

Conductometric Investigations on Cerium Soaps in Mixed Organic Solvents

Abstract

The critical micellar concentration (CMC) of Cerium soaps in a mixture of benzene methanol were determined by using conductometric measurements. The molar conductance at infinite dilution, degree of ionization and ionization constant have been evaluated. The result show that Cerium soaps behave as simple electrolytes in dilute solution and CMC was found to decrease with increasing chain length of the fatty acid constituent of the soap.

Keyword: Cerium Soaps, Specific Conductance, Molar Conductance, Degree of Ionization Critical Micellar Concentration.

Introduction

In recent past, metal soap has been a subject of intense investigation on account of its role in such diversified field as an emulsifiers, plasticizers, stabilizers, softeners catalysts, antioxidants, lubricants, germicides, medicines, preservatives. Cosmetics, thickeners, insecticides, water proofing and wetting agents. The physico chemical characteristics and structure of metal soaps can be controlled up to an extent by the methods and conditions of their preparations and so detailed studies of metal soaps are of great importance for their uses in various industries under different conditions.

Several workers¹⁻⁴ prepared the heavy metal soaps by double decomposition, metathesis, and fusion or by direct reaction of metal oxide with an organic acid. Mehrotra et al⁵ reported the IR-spectra and X-ray diffraction pattern and magnetic moment of some Lanthanide soaps and also suggested a probable mechanism for thermal decomposition of these metal soaps. Da-Guang et al.⁶ determined the structure of neodymium soaps by IR-spectra and X-ray diffraction pattern. Casellato et al.⁷ correlated The available structural information of actinide soaps with their spectral and thermal characteristics. The Solubility of Different lanthanide soaps was determined by brzyska and Hubicki⁸. Kapoor et al.⁹ measured the viscosity and conductivity of the uranyl soaps. Shukla et al.¹⁰ investigated various physico-chemical properties of Dysprosium soaps in solid state as well as in solutions. Mehrotra et al.¹¹ carried out the conductometric, viscometric and ultrasonic studies on soaps of Ce, Sm, and Nd in pure and mixed organic solvents and determined the micellar and acoustic behavior of these soap solution. Now a days metal soaps are being used¹²⁻¹⁴ as eco-friendly thermal stabilizer in PVC products, as lubricant in medicines and for making soft and water proofing leather.

The present work has been initiated with a view to determine the CMC, molar conductance, degree of ionization and ionization constant of cerium soaps (laurate and myristate) in a mixture of benzene and methanol.

Experimental

All chemicals used were of BDH/AR grade. Solvents Benzene and Methanol were purified by distillation under reduced pressure. Cerium soaps (laurate and myristate) were synthesized by direct metathesis Of corresponding their potassium soap with slight excess of the solution of cerium acetate at 50-55°C under vigorous stirring. The precipitated soaps were washed several times with water and then acetone. The metal soaps thus obtained were first dried in an air oven at 50-60°C and final drying of the soaps was carried out under reduced pressure. The soaps were purified by recrystallization with Benzene – Methanol mixture. The purity was checked by their melting points (Cerium laurate-175°C, cerium myristate-180°C and absence of hydroxylic group was confirmed by IR spectra. The reproducibility of the result was checked by preparing two samples of the same soaps under similar conditions.



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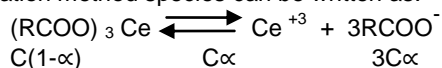
The solutions of soaps were prepared by dissolving a known amount of soap in a 70%benzene 30% methanol mixture (v/v) and were kept for 2 hr in a thermostat at a constant temperature of 40 ± 0.05 °C. The soap do not possess high solubility in pure solvents thus measurements were conducted in benzene – methanol mixture. 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 soap solutions at 40 ± 0.05 °C.

Results and Discussion

Cerium Soaps

The specific conductance, k of the dilute solutions of Cerium soaps (laurate and myristate) in a mixture of Benzene and Methanol (7:3v/v) increases with increasing soap concentration, C (g mol l^{-1}) and decreasing chain length of fatty acid constituent of soap.(Table:I&II).The increase in the specific conductance with the increase in soap concentration may be due to the ionization of Cerium soap into simple metal cations, Ce^{3+} and fatty acids anions, RCOO^- (where R is $\text{C}_{11}\text{H}_{23}$ and $\text{C}_{13}\text{H}_{27}$ for laurate and myristate respectively) in dilute solutions due to the formation of micelles at higher soap concentrations. The decrease in specific conductance with increasing chain length of soap may be due to the increasing size and decreasing mobility of anions with increasing chain length of the soap. The plots of specific conductance, k , vs Soap concentrations, C (fig) are characterized by intersection of two straight lines at definite soap concentration which corresponds to the CMC of soaps. The CMC is defined as the concentrations of the soap in the bulk at which micelles starts forming and above which micelles are spontaneously formed .It is suggested that the soap is considerably ionized in dilute solutions and the anions begin to aggregate to form micelles. The results show that the values of CMC decreases with increasing chain length of fatty acids constituent of soap molecule Table (III).

The molar conductance, μ of the solutions of cerium soap decreases with increasing soap concentration as well as increases with chain length of fatty acid constituent of soap. The decreases in molar conductance may be due to combined effects of ionic atmosphere, salvation of ions, decrease of mobility and ionization and formation of micelles. The plots of molar conductance, μ vs. Square root of soap concentration, $C^{1/2}$ are concave upward with increasing slopes, which indicates that these soap behave as simple electrolyte. The Debye-Huckel – Onsager's equation is not applicable to these soap solutions and the limiting molar conductance, μ_0 cannot be determined by usual extrapolation method species can be written as:



Where R is $\text{C}_{11}\text{H}_{23}$ and $\text{C}_{13}\text{H}_{27}$ for laurate and myristate respectively.

The ionization constant, K can be expressed as:

$$K = \frac{[\text{Ce}^{3+}][\text{RCOO}^-]^3}{\text{Ce}[\text{RCOO}^-]_3} = \frac{C\alpha(3C\alpha)^3}{C(1-\alpha)} = \frac{27C^3\alpha^4}{(1-\alpha)} \dots\dots(1)$$

Since the ionic concentration are low and interionic effects are almost negligible in dilute solutions , the

Solutions of soaps will not deviate appreciably from Ideal behavior and so the activities of ions can be taken as almost equal to the concentrations. The degree of ionization, α may be. May be replaced by the conductance ratio, μ/μ_0 is the molar conductance at finite concentration and μ_0 is the limiting molar conductance at infinite dilution. On substituting the value of α and rearranging, equation (1) can be written as:

$$\mu^3 C^6 = \frac{K \mu_0^4}{27 \mu} - \frac{K \mu_0^3}{27} \dots\dots(2)$$

The value of the ionization constant, K and limiting molar conductance, μ_0 have been obtained from the slope, $(K \mu_0^4/27)$ and intercept, $(-K \mu_0^3/27)$ of the linear plots of $\mu^3 C^3$ vs. $1/\mu$ below the CMC and are recorded (Table: III). The results show that the values of limiting molar conductance increase while of ionization constant decreases with increasing chain length of the soap. The value of the degree of ionization α at different soap concentrations have been evaluated by assuming it as equal to the conductance ratio μ/μ_0 . The plots of degree of ionization vs soap concentration show that the degree of ionization decreases rapidly in dilute solutions with the increase in soap concentration. The value of K calculated by using equation(1)and assuming the degree of ionization as equal to the conductance ratio are presented in Table: 1(I&II). The values show that K decreases with increasing chain length of the soap. The values of K show approximately constancy in dilute solutions but exhibit a drift with increasing soap concentrations which shows that the soap does not behaves as a very weak electrolyte. The drift in the values of ionization constant with increasing soap concentration may be partly due to the fact that Degree ionization is not exactly equal to the conductance ratio, μ/μ_0 and mainly due to the fact that the activities coefficient of ions are not equal to unity. The deviations at higher soap concentration may also be due to the failure of simple Debye-Huckel activity equation.

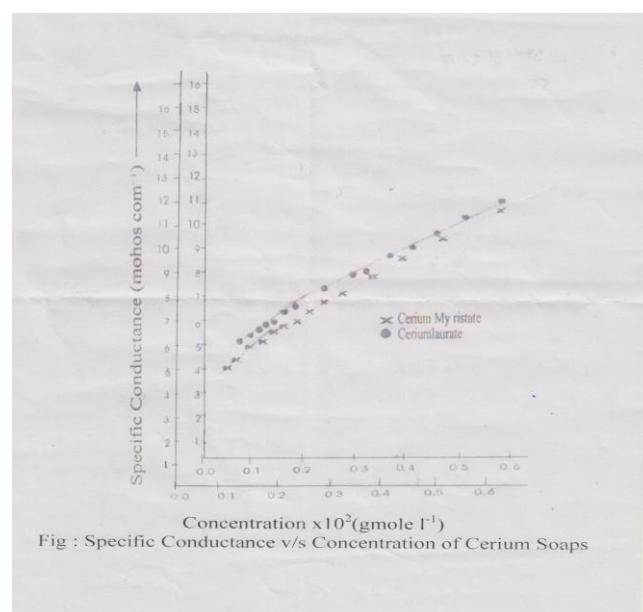


Fig : Specific Conductance v/s Concentration of Cerium Soaps

Table- I
Conductance of Cerium Laurate Soaps in 70% Benzene and 30% Methanol at 40 ± 0.05°C

S. No.	Concentration C(g mole l ⁻¹)	Specific conductance K	Molecule conductance $\mu \times 10^6$	Degree of association α	Dissociation constant $K \times 10^{10}$
1.	0.0010	5.36	5.360000	0.299	2.9
2.	0.0011	5.40	4.9090906	0.274	2.7
3.	0.0012	5.54	4.6166667	0.258	2.7
4.	0.0013	5.70	4.3846154	0.245	2.7
5.	0.0014	5.88	4.200000	0.234	2.7
6.	0.0015	6.08	4.053333	0.226	2.9
7.	0.0016	6.28	2.6941176	0.206	2.4
8.	0.0017	6.60	3.6666667	0.204	2.8
9.	0.0016	6.84	3.4200000	0.191	2.5
10.	0.0020	7.20	3.2727277	0.182	2.8
11.	0.0022	7.51	3.0040000	0.167	2.6
12.	0.0025	7.85	2.8035714	0.156	2.9
13.	0.0028	8.42	2.8066667	0.156	3.9
14.	0.0030	9.00	2.5000000	0.139	3.1
15.	0.0033	9.70	2.204545	0.123	2.3
16.	0.003 b	10.65	2.1734694	0.121	3.0

Table - II
Conductance of Cerium Myrestate in 70% Benzene and 30% Methanol at 40 ± 0.05°C

S. No.	Concentration C(g mole l ⁻¹)	Specific conductance K	Molecule conductance $\mu \times 10^6$	Degree of association α	Dissociation constant $K \times 10^{10}$
1.	0.0010	5.02	5.020000	0.280	2.3
2.	0.0011	5.16	4.6909091	0.262	2.2
3.	0.0012	5.28	4.400000	0.246	2.1
4.	0.0013	5.37	4.1307692	0.231	2.0
5.	0.0014	5.57	3.9785714	0.272	2.2
6.	0.0018	5.79	3.8600000	0.215	2.3
7.	0.0017	6.04	3.5829412	0.198	2.5
8.	0.0018	6.36	3.5333333	0.197	2.9
9.	0.0020	6.52	3.260000	0.182	2.6
10.	0.0022	6.85	3.1136364	0.174	3.1
11.	0.0025	7.23	2.8920000	0.161	3.3
12.	0.0028	7.60	2.7142857	0.151	3.4
13.	0.0032	8.36	2.6128000	0.146	4.5
14.	0.0038	9.05	2.200000	0.123	3.8
15.	0.0044	9.96	2.0563182	0.144	4.3
16.	0.0052	10.08	1.9153845	0.107	5.5
17.	0.0056	11.62	2.07500	0.116	9.4

Table - III
Value of CMC, Limiting Molar Conductance, and Ionization, μ_0 Constant, K of Cerium Soap.

Name of soap	CMC $\times 10^2$ (gmol l ⁻¹)	μ_0	K
Cerium Laurate	00.26	10.35	7.2010 ⁻³
Cerium Myristate	00.16	12.55	5.8710 ⁻³

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