  vs C show that the Dysprosium myristate and palmitate behave as a weak electrolyte in methanol. The values of dissociation constants 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 concentration. The various parameters of dissociation and association process have also been calculated by using thermodynamic equation.

The heat of dissociation is given by the relationship

$$\frac{\partial \ln K}{\partial T} = \frac{\Delta H_D^\circ}{RT^2}$$

Or 
$$\log K = -\frac{\Delta H_D^\circ}{2.303RT} + \text{constant} \quad (5)$$

The values of the heat of dissociation,  $\Delta H_D^\circ$  have been obtained from the slope of the linear plot of  $\log K$  vs  $1/T$  (Fig.2). The negative values of heat of dissociation indicate that the dissociation process is exothermic.



**Figure 2** Log K vs 1/T

The values of the change in free energy,  $\Delta G_D^0$  and entropy  $\Delta S_D^0$ , per mole for the dissociation process have been calculated using the relationship (table-2).

$$\Delta G_D^0 = -RT \ln K_D \quad (6)$$

$$\Delta S_D^0 = \frac{[\Delta H_D^0 - \Delta G_D^0]}{T} \quad (7)$$

**Table 2** Thermodynamic parameters of Dysprosium carboxylates for the dissociation process

S.No.	Temperature (K)	Dysprosium Myristate			Dysprosium Palmitate		
		$-\Delta H_D^0$ kJ/mol	$\Delta G_D^0$ kJ/mol	$-\Delta S_D^0 \times 10^2$ kJ/mol K	$-\Delta H_D^0$ kJ/mol	$\Delta G_D^0$ kJ/mol	$-\Delta S_D^0 \times 10^2$ kJ/mol K
1	303.15	10.310	4.83	2.08	10.545	4.43	1.94
2	313.15	10.465	4.34	2.21	10.864	3.99	2.02
3	323.15	10.732	3.75	2.32	11.248	3.92	2.10

For the aggregation process, the standard free energy of micellization (per mole of monomer)  $\Delta G_A^0$  for the phase separation model [7,8] is given by the relationship.

$$\Delta G_A^0 = 2 RT \ln X_{CMC} \quad (8)$$

where  $X_{CMC}$  is the CMC expressed as a mole fraction and defined as :

$$X_{CMC} = \frac{n_s}{n_s + n_o}$$

**Table 3** Values of the standard free energy of micellization  $\Delta G_A^0$  (kJ mol<sup>-1</sup>) and  $\Delta H_A^0$  (kJ mol<sup>-1</sup>) of Dysprosium carboxylates for association process

S.No.	Temperature (K)	$\Delta G_A^0$	$\Delta H_A^0$	$\Delta G_A^0$	$\Delta H_A^0$
		Dysprosium Myristate	Dysprosium Myristate	Dysprosium Palmitate	Dysprosium Palmitate
1	303.15	-5.02	-1.45	-5.07	-1.47
2	313.15	-5.13	-1.48	-5.18	-1.51
3	323.15	-5.26	-1.52	-5.28	-1.57

Since the number of moles of free surfactant,  $n_s$  is small as compared to the number of moles of solvent,  $n_0$ .

$$X_{CMC} = \frac{n_s}{n_0}$$

the standard enthalpy change of micellization per mole of monomer for the phase separation model[9,10].  $\Delta H_A^0$  is given by the relationship.

$$\begin{aligned} \frac{\partial(\ln X_{CMC})}{\partial T} &= -\frac{\Delta H_A^0}{2RT^2} \\ \ln(X_{CMC}) &= \frac{\Delta H_A^0}{2RT} + \text{Constant} \end{aligned} \quad (9)$$

The values of  $\Delta H_A^0$  of dysprosium myristate and palmitate have been calculated from the slope of the plots of  $-\ln X_{CMC}$  vs  $1/T$ . The value of  $\Delta H_A^0$  decreases as the CMC also decreases with increasing chain length of the carboxylates (table-3).

The values of enthalpy, free energy and entropy changes ( $\Delta H_D^0 < 0$ ,  $\Delta G_D^0 > 0$ ,  $\Delta S_D^0 < 0$ ,  $\Delta H_A^0 < 0$ ) confirm the exothermic nature of dissociation process and the decrease in free energy for association process shows that the micellization is favoured over dissociation process.

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