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Conductometric and Thermodynamic Studies on Gadolinium Tri-Soaps in Benzene-Dimethylformamide Mixture

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Abstract: **Conductometric measurements were made on gadolinium caprylate and laurate in 50% benzene-50% dimethylformamide mixture(V/V), to determine the critical micellar concentration (CMC), limiting molar coductance at infinite dilution, degree of dissociation, dissociation constant and free energy change for dissociation and micellization process. The conductivity results showed that gadolinium soaps behave as weak electrolyte in dilute solutions below the CMC and Debye-Huckel-Onsager's equation is not applicable to these soaps solutions. The micellization process of these soaps has been found to be predominant over the dissociation process.**

Keywords: **Micelles, Critical micellar concentration, Conductance, Dissociation constant.**

1. INTRODUCTION

The metallic soaps are soluble in variety of pure and mixed organic solvents and yield liquids dispersion and gels with characteristics colloidal properties. These soaps are widely used in industries, their appreciable solubility in organic solvents and availability at a reasonable cost make them potentially useful as detergents, softeners, plasticizers, greases, lubricants, cosmetics, medicines, emulsifiers and water proofing agents. Metal soaps with elements from the lanthanide series were synthesized for the first time by Mishra et al [1]. Mehrotra et al [2-5] investigated acoustical and thermodynamic properties of gadolinium soaps and concluded that these soaps behave as weak electrolyte in dilute solutions. Upadhyaya et al studied thermodynamic [6, 7] and ultrasonic [8] behavior of metallic soaps .They inferred that there is a significant interaction between soap-solvent molecules in dilute solution and soap molecule do not aggregate appreciably below the CMC. The present paper deals with the conductivity measurements of solutions of gadolinium caprylate and laurate in 50/50 benzene – dimethylformamide mixture. The results have been used to find out the nature of these soaps in non-aqueous medium and to determine various thermodynamic parameters both for dissociation and micellization processes.

2. EXPERIMENTAL

Analytical R grade caprylic acid, lauric acid, benzene, dimethylformamide, acetone and gadolinium acetate (purity 99.9% Indian rare earth limited ,Kerala) were used for the present investigations. The gadolinium caprylate and laurate were prepared by direct metathesis of potassium soaps (potassium caprylate and potassium laurate) by pouring a slight stoichiometric excess of aqueous gadolinium acetate solution into clear potassium caprylate and laurate dispersion at raised temperature with vigorous stirring. The precipitates were filtered off and washed with hot distilled water and acetone. After initial drying in an air oven at 50-60^{0}C, final drying was carried out under reduced pressure. The purity of soaps was checked by elemental analysis and the results were found in agreement with the theoretically calculated values. The general chemical reactions for the synthesis of these soaps are as follows

$$(CH_3\,COO)_3\,Gd + 3RCOOK \longrightarrow (RCOO)_3\,Gd + 3CH_3\,COOK$$

(Gadolinium soap)

Where R is C_7H_{15}, $C_{11}H_{23}$,for caprylate and laurate respectively.

A digital conductivity meter (Systronics conductivity Bridge 305) and a dipping type conductivity cell with platinised electrode(cell constant 1.0) were used for measuring the conductance of the gadolinium soap solutions at different concentrations temperatures and in non-aqueous medium.

3. RESULTS AND DISCUSSION

Specific conductance, k of the solution of gadolinium caprylate and laurate in a mixture of 50/50 benzene-dimethylformamide mixture (V/V) increases with increasing soap concentration, C and temperature (Fig. 1). The increase in specific conductance with soap concentration may have been due to dissociation of these soaps into simple gadolinium metal cations (Gd^{3+}) and fatty acid anions ($RCOO^-$).

The decrease of the 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. The plots (Fig. 1) of specific conductance, k Vs. soap concentration C are characterized by a break, corresponding to C.M.C (Table 1) indicates that micelle formation takes place at a definite soap concentration .

Molar conductance μ of gadolinium soap (caprylate and laurate) solution in 50/50 benzene – dimethylformamide mixture (V/V) decrease with increasing concentration. The decrease in molar conductance is attributed to the combined effects of ionic atmosphere, solvation of ions and decrease in mobility and ionization with formation of micelles.

The plots of molar conductance Vs square root of soap concentration indicates that Debye– Huckel-Onsager‘s equation [9] is not applicable to these soaps solution. Molar conductance results indicates that gadolinium caprylate and laurate behave as weak electrolytes in dilute solution If C is the concentration in g mole/lit and α is the degree of dissociation of the soaps, the equivalent concentration of different species can be represented as

$$Gd(RCOO)_3 \longrightarrow Gd(RCOO)^{2+} + 2RCOO$$

$C\,(1-\alpha)$ $C\alpha$ $2\,(C\alpha)$

Where R = C_7H_{15} and $C_{11}H_{23}$ for caprylate and laurate, respectively.

The dissociation constant K_D can be expressed as,

$$K_D = \frac{4\,C^2\alpha^3}{(1-\alpha)} \text{ ------------------------------- (1)}$$

The following expression for their dissociation can be derived.

$$\mu^2C^2 = \frac{K_D\mu_0^3}{4\mu} - \frac{K_D\mu_0^2}{4} \text{ -------------------------- 2)}$$

The dissociation constant $k_{D\text{ and}}$ limiting molar conductance,μ_0 have obtained from the slope , $\frac{K_D\mu_0^3}{4\mu}$ and the intercept $\frac{K_D\mu_0^2}{4}$ of the linear plots μ^2C^2 Vs 1 / μ for dilute soap solution .

It is observed that an increase of temperature causes an increase of the limiting molar conductance at infinite dilution μ_0 and decrease of dissociation constant K_D . The decease of the value of dissociation constant with increasing temperature indicates the exothermic nature of the dissociation of gadolinium soaps in a mixture of 50/50 benzene –dimethyl formamide. The degree of dissociation,α at various soap concentration can be calculated by using it to be equal to the conductance ratio, μ/μ_0 .

The heat of dissociation, ΔH_D for gadolinium caprylate and laurate is determined by using following equation

$$\log K_D = -\frac{\Delta H_D}{2.303RT} + c \text{ ------------------------------- (3)}$$

The values of heat of dissociation, ΔHD were obtained from the slope of the linear plots of log K_D Vs 1/T (Fig 2)and mentioned in table 3 . The values of heat of dissociation, ΔH_D, are negative, which indicates that the dissociation process for gadolinium soaps is exothermic in nature .

The values of change in free energy, ΔG_D and entropy $T\Delta S_D$ per mole for the dissociation process are computed by using following relationship.

$$\Delta G_D = -RT \text{ in } K_D \text{ ---------------------------------- } (4)$$

$$T\Delta S = \Delta H_D - \Delta G_D \text{ ---------------------------------- } (5)$$

The calculated values of ΔG_D and $T\Delta S_D$ are recorded in table 4.

In case of micellization i.e. aggregation process , when counter –ions are bound to a micelle , the standard free energy change of micellization ,ΔG_M for phase separation mode [10-12] is given by

$$\Delta G_M = 2RT \text{ in } X_{CMC} \text{ -------------------------------- } (6)$$

Where X_{CMC} is the CMC expressed as a mole fraction and is defined as.

$$X_{CMC} = \frac{n_s}{n_s + n_0} = \frac{n_s}{n_0} \text{ ---------------------------------- } (7)$$

Since the number of moles of free soap n_s are small as compared to the number of moles of solvent ,n_0

The standard enthalpy change of micellization, ΔH_M per mole of monomer for phase separation model is evaluated as follows.

$$\text{In } X_{CMC} = \frac{\Delta H_M}{2RT} + c \text{ -------------------------------- } (8)$$

The values of ΔH_M have been determined from the slope of linear plots of In X_{CMC} Vs 1/T and mentioned in table 3. The positive enthalpy for micellization ,ΔH_M indicates that the association of gadolinium caprylate and laurate in 50/50 benzene – dimethyl formamide (V/V) is endothermic .

The standard entropy change for micellization is then calculated as

$$T\Delta S_M = \Delta H_M - \Delta G_M \text{ -------------------------------- } (9)$$

The calculated values of ΔG_M and $T\Delta S_M$ are recorded in table 3.

The micellization of the soap in a mixture of 50/50 benzene – dimethyl formamide is consistent with $\Delta H_M>0$, $\Delta G_M<0$, $T\Delta S_M>0$. However, dissociation of these soaps is consistent with $\Delta H_D<0$, $\Delta G_D>0$,$T\Delta S_D<0$.

4. CONCLUSION

The conductivity result show that gadolinium soaps in 50/50 benzene-dimethylformamide (V/V) mixture behave as weak electrolyte in dilute solution.

The value of CMC increase with increasing temperature In case of gadolinium caprylate and laurate the CMC values also increase with the rise in temperature [13].A careful scrutiny of the thermodynamic parameter indicate that micellization process is favoured over the dissociation process.

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APPENDIX – A

List Of Tables:

Table.1: Critical micellar concentration, CMC of Gadolinium caprylate and laurate in a mixture of 50/50 benzene-dimetylformamide V/V at various temperature.

Soap	CMC x 10^3 mol l^{-1}			
	303^0K	308^0K	313^0K	318^0K
Gadolinium caprylate	5.45	5.95	6.20	6.60
Gadolinium laurate	5.20	5.85	6.05	6.40

Table.2: Heat of dissociation, ΔH_D and heat of micellization ΔH_M of Gadolinium caprylate and laurate in a mixture of 50/50 benzene dimetylformamide V/V at various temperature.

Soap	$-\Delta H_D$ (KJ moI^{-1})	ΔH_M (KJ moI^{-1})
Gadolinium caprylate	22.66	33.55
Gadolinium laurate	23.05	38.34

Table 3: Thermodynamic parameter of dissociation and micellization of Gadolinium caprylate and laurate in a mixture of 50/50 benzene dimetylformamide V/V at various temperature.

T ^{0}K	Gadolinium caprylate				Gadolinium laurate			
	ΔG_D (KJ moI^{-1})	ΔG_M (KJ moI^{-1})	- $T\Delta S_D$ (KJ mol^{-1})	-$T\Delta S_M$ (KJ mol^{-1})	ΔG_D (KJ moI^{-1})	ΔG_M (KJ moI^{-1})	- $T\Delta S_D$ (KJ mol^{-1})	-$T\Delta S_M$ (KJ mol^{-1})
303^0K	33.22	27.25	55.88	60.80	33.50	27.20	56.55	65.54
308^0K	34.15	27.32	56.81	60.87	34.40	27.39	57.45	65.73
313^0K	35.08	27.41	57.74	60.96	35.32	27.57	58.37	65.91
318^0K	36.09	27.58	58.75	61.13	36.31	27.75	59.36	66.09

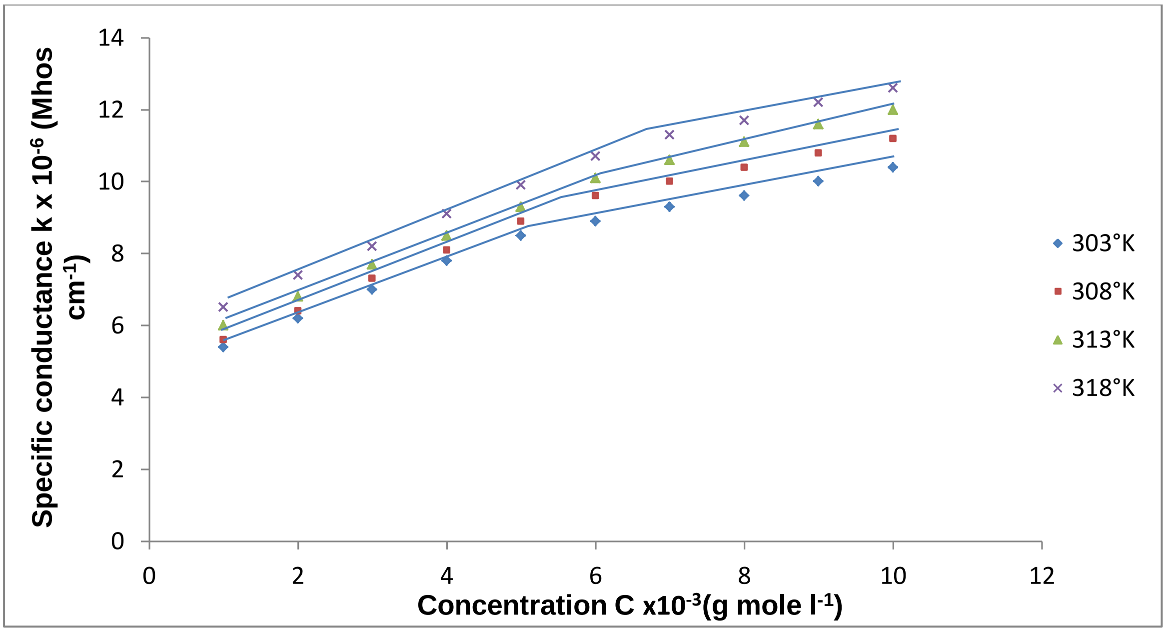

Figure.1: Specific conductance, k Versus soap Concentration, C plots of Gadolinium caprylate

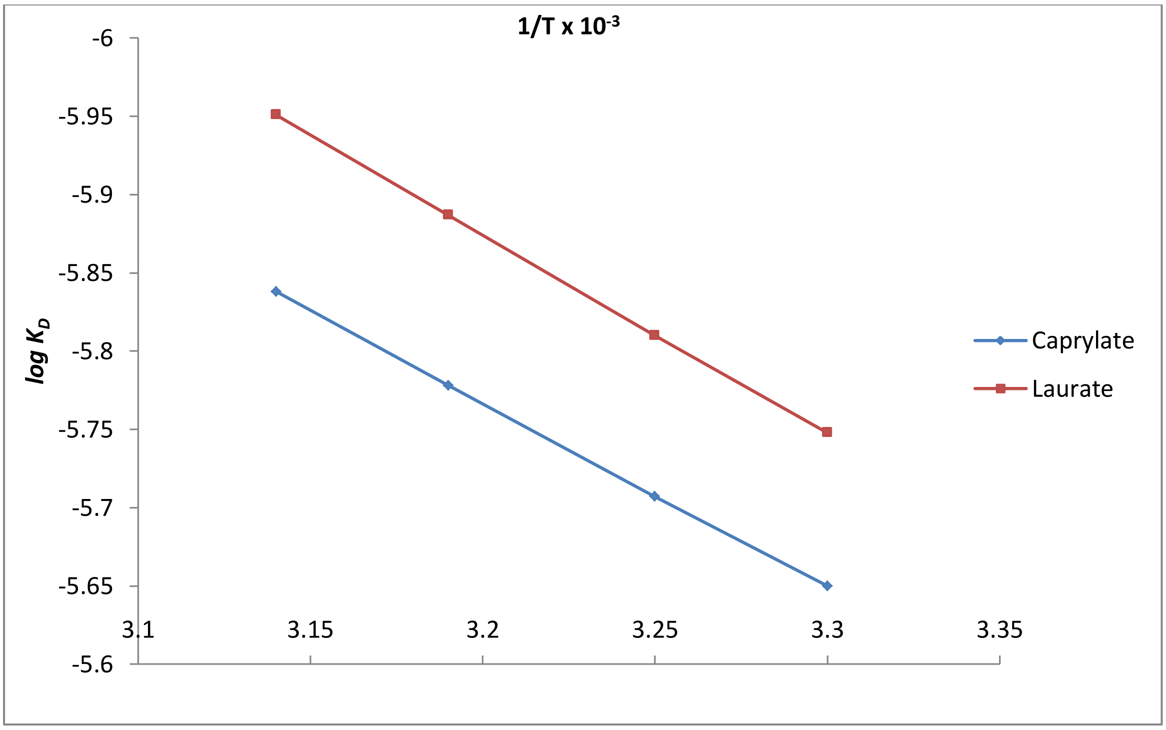

Figure.2: log K_D vs. 1/T for gadolinium caprylate and laurate