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Micellization and Conductometric Studies on Lithium Soaps in Aqueous Medium

Yadvendra Sharma

F.E.T. Agra College, Agra, **INDIA**

Email: yadvendra.fet@gmail.com

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ABSTRACT

The critical micelle concentration (CMC) of Lithium soaps (Laurate and Myristate) have been determined by using condctometric measurements. The molar conductance at infinite dissociation constant has been evaluated. The results show that Lithium soaps (Laurate and Myristate) behave as a weak electrolyte in dilute solutions and CMC has been found to decrease with increasing chain length of the fatty acid constituent of the soap.

Keywords: Lithium soaps, CMC and conductivity.

INTRODUCTION

Metal soaps have been a subject of intense investigation on account of its role in diverse fields. The importance of metallic soaps in academic and technological fields is on account of their unique characteristics due to the presence of lyphobic and luphobhilic moieties in the same molecule. The physico – chemical characteristics and the structure of metallic soaps depend largely on the method and conditions of preparations, properties and uses of metal saps were investigated by several workers [1 - 6].

Ogino et.al [7] studied the use of metal soaps as binding material. Several workers [8 - 10] investigated the uses of metal soaps as cosmetic gel polymer and coating pigment in paper industry.

In the present manuscript the work has been initiated with a view to determine the CMC (Critical Micelle Concentration), molar conductance, degree of dissociation and dissociation constant of Lithium Soaps.

MATERIALS AND METHODS

All chemical used were AR/GR (E – Merck) grade. Lithium soaps (Laurate and Myristate) have been prepared by direct metathesis of corresponding potassium soaps with the required amount of aqueous solution of lithium hydroxide at 50^{o}C – 55^{o}C under vigorous stirring. The precipitated soaps were washed with water and acetone to remove the excess of metal ions and unreached fatty acid. The purity of the soaps was checked by the M.P., elemental analysis and by their IR spectrum.

The solutions of Lithium Soaps have been prepared by dissolving acquired amount of soap in water. The conductance was measured by Toshniwal Digital Conductivity Meter, Type CL 01,10A using dipping Type Conductivity cell with Platonized electrode.

RESULTS AND DISCUSSION

The specific conductance, k of the solutions of Lithium Soaps (Laurate and Myristate) in water increases with increasing soap concentration and decreasing chain length of the fatty acid constituent of the soap molecule (Table 1 and 2). The increase in the specific conductance may be due to the ionization of Lithium Soaps into Lithium Cation Li^+ and fatty acid anions, $RCOO^-$ (where R is $C_{11}H_{23}$ and $C_{13}H_{27}$ for Laurate and Myristate) and due to the formation of micelle at higher soap concentrations. The plots of specific conductance vs. soap concentration are characterized by an intersection of two straight lines at definite soap concentration which corresponds to the CMC. The results show that the CMC (Critical Micelle Concentration) decreases with increasing chain length of the soap molecule (Fig. 1).

Table 1. Conductivity Measurement of Lithium Laurate in water at 40 ± 0.05^oC

S. No.	Concentration $C * 10^3$ (mol l^{-1})	Specific Conductance $K*10^6$ (mhos em^{-1})	Molar Conductance μ (mhos cm^2 mol^{-1})	Degree of Dissociation α	Dissociation Constant -log K
1	20.0	11.0	0.5500	0.5000	1.0000
2	18.1	10.5	0.5801	0.5274	1.0274
3	16.6	10.0	0.6024	0.5476	1.0416
4	15.3	9.7	0.6340	0.5764	1.0791
5	14.2	9.4	0.6620	0.6018	1.1111
6	13.3	9.2	0.6917	0.6288	1.1514
7	12.5	9.0	0.7200	0.6545	1.1904
8	11.7	8.6	0.7350	0.6682	1.1972
9	11.1	8.3	0.7477	0.6798	1.2046
10	10.5	8.0	0.7619	0.6926	1.2146
11	10.0	7.9	0.7900	0.7182	1.2625
12	9.5	7.5	0.7895	0.7177	1.2389
13	9.1	7.3	0.8022	0.7293	1.2523
14	8.6	7.1	0.8256	0.7505	1.2882
15	8.3	6.9	0.8313	0.7558	1.2880
16	8.0	6.6	0.8277	0.7525	1.2624
17	7.4	6.2	0.8381	0.7619	1.2564
18	6.8	5.8	0.8466	0.7696	1.2426
19	6.6	5.7	0.8572	0.7793	1.2591
20	6.2	5.4	0.8709	0.7917	1.2708

Table 2. Conductivity Measurement of Lithium Myristate in water at 40 ± 0.05^oC

S. No.	Concentration $C * 10^3$ (mol l^{-1})	Specific Conductance $K*10^6$ (mhos em^{-1})	Molar Conductance μ (mhos cm^2 mol^{-1})	Degree of Dissociation α	Dissociation Constant -log K
1	20.0	9.7	0.4850	0.6467	23.670
2	18.1	9.3	0.5138	0.6851	26.975
3	16.6	8.8	0.5301	0.7068	28.289
4	15.3	8.5	0.5556	07407	32.381
5	14.2	8.1	0.5704	0.7606	34.306

6	13.3	7.7	0.5789	0.7719	34.749
7	12.5	7.3	0.5840	0.7787	34.243
8	11.7	6.9	0.5897	0.7863	33.856
9	11.1	6.6	0.5946	0.7928	33.670
10	10.5	6.2	0.5905	0.7873	30.599
11	10.0	6.1	0.6100	0.8133	35.438
12	9.5	5.8	0.6105	0.8140	33.852
13	9.1	5.7	0.6264	0.8350	38.507
14	8.6	5.4	0.6279	0.8372	37.029
15	8.3	5.3	0.6386	0.8514	40.490

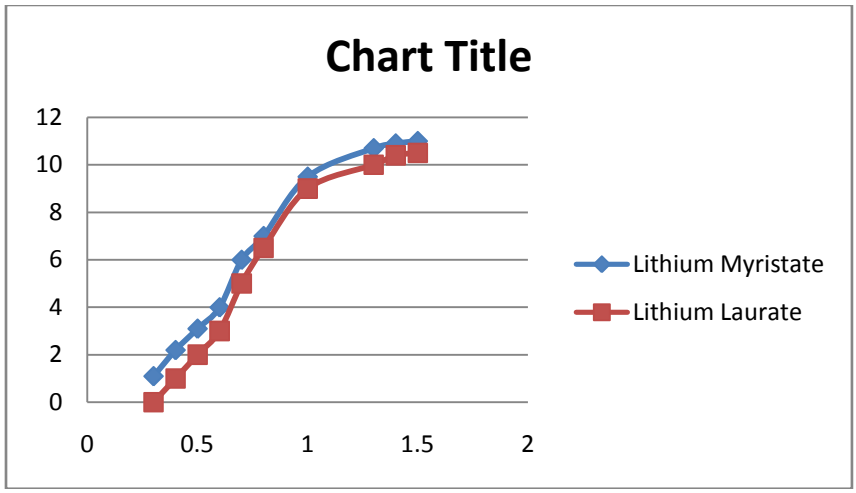

Fig. 1

The molar conductance, μ of the solution of Lithium Soaps in water decreases with decreasing soap concentration. The plots of molar conductance, μ vs square root of concentration, C½ are not linear indicating that the Debye – Hackle Onsager's equation is not applicable to these soap solutions and values of limiting molar conductance μ cannot be obtained by usual extrapolation method.

An expression for the dissociation of Lithium Soaps may be obtained in Ostwald's manner.

$$RCOOLi \leftrightarrow Li^{+} + RCOO^{-}$$

$$C(1-\alpha) \quad C\alpha \quad C\alpha$$

where C is the concentration and α is the degree of dissociation of soaps.

The dissociation constant, K for the above dissociation may be written as –

$$K = \frac{[Li^{+}][RCOO^{-}]}{(RCOO)Li}$$

$$= \frac{C\alpha \cdot C\alpha}{C(1-\alpha)}$$

$$= \frac{C\alpha^{2}}{1-\alpha} \quad \longrightarrow \quad (1)$$

The degree of dissociation α may be replaced by the conductance ratio, μ/ μ_0 where μ is the molar conductance at finite concentration and μ_0 is the limiting molar conductance at infinite dilution.

On substituting the values of α and re – arranging, equation (1)

$$\mu C = K\mu_0^2$$
$$\frac{}{M} - K\mu_0$$

The values of μ_0 and K have been obtained from the scope and intercept of linear portion of the plots of K μC vs. 1/μ for dilute solutions and are recorded in table 3. The results shows that the value of limiting molar conductance μ_0 decrease while the dissociation constant, K increase with increasing number of carbon atoms in soap molecules. The values of the degree of dissociation, α at different concentrations were calculated assuming it as equal to the conductance ratio μ/μ_0. The plots of the degree of dissociation, α vs soap concentration C show that Lithium Soaps (Laurate and Myristate) behave as a weak electrolyte in these solutions.

Table 3.

S. No.	Name of Metal Soap	CMC*10^3 (mol l^{-1})	μ_o (mhos cm^2 mol^{-1})
1	Lithium Laurate	$0.0120 * 10^{-3}$	0.9524
2	Lithium Myristate	$0.0110 * 10^{-3}$	1.0000

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AUTHORS' ADDRESSES

1. **Yadvendra Sharma**
F.E.T. Agra College, Agra, India
Email: yadvendra.fet@gmail.com