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Research Article

CONDUCTOMETRIC AND MICELLIZATION EFFECT ON C.M.C. OF COPPER CARBOXYLATES IN MIXED ORGANIC SOLVENTS

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A R T I C L E   I N F O

A B S T R A C T

The conductance of the solutions of copper carboxylates (caproate, caprylate, caprate, laurate and myristate) has been measured with a view to determine the C.M.C. (critical micellar concentration), molar conductance at infinite dilution. The results show that the specific conductance of the solutions of copper carboxylates increases with increase carboxylate concentration and also increases with the chain length of the carboxylates. The value of C.M.C decreases with the increase in the chain length of the carboxylates. The molar conductances at infinite dilute and degree of ionization have been evaluated.

INTRODUCTION

In the recent years there has been considerable progress in the determination of thermodynamic, rheological and acoustical properties of metallic soaps from speed density and viscosity measurements [1-3]. The kinetics of the thermal decomposition of zinc stearate nd copper caprate studies by Upadhyaya *et.al*[4] and Mehrotra *et.al*[5]. Tomar *et.al*[6] investigated the molar volume, rheological and acoustic parameters of Cadmium soaps. Uranyl carboxylates in mixed organic solvents have been investigated by several workers [7-10].

In the present manuscript attempts have been to determine the conductivity to study the micellar properties.

Experimental

Copper carboxylates (caproate, caprylate, caprate, laurate and myristate) were synthesized by metathesis of the corresponding potassium carboxylates with the required amount of aqueous solution of copper nitrate. Purity of metal carboxylates were checked by Melting point, element of analysis and IR spectra. The conductance of carboxylate solutions in benzene and methanol (50%-50% v/v) have been measured with Ellico conductivity meter -183 using dipping type conductivity cell with platinized electrodes.

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RESULTS AND DISCUSSION

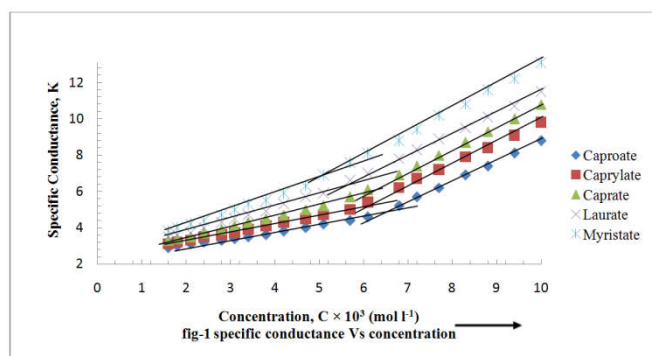### Specific Conductance, k and Molar Conductance

The specific conductance, k of the solutions of Copper carboxylates (caproate, caprylate, caprate, laurate and myristate) in a mixture of benzene-methanol(50%-50% v/v) increases with the increasing concentration, C (Table-1) and this may be due to ionization of Copper carboxylates (caproate, caprylate, caprate, laurate and myristate)

Table 1 Conductivity measurement of copper carboxylates in a mixture of benzene-methanol (50%-50%v/v) at 40±0.05^{0}C

S.N.	Concentration $C \times 10^3$ (mol l^{-1})	Specific Conductance K, mhos cm^{-1}				
		Caproate	Caprylate	Caprate	Laurate	Myristate
1.	1.6	2.9	3.1	3.3	3.5	3.8
2.	1.8	3.0	3.2	3.4	3.6	4.0
3.	2.1	3.1	3.3	3.5	3.7	4.2
4.	2.4	3.2	3.5	3.7	4.0	4.4
5.	2.8	3.3	3.6	3.9	4.3	4.7
6.	3.1	3.4	3.7	4.1	4.5	5.0
7.	3.4	3.5	3.9	4.3	4.7	5.3
8.	3.8	3.6	4.1	4.5	4.9	5.5
9.	4.2	3.8	4.3	4.7	5.3	5.9
10.	4.7	4.0	4.5	5.0	5.7	6.3
11.	5.1	4.2	4.7	5.2	5.9	6.9
12.	5.7	4.4	5.0	5.7	6.6	7.6
13.	6.1	4.6	5.4	6.1	7.0	8.1
14.	6.8	5.2	6.2	6.9	7.8	8.8
15.	7.2	5.7	6.7	7.4	8.3	9.4
16.	7.7	6.2	7.2	8.0	8.9	10.2
17.	8.3	6.9	7.9	8.7	9.5	10.8
18.	8.8	7.4	8.4	9.3	10.1	11.6
19.	9.4	8.1	9.1	10.0	10.7	12.2
20.	10.0	8.8	9.8	10.8	11.5	13.1

(caproate, caprylate, caprate, laurate and myristate) into simple metal cation M^{2+} and fatty acids Anions $RCOO^-$ [where M is copper and R is C_5H_{11}, C_7H_{15}, C_9H_{19}, $C_{11}H_{23}$ and $C_{13}H_{37}$ for caproate, caprylate, caprate, laurate and myristate respectively] in solutions and also due to the formation of micelles at higher soap concentration.

The plots of k Vs C (Fig.-1) are characterized by an intersection of two straight lines at a definite soap concentration which corresponds to the CMC of the soaps indicating the formation of ionic micelles at this concentration. The results show that the CMC decreases with increasing chain length of fatty acid (Table-3).


fig-1 specific conductance Vs concentration

The molar conductance, μ of the solutions of Copper carboxylates (caproate, caprylate, caprate, laurate and myristate) decreases with increasing concentration (Table -2). The decrease in molar conductance may be attributed to combined effects of ionic atmosphere, solvation of ions and decreases of mobility and ionization with the formation of micelles.

Table 2 Conductivity measurement of copper carboxylates in a mixture of benzene-methanol (50%-50%v/v) at 40 ± 0.05^0C

S.N.	Concentration $C \times 10^3$ (mol l⁻¹)	Molar Conductance μ mhos cm² mol⁻¹				
		Caproate	Caprylate	Caprate	Laurate	Myristate
1.	1.6	1.813	1.938	2.063	2.188	2.375
2.	1.8	1.666	1.777	1.888	2.000	2.222
3.	2.1	1.476	1.571	1.666	1.762	2.000
4.	2.4	1.333	1.458	1.541	1.666	1.750
5.	2.8	1.178	1.285	1.393	1.536	1.678
6.	3.1	1.098	1.193	1.323	1.452	1.62
7.	3.4	1.029	1.147	1.264	1.382	1.558
8.	3.8	0.947	1.078	1.184	1.289	1.447
9.	4.2	0.904	1.023	1.119	1.261	1.404
10.	4.7	0.851	0.957	1.063	1.212	1.340
11.	5.1	0.823	0.921	1.019	1.156	1.350
12.	5.7	0.771	0.877	1.000	1.157	1.333
13.	6.1	0.754	0.885	1.000	1.147	1.327
14.	6.8	0.764	0.911	1.014	1.147	1.294
15.	7.2	0.791	0.930	1.027	1.152	1.305
16.	7.7	0.805	0.935	1.038	1.155	1.324
17.	8.3	0.831	0.951	1.048	1.144	1.301
18.	8.8	0.840	0.954	1.056	1.147	1.318
19.	9.4	0.861	0.968	1.063	1.138	1.297
20.	10.0	0.880	0.980	1.080	1.150	1.310

The plots of the molar conductance, μ against the square root of the concentration, $C^{1/2}$ (fig-2) is not linear which indicates that these soaps behaves as a weak electrolyte in these solutions.

fig-2 molar conductance Vs square root of concentration
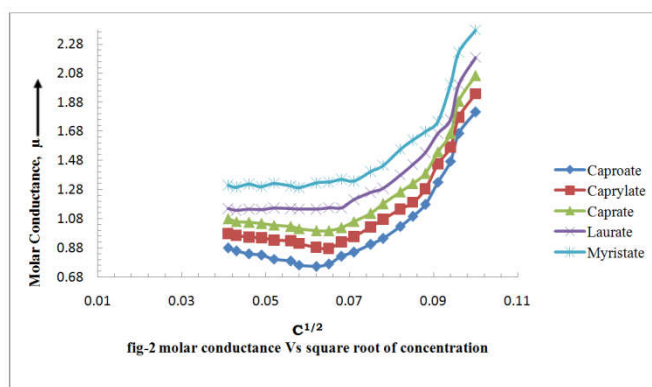
The molar conductance, $μ_0$ cannot be obtained by the usual extrapolating method as the Debye-Huckel Onsanger's equation is not applicable to these solutions. Assuming that these carboxylates are completely associated in to M^{2+} and $RCOO^-$ ions. The dissociation of metal carboxylates may be represented as :

$$M[R\,COO^-]_2 \longrightarrow M^{2+} + 2\,R\,COO^-$$

$$C(1-\alpha) \qquad\qquad (C\alpha) \quad 2(C\alpha)$$
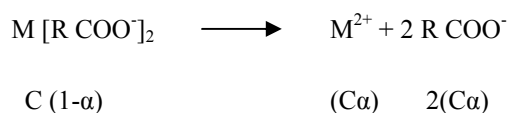
Where M is copper and R denotes C_5H_{11}, C_7H_{15}, C_9H_{19}, $C_{11}H_{23}$ and $C_{13}H_{27}$ for caproate, caprylate, caprate, laurate and myristate respectively.

The dissociation constant, K for the above dissociation may be expressed as:

$$K = \frac{[M^{+2}][RCOO^-]^2}{[M(RCOO)_2]}$$

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

$$\qquad\qquad\qquad\qquad ...... (1)$$

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

Assuming that the dilute solutions do not deviate appreciably from ideal behaviour and the activities of ions can be taken as almost equal to concentration. Thus α may be defined by conductance ratio $μ/μ_0$. Where μ is the molar conductance at a finite concentration that is attributed to the ions formed by the dissociation of metal soaps and $μ_0$ is the limiting molar conductance of these ions.

On substituting the value of α and rearranging, equation (1) can be written as:

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

The values of K and $μ_0$ have been obtained from the slope and intercept of the linear plots of $μ^2c^2$ vs $1/μ$ below the CMC and are recorded in (Table-3). The results show that the values of

limiting molar conductance increases while the dissociation constant decreases with increasing concentration.

Table 3 CMC, and values of various constants of copper carboxylates at 40 ± 0.05^0C

S.No.	Name of metal carboxylate	CMC	μ_0	K
1	Copper caproate	0.0064	2.399	1.86
2	Copper caprylate	0.0058	2.454	1.99
3	Copper caprate	0.0054	2.516	2.50
4	Copper laurate	0.0052	2.574	2.85
5	Copper myristate	0.0050	2.645	3.33

The values of degree of dissociation, α and dissociation constant, K have been calculated at different concentrations by using the values of μ_0 and equation (1). The plots of α vs C show that the Copper carboxylates (caproate, caprylate, caprate, laurate and myristate) behave as a simple electrolyte in these solutions. The values of dissociation constant remain almost constant in dilute solutions but show a drift at higher concentration which may be due to the failure of Debye-Huckel's activity equation at higher concentration.

Acknowledgement

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