

Investigations into the Micellization and Conductance Behavior of Cerium Soaps in a Benzene–DMF Mixture

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SYNOPSIS

Conductivity measurements were employed to determine the critical micelle concentration (CMC), degree of dissociation and dissociation constant of dilute solutions of cerium soaps in 50% benzene and 50% *N-N*-dimethyl formamide (DMF) mixture (v/v). The results show that the soaps behave as weak electrolytes below the CMC. The various thermodynamic parameters were also evaluated for both dissociation and association process. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

In recent years metal soaps have been used in industries and various branches of technology: rubber, plastics, pharmaceuticals, detergency, soil sciences, lubrication, etc. The physicochemical properties of rare earth metal soaps in solutions have not been carried out systematically and few references^{1–15} are available in this field. The application of these metal soaps depends largely on their physical state, stability, and chemical reactivity together with volatility and solubility in common solvents. Keeping in view the manifold uses of metal soaps, a study on micellar behavior of cerium soaps was carried out.

The recent work was initiated to study the micellar behavior and to evaluate various thermodynamic parameters of cerium soaps in a benzene–DMF (dimethyl formamide) mixture at different temperatures.

EXPERIMENTAL

All chemicals used were of British drughouse/analytical reagent (BDH/AR) grade. Cerium soaps (caprate and laurate) were prepared and purified as described in an earlier study.^{16,17} The melting points of the purified soaps were 144°C for cerium caprate and 149°C for cerium laurate.

The solutions of cerium soaps were prepared by dissolving a requisite amount of soap in benzene–DMF mixture and were kept for 2 h in a thermostat at desired constant temperature. The soaps possess high solubility in a mixture but not in a pure solvent so measurements were made in a mixture of benzene and DMF.

A digital conductivity meter (Toshniwal CL 01.10A) and a dipping type conductivity cell with platinized electrodes (cell constant 0.895) were used for measuring the conductance of the solutions.

RESULTS AND DISCUSSION

The increase in specific conductance of the soap solutions with the increase in soap concentration and with increasing temperature (Fig. 1) may be due to the fact that cerium soaps (caprate and laurate) behave as simple electrolytes in dilute solutions, and are considerably ionized into a simple metal cation, Ce^{3+} and fatty acid anions, RCOO^- (where R is C_9H_{19} and $\text{C}_{11}\text{H}_{23}$ for caprate and laurate, respectively). The plots of specific conductance, vs. concentration are characterized by an intersection of two straight lines at a definite soap concentration (Fig. 1) that corresponds to the critical micelle concentration (CMC) of metal soaps. It is suggested that these soaps are considerably ionized in dilute solutions and the anions begin to aggregate to form ionic micelles at CMC. These micelles are in thermodynamic equilibrium with the metal ion, Ce^{3+} and

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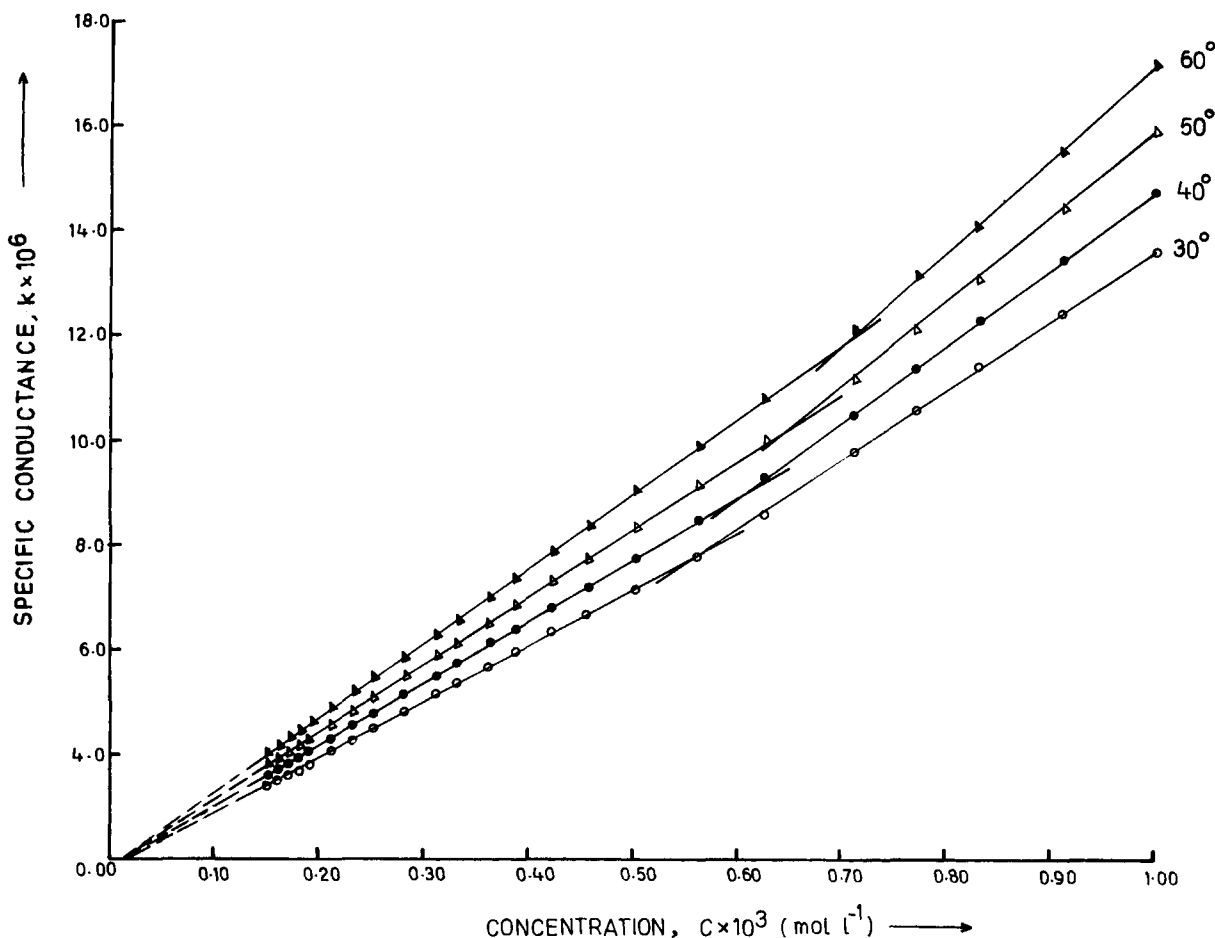
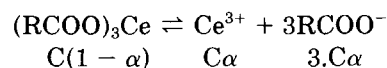


Figure 1 Specific conductance vs. concentration of cerium laurate.

the carboxylate ion, RCOO^- present in the solution. The increase in conductance above the CMC may be due to the production of ionic micelles or may be due to the liberation of some of the attached counterions from the micelles. The values of CMC increase with increasing temperature and decreasing chain length of fatty acid constituents of the soap (Table I).

The molar conductance of the solutions of cerium soaps decreases with increasing soap concentration. However, the CMC cannot be obtained from the plots of molar conductance vs. square root of con-

centration that are concave upward with increasing slope indicating that cerium soaps behave as weak electrolytes in dilute solutions. Therefore, the Debye-Huckel-Onsager equation is not applicable to these soap solutions. Because cerium soaps behave as weak electrolytes in dilute solutions the expression for the ionization may be developed in Ostwald's manner.



where C and α are the concentration and degree of dissociation of soap, respectively. The dissociation constant, K can be expressed as:

$$K = \frac{27C^3\alpha^4}{(1-\alpha)} \quad (1)$$

Because α is small, interionic effects may be treated as negligible. Assuming α as equal to the conductance ratio, μ/μ_0 and rearranging eq. (1):

Table I CMC Values of Cerium Soaps (gmol L^{-1})

Soap	CMC $\times 10^2$			
	30°	40°	50°	60°
Cerium caprate	6.70	7.10	7.60	8.10
Cerium laurate	5.60	6.00	6.50	7.00

Table II Values of Limiting Molar Conductance, μ_o , and Dissociation, K , at Different Temperatures

Soap	μ_o	30°	40°	50°	60°
		$K_D 10^{11} : \mu_o$	$K_D 10^{11} : \mu_o$	$K_D 10^{11} : \mu_o$	$K_D 10^{11} : \mu_o$
Cerium caprate	37.77	12.03 : 39.26	10.11 : 42.00	8.89 : 43.77	7.26
Cerium laurate	35.41	9.73 : 37.06	7.96 : 39.19	6.28 : 41.70	4.84

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

where μ and μ_o are the molar conductance at finite and at infinite dilution, respectively.

The values of K and μ_o were obtained from the slope, $(K\mu_o^4/27)$ and intercept $(-K\mu_o^3)/27$ of the linear parts of the plots of $\mu^3 C^3$ vs. $1/\mu$ for dilute soap solution and are recorded in Table II.

The values of degree of dissociation and dissociation constant decrease rapidly in dilute solutions but decrease slowly above the CMC with increasing soap concentration. The dissociation constant increases from cerium caprate to cerium laurate but it decreases with an increase of temperature. The decrease in the value of K with increasing temperature indicates the exothermic nature of cerium soaps in a benzene-DMF mixture.

The heat of dissociation, ΔH_D° , for cerium soaps

in benzene-DMF mixture were obtained from the slope of the linear plots of $\log K_D$ vs. $1/T$ (Fig. 2) and are recorded in Table III. The dissociation of the metal soaps was found to be exothermic. However, the heat of dissociation decreases from cerium caprate to cerium laurate with the increase in chain length of the soap. The standard free energy change ($\Delta F_D^\circ = -RT \ln K$, where K is the equilibrium constant) and standard entropy change ($T\Delta S_D^\circ = \Delta H_D^\circ - \Delta F_D^\circ$) were evaluated for the dissociation process (Table IV).

For the micellization process, when counterions are bound to micelles, the standard free energy of micellization per mole of monomer, ΔF_A° (Table V), for the phase separation model¹⁸⁻²⁰ is given by the relationship:

$$\Delta F_A = 2RT \ln X_{cmc}$$

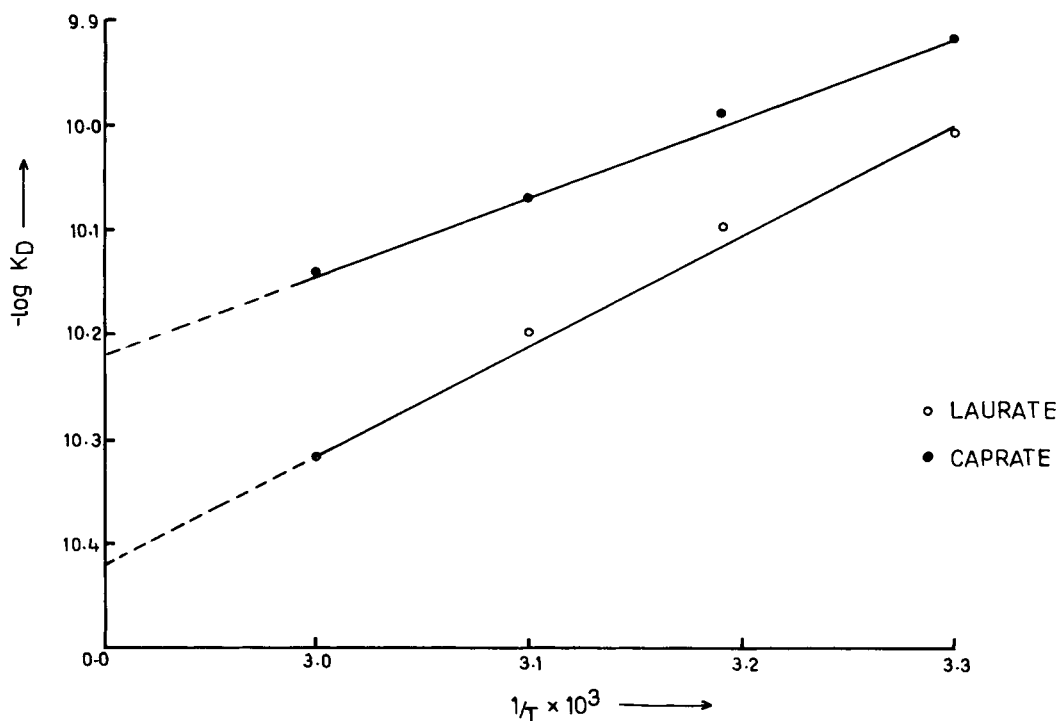

Figure 2 $\log K_D$ vs. $1/T$ plots for cerium soaps in benzene-DMF mixture.

Table III Heat of Dissociation, ΔH_D° , and Heat of Association, ΔH_A° , of Cerium Soaps

Soap	$-\Delta H_D^\circ$ (kJ mol ⁻¹)	ΔH_A° (kJ mol ⁻¹)
Cerium caprate	0.80	2.48
Cerium laurate	1.06	2.84

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

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

As the number of moles of free surfactant, n_s is small as compared to the number of moles of solvent, n_o , then

$$X_{cmc} = \frac{n_s}{n_o}$$

The standard enthalpy change of micellization per mole of monomer, ΔH_A° , for the phase separation model¹⁸⁻²⁰ is given by the relationship:

$$\frac{\partial(\ln X_{cmc})}{\partial T} = \frac{-\Delta H_A^\circ}{2RT^2}$$

$$\ln X_{cmc} = \frac{\Delta H_A^\circ}{2RT} + C.$$

The values of ΔH_A° were obtained from the slope of the linear plots of the $\ln X_{cmc}$ vs. $1/T$ (Fig. 3) and are recorded in Table III. The positive values of ΔH_A° indicate that the association of cerium soaps in 50% benzene and 50% DMF (v/v) is endothermic. The standard entropy change per mole of monomer (Table V) is calculated as: $T\Delta S_A^\circ = \Delta H_A^\circ - \Delta F_A^\circ$. The negative enthalpy change of dissociation (Table III) tends to make up for the unfavorable change in free energy and entropy of the dissociation process (Table IV). On the other hand, the negative free energy and positive entropy (Table V) favor micellization and compensate for the unfavorable enthalpy change for the process (Table III). The results show that the association process is dominant over the dissociation process.

It is therefore concluded that the thermodynamics of dissociation and association can be satisfactorily explained in the light of the phase separation model by conductivity measurements. The results showed that dissociation of cerium soaps was found to be

Table IV Free Energy of Dissociation, F_D° , and Entropy of Dissociation, S_D° , of Cerium Soaps at Different Temperatures

Temperature (°C)	Cerium Caprate		Cerium Laurate	
	ΔF_D° (kJ mol ⁻¹)	$-T\Delta S_D^\circ$ (kJ mol ⁻¹)	ΔF_D° (kJ mol ⁻¹)	$-T\Delta S_D^\circ$ (kJ mol ⁻¹)
30	13.75	12.95	13.88	12.82
40	14.32	13.52	14.46	13.40
50	14.88	14.08	15.08	14.02
60	15.45	14.65	15.72	14.66

Table V Values of Free Energy of Association, F_A° , and Entropy of Association, S_A° , of Cerium Soaps at Different Temperatures

Temperature (°C)	Cerium Caprate		Cerium Laurate	
	$-\Delta F_A^\circ$ (kJ mol ⁻¹)	$T\Delta S_A^\circ$ (kJ mol ⁻¹)	$-\Delta F_A^\circ$ (kJ mol ⁻¹)	$T\Delta S_A^\circ$ (kJ mol ⁻¹)
30	6.25	8.73	6.47	9.31
40	6.34	8.87	6.60	9.44
50	6.50	8.98	6.71	9.55
60	6.62	9.10	6.82	9.66

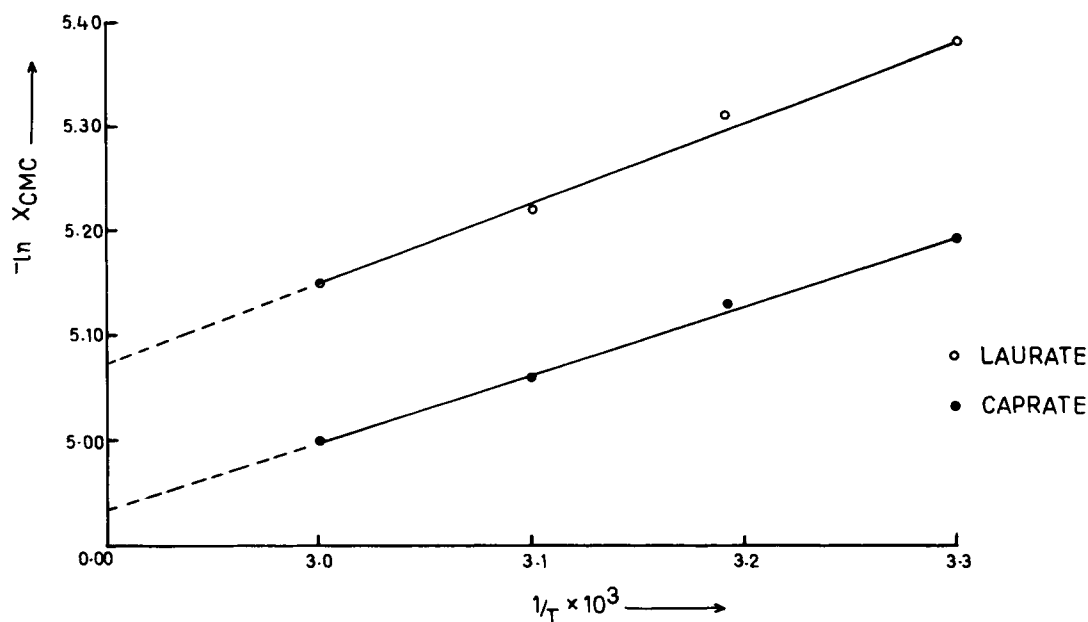


Figure 3 $\ln X_{cmc}$ vs. $1/T$ plots for cerium soaps in benzene-DMF mixture.

exothermic while the association process was endothermic in nature.

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REFERENCES

- J. H. Skellon and K. E. Andrews, *J. Appl. Chem. (London)*, **5**, 245 (1955).
- H. W. Chatfield, *Paint Manufacturing*, **6**, 112 (1936).
- F. Mains, D. Mills, and D. W. White, U.S. Pat. 3,320,172 (May 16, 1967).
- S. N. Misra, T. N. Misra, and R. C. Mehrotra, *J. Inorg. Nucl. Chem.*, **25**, 195 (1963).
- K. N. Mehrotra, A. S. Gahlaut, and M. Sharma, *J. Am. Oil Chemist's Soc.*, **63**, 1571 (1986).
- K. N. Mehrotra, M. Sharma, and A. S. Gahlaut, *J. Indian Chem. Soc.*, **64**, 331 (1987).
- A. M. Bhandari, S. Dubey, and R. N. Kapoor, *J. Am. Oil Chemist's Soc.*, **4**(47), 115 (1970).
- W. Brzyska and W. Hubicki, *Ann. Univ. Mariae Curie Sklodowska, Sect. A.A. Pub.*, **24/25**(9), 63 (1970).
- R. P. Varma and R. Jindal, *Tenside Detergents*, **20**(4), 193 (1983).
- M. Singh and S. N. Misra, *Synth. React. Inorg. Methods Org. Chem.*, **8**, 389 (1978).
- K. N. Mehrotra, A. S. Gahlaut, and M. Sharma, *J. Colloid Interface Sci.*, **120**, 110 (1987).
- K. N. Mehrotra and S. K. Upadhyaya, *J. Chem. Eng. Data*, **33**, 465 (1988).
- G. Marwedel, *Farbe, U. Lack*, **60**, 530 (1954); **62**, 92 (1956).
- W. Casellato, P. A. Vigato, and M. Vidali, *Coord. Chem. Rev.*, **26**, 85 (1978).
- K. W. Bagnall, *Int. Rev. Sci.; Inorg. Chem. Ser., Z.*, **7**, 41 (1975).
- K. N. Mehrotra, M. Chauhan, and R. K. Shukla, *J. Phys. Chem. Liquids*, **18**, 295 (1988).
- K. N. Mehrotra, R. K. Shukla, and M. Chauhan, *Acoustic Lett.*, **12**(4), 66 (1988).
- B. W. Barry and G. F. J. Russel, *J. Colloid Interface Sci.*, **40**, 174 (1972).
- D. C. Robins and I. L. Thomas, *J. Colloid Interface Sci.*, **26**, 407 (1968).
- D. Attwood and A. T. Florence, *Surfactant Systems*, Chapman and Hall, London, 1983, p. 100.

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