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# Conductometric Investigations on Cerium and Thorium Soaps

**Abstract**

The critical micellar concentration (Cmc) of Cerium and Thorium 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 and Thorium 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.

**Keywords:** Cerium and Thorium Soaps, specific conductance, molar conductance, degree of ionization critical micellar concentration).

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## 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, thickners, insecticides,water proofing and wetting agents. The physico chemical charecteristics 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 workers [1-4] prepared the heavy metal soaps by double decomposition, metathesis, and fusion or by direct reaction of metal oxide with an organic acid. Mehrotra et al[5] 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 Hubicki[8] . 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 coductometric, viscometric and ultra sonic 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 used[12-14] 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 inonization constant of cerium and thorium soaps (laurate and myristate) in a mixture of benzene and methanol.

## Experimental

All chemicals used were of Bdh/Ar grade. Solvents Benzne and Methanol were purified by distillation under reduced pressure.Cerium and Thorium soaps (laurate and myristate) were synthesized by direct metathesis Of corresponding their potassium soap with slight excess of the solution of cerium and thorium acetate at 50-55$^oC$ 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$^oC$ 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$^oC$, cerium myristate-180$^oC$ thorium laurate-250$^o$ and Thourium myristate-270$^oC$) 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.

in a thermostat at a constant temperature of 40±0.05 $^0$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 $^0$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 (5:5v/v) increases with increasing soap concentration, C (g mol $l^{-1}$) and decreasing chain length of fatty acid constituent of soap.(Table:1a&b).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 $C_{11}H_{23}$and $C_{13}H_{27}$ 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 deceasing 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 from micelles. The results show that the values of Cmc decreases with increasing chain length of fatty acids constituent of soap molecule Table (II)

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 slops, 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, $\mu_0$ cannot be determined by usual extrapolation method species can be written

$$(RCOO)_3 Ce \Leftrightarrow Ce^{+3} + 3RCOO^-$$

$$C(1-\alpha) \qquad C\alpha \qquad 3C\alpha$$

Where R is $C_{11}H_{23}$ and $C_{13}H_{27}$ for laurate and myristate respectively.

The ionization constant, K can be expressed as

The solutions of soaps were prepared by dissolving a known amount of soap in a 50%benzene 50% methanol mixture (v/v) and were kept for 2 hr

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

Since the ionic concentration are low and interionic effects are almost negligible in dilute solutions , the Solutions of soaps will note 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,$\mu/\mu_0$ is the molar conductance at finite concentration and $\mu_0$ is the limiting molar conductance at infinite dilution. On substituting the value of α and rearranging, equation (1) can be written as:

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

The value of the ionization constant, K and limiting molar conductance, $\mu_0$ have been obtained from the slope, (K $\mu_0^4$/27) and intercept, (-K $\mu_0^3$/27) of the linear plots of$\mu^3C^3$vs.1/μ below the CMC and are recorded (Table:II) . 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 $\mu/\mu_0$. 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(a&b).

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 iqual to the conductance ratio, $\mu/\mu_0$ 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.

**Thorium soaps**

The specific conductance, K of the dilute solutions of Thorium soaps (laurate,myristate ) in a mixture of Benzene and Methanol (5:5v/v) increases with increasing soap concentration C (g mol $l^{-1}$) and decreasing chain length of fatty acid constituent of soap.(Table:Ia&b). The increase in the specific conductance with the increase in soap concentration may be due to the ionization of Thorium soaps into simple metal Cations, $Th^{4+}$ and fatty acid anions, $Rcoo^-$ (where R is $C_{11}H_{23}$ and $C_{13}H_{27}$ for laurate and myristate respectively) in dilute solution 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 deceasing mobility of anions with increasing chain length of the soap. The plots of specific conductance, k vs. shop concentration,C(fig) are characterized by intersection of two straight lines at definite soap concentration which corresponds to the Cmc of the soaps.

The molar conductance, μ of the solutions of thorium Soaps decreases with increasing soap concentration as well as increases with chain length of fatty acid constituent of soap. The decrease in molar conductance maybe due to the combined effects of ionic atmosphere, salvation of ions, decrease of mobility and ionization and formation of micelles. The value of limiting molar conductance, $\mu_0$ may be determined by developing an expression for ionization of the thorium soaps in Ostwald's manner .

$(RCOO)_4$ Th $\Leftrightarrow$ $Th^{+4}$ 4RCOO $^{-1}$
C(1-α) Cα 4Cα

Where R is $C_{11}H_{23}$ and $C_{13}H_{27}$ for laurate and myristate respectively.
The ionization constant, K can be expressed as

$$K = \frac{[Th^{4+}][RCOO^-]^4}{Th[RCOO^-]_4} = \frac{C\alpha(4C\alpha)^4}{C(1-\alpha)} = \frac{256C^4\alpha^5}{(1-\alpha)} \text{..........(3)}$$

Since the degree of ionization for dilute solutions of orium soaps is small, the degree of ionization α may be taken as equal to the conductance ratio $\mu/\mu_0$ On substituting the value of α and rearranging equations(3)

$$\mu^4C^4 = \frac{K\mu_0^5}{256\mu} - \frac{K\mu_0^5}{256} \text{........(4)}$$

The values of Cmc obtained from the plots $\mu^4C^4$ vs. 1/μ are in close agreement with the value obtained from the plots of specific conductance k vs. soap concentration C. The ionization constant, k and limiting molar conductance, $\mu_0$ have been obtain obtained from the slope,

($k\mu_0^5/256$) and intercept, ($-k\ \mu_0^4/256$) of the linear plots of $\mu^4C^4$ vs. 1/μ below the Cmc. The result show that the value of limiting molar conductance increase while of ionization constant decreases with increasing chain length of the soap.

The variation of the degree of ionization α of dilute solution of thorium soaps is similar to that exhibited by cerium soaps. The values of ionization constant, k are record in table, the values of ionization constant increases slowly with the increase in the soap concentration below the Cmc but increase rapidly above the Cmc. It is also found that Thorium soaps have high spicific conductance them cerium soaps. the conductivity. results confirm that Cerium and thorium soaps behaves as weak electrolytes in dilute solutions and the dibye-Huckel-on sagars equation is not applicable to these soap solutions.

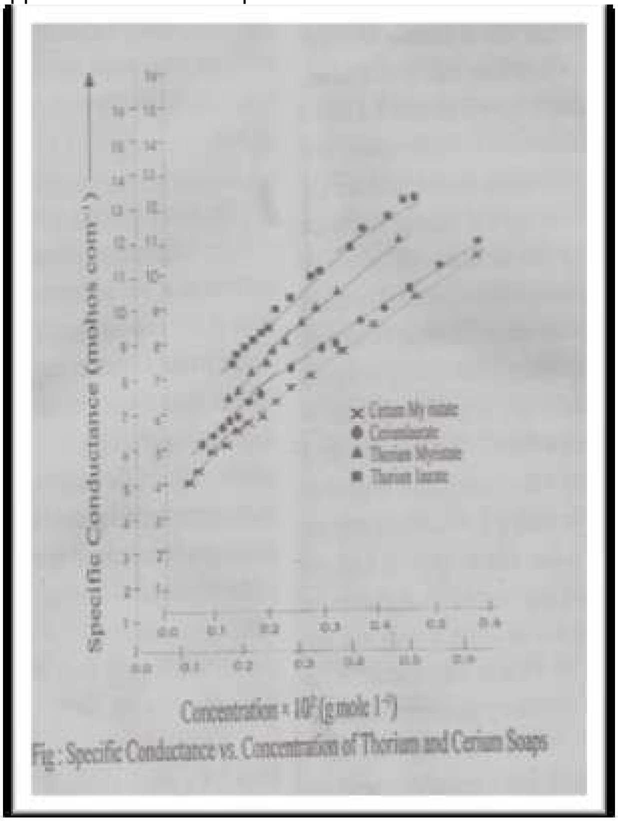


Fig : Specific Conductance vs. Concentration of Thorium and Cerium Soaps

**Table – 1a** Conductivity of Thorium Lourate in 50% benzene and 50% methanol at 40 ± 0.05°C

| S. No | Concentration C(g mole $l^{-1}$) | Specific conductance K | Molecule conductance μ × $10^6$ | Degree of association | Dissociation constant K × $10^{12}$ |
|---|---|---|---|---|---|
| 1. | 0.0012 | 9.49 | 7.908 | 0.391 | 7.7 |
| 2. | 0.0013 | 9.63 | 7.407 | 0.366 | 7.9 |
| 3. | 0.0014 | 9.88 | 7.057 | 0.349 | 8.1 |
| 4. | 0.0015 | 10.01 | 6.673 | 0.330 | 7.5 |
| 5. | 0.0016 | 10.22 | 6.387 | 0.315 | 6.9 |
| 6. | 0.0017 | 10.48 | 6.164 | 0.304 | 7.6 |
| 7. | 0.0018 | 10.62 | 5.899 | 0.291 | 7.5 |
| 8. | 0.0019 | 10.80 | 5.684 | 0.281 | 8.1 |
| 9. | 0.0020 | IO.99 | 5.495 | 0.271 | 8.2 |
| 10. | 0.0022 | 11.39 | 5.177 | 0.256 | 8.7 |
| I1. | 0.0024 | 11.84 | 4.933 | 0.243 | 9.5 |
| 12. | 0.0026 | 12.23 | 4.703 | 0.232 | 10.1 |
| 13. | 0.0028 | 12.58 | 4.492 | 0.222 | 10.8 |
| 14. | 0.0033 | 13.38 | 4.054 | 0.200 | 12.1 |
| 15. | 0.0036 | 13.81 | 3.836 | 0.189 | 12.7 |

| | | | | | |
|---|---|---|---|---|---|
| 16. | 0.0040 | 14.33 | 3.582 | 0.177 | 13.8 |

**Table – 1b.** Conductivity of cerium myrestate in 50% benzene and 50% methanol at 40 $\pm$ 0.05°C

| S. No. | Concentration C(g mole $l^{-1}$) | Specific conductance K | Molecule conductance $\mu \times 10^6$ | Degree of association | Dissociation constant $K \times 10^{10}$ |
|---|---|---|---|---|---|
| 1. | 0.0010 | 7.16 | 7.160000 | 0 .4001 | 1.1 |
| 2. | 0.0011 | 7.35 | 6.6818182 | 0.373 | 1.0 |
| 1 | 0.0012 | 7.56 | 6.30000 | 0.352 | 1.0 |
| 4. | 0.0013 | 7.84 | 6.0607692 | 0.337 | 1.1 |
| 5. | 0.0014 | 8.18 | 5.8428571 | 0.326 | 1.2 |
| 6. | 0.0015 | 8.66 | 5.7733333 | 0.323 | 1.4 |
| 7. | 0.0017 | 8.80 | 5.1764705 | 0.289 | 1.2 |
| 8. | 0.00 16 | 9.20 | 5.1111111 | 0.285 | 1.2 |
| 9. | 0.0020 | 9.66 | 4.830000 | 0.270 | 1.6 |
| 10. | 0.0022 | 9.87 | 4.48636 | 0.270 | 2.0 |
| 11. | 0.0025 | 10.16 | 4.064000 | 0.251 | 2.2 |
| 12. | 0.0028 | 10.66 | 2.807429 | 0.227 | 1.9 |
| 13. | 0.0032 | 11.45 | 3.578125 | 0.212 | 2.2 |
| 14. | 0.0038 | 12.24 | 3.2210526 | 0.199 | 2.8 |
| 15. | 0.0044 | 13.06 | 2.9681818 | 0.180 | 2.9 |
| 16. | 0.0052 | 14.14 | 2.7192308 | 0.166 | 3.3 |
| 17. | 0.0056 | --- | --- | 0.152 | 2.8 |

**Table – 2 Value of Cmc, limiting molar conductance, and ionization, $\mu_0$ constant, k of cerium and thorium Soaps**

| Name of soap | CMC10$^2$ (gmol $l^{-1}$) | $\mu_0$ | K |
|---|---|---|---|
| Cerium Laurate | 00.26 | 10.35 | 7.2010$^{-3}$ |
| Cerium Myristate | 00.16 | 12.55 | 5.8710$^{-3}$ |
| Thorium Laurate | 00.34 | 12.87 | 5.8410$^{-3}$ |
| Thorium Myristate | 00.20 | 11.08 | 3.3410$^{-3}$ |

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