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Conductometric behaviour of Carboxylates of Calcium in non-aqueous medium

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ABSTRACT

In the present manuscript critical micelle concentration (CMC), degree of dissociation and dissociation constant of Calcium carboxylates (caproate, caprylate, caprate, laurate, myristate, palmitate and stearate) in 70% chloroform - 30% propylene glycol have been determined from conductivity measurement. The results show that Calcium carboxylates behave as a weak electrolyte in dilute solution and the values of CMC decreases with increasing chain length of fatty acid constituent of the molecule.

Keywords: Calcium carboxylates, conductivity, micellization and CMC value.

INTRODUCTION

Metal carboxylates are materials of considerable commercial importance. Significant areas [1-3] for metal carboxylates include lubricating greases which is intended to improve flow, coating smoothness, printability, driers in paints, cosmetic gels and heat stabilizers for plastics and in the development of PVC (Poly vinyl chloride) as an important commercial polymer. Metal carboxylates used as coating pigment in paper industries [4], optical polymer fiber [5,6] and also uses as a fungicides and pesticides [7].

The investigation are aimed at obtaining accurate information on the conductivity of Calcium carboxylates (caproate, caprylate, caprate, laurate, myristate, palmitate and stearate) in 70% chloroform - 30% propylene glycol (v/v) mixture in order to clarify the solute- solvent interaction and to evaluate the CMC.

MATERIALS AND METHODS

Preparation of Carboxylates: The chemicals used were of AR/GR grade. Calcium carboxylates (caproate, caprylate, caprate, laurate, myristate, palmitate and stearate) were prepared by direct metathesis of the corresponding potassium carboxylates with slight excess of aqueous solutions of Calcium Nitrate at 50-55ºC under vigorous stirring. The precipitated carboxylates were filtered off and washed with distilled water and Acetone to remove the excess of metal ions and unreacted fatty acid. The carboxylates were purified by recrystallisation, dried in an air oven at 50-60ºC and the final drying was carried out under reduced pressure. The purity of these carboxylates have been checked by elemental analysis, IR spectra and by determination of their melting point.

Measurements: The conductance of the solutions was measured with a digital conductivity meter (Toshniwal Model CL 01, 01 10A) and a dipping type conductivity cell (cell constant 0.90cm^{-1}) with plantinized electrode.

RESULTS AND DISCUSSION

Specific conductance, k and molar conductance: The specific conductance, k of the solutions of calcium carboxylates (caproate, caprylate, caprate, laurate, myristate, palmitate and stearate) in methanol increases with the increasing concentration, C (tables-1-7) and this may be due to ionization of calcium carboxylates into simple metal cation M^{2+} and fatty acids anions $RCOO^-$ (where M is calcium and R is C_5H_{11}, C_7H_{15}, C_9H_{19}, $C_{11}H_{23}$, $C_{13}H_{27}$, $C_{15}H_{31}$ and $C_{17}H_{35}$ for caproate, caprylate, caprate, laurate, myristate, palmitate and stearate respectively) in solutions and also due to the formation of micelles at higher concentration. The plots of k Vs C (fig.1) are characterized by an intersection of two straight lines at a definite carboxylate concentration which corresponds to the CMC of the carboxylates indicating the formation of ionic micelles at this concentration. The results show that the CMC decreases with increasing chain length of fatty acid (table 8)

Table 1. Conductivity measurements of Calcium caproate in 70% chloroform - 30% propylene glycol (v/v) at 30±0.05^{0}C

S.N.	Concentration $C\times10^3$ mol l^{-1}	Specific conductance $k\times10^3$ mhos cm^{-1}	Molar conductance (μ) mhos cm^{2}mol^{-1}	1/μ	Degree of dissociation α
1.	20.0	18.1	0.905	1.105	0.411
2.	18.2	17.4	0.956	1.046	0.435
3.	16.6	16.9	1.018	0.982	0.463
4.	15.3	16.4	1.072	0.933	0.487
5.	14.2	16.0	1.127	0.887	0.512
6.	13.3	15.7	1.181	0.847	0.537
7.	12.5	15.3	1.214	0.824	0.552
8.	11.7	14.4	1.231	0.812	0.559
9.	11.1	14.1	1.259	0.794	0.572
10	10.5	13.5	1.286	0.778	0.585
11.	10.0	13.1	1.310	0.763	0.595
12.	9.5	12.8	1.347	0.742	0.612
13.	9.0	12.3	1.367	0.732	0.621
14.	8.6	12.0	1.395	0.717	0.634
15.	8.0	11.5	1.438	0.695	0.654
16.	7.4	10.8	1.459	0.685	0.663
17.	6.8	10.4	1.529	0.654	0.695
18.	6.4	10.1	1.578	0.634	0.717
19.	5.2	9.3	1.789	0.559	0.813
20.	4.8	8.8	1.833	0.546	0.833

The molar conductance, μ of the solutions of Calcium carboxylates decreases with increasing concentration (tables 1-7) .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 measurements of Calcium caprylate in 70% chloroform - 30% propylene glycol (v/v) at 30±0.05^{0}C

S.N.	**Concentration** $C\times10^3$ **mol** l^{-1}	**Specific conductance** $k\times10^3$ **mhos** cm^{-1}	**Molar conductance** (μ) **mhos** cm^2mol^{-1}	$1/\mu$	**Degree of dissociation** α
1.	20.0	18.9	0.945	1.058	0.394
2.	18.2	18.3	1.006	0.994	0.419
3.	16.6	17.7	1.067	0.937	0.445
4.	15.3	17.3	1.131	0.884	0.471
5.	14.2	16.9	1.190	0.840	0.496
6.	13.3	16.6	1.248	0.801	0.520
7.	12.5	16.4	1.302	0.768	0.543
8.	11.7	15.5	1.325	0.754	0.553
9.	11.1	15.1	1.348	0.742	0.562
10	10.5	14.6	1.391	0.719	0.579
11.	10.0	14.0	1.400	0.714	0.583
12.	9.5	13.6	1.432	0.698	0.597
13.	9.0	13.2	1.467	0.682	0.611
14.	8.6	12.8	1.488	0.672	0.620
15.	8.0	12.3	1.538	0.650	0.641
16.	7.4	11.7	1.581	0.633	0.659
17.	6.8	11.2	1.647	0.607	0.686
18.	6.4	10.7	1.672	0.598	0.697
19.	5.2	9.9	1.800	0.556	0.750
20.	4.8	9.3	1.938	0.516	0.808

Table 3. Conductivity measurements of Calcium caprate in 70% chloroform - 30% propylene glycol (v/v) at 30±0.05^{0}C

S.N.	**Concentration** $C\times10^3$ **mol** l^{-1}	**Specific conductance** $k\times10^3$ **mhos** cm^{-1}	**Molar conductance** (μ) **mhos** cm^2mol^{-1}	$1/\mu$	**Degree of dissociation** α
1.	20.0	19.7	0.985	1.015	0.365
2.	18.2	19.1	1.049	0.953	0.389
3.	16.6	18.6	1.121	0.892	0.415
4.	15.3	18.2	1.189	0.841	0.440
5.	14.2	17.8	1.254	0.797	0.464
6.	13.3	17.5	1.316	0.759	0.487
7.	12.5	17.3	1.373	0.728	0.509
8.	11.7	16.7	1.427	0.701	0.539
9.	11.1	16.3	1.455	0.687	0.539
10	10.5	15.7	1.495	0.669	0.554
11.	10.0	15.0	1.500	0.667	0.556
12.	9.5	14.6	1.537	0.651	0.569
13.	9.0	14.1	1.567	0.638	0.580
14.	8.6	13.8	1.605	0.623	0.594
15.	8.0	13.1	1.638	0.610	0.607
16.	7.4	12.6	1.703	0.587	0.631
17.	6.8	12.0	1.765	0.567	0.654
18.	6.4	11.4	1.781	0.561	0.659
19.	5.2	10.6	2.039	0.490	0.755
20.	4.8	9.8	2.042	0.489	0.756

Table 4. Conductivity measurements of Calcium laurate in 70% chloroform - 30% propylene glycol (v/v) at 30 ± 0.05^0C

S.N.	Concentration $C\times10^3$ mol l^{-1}	Specific conductance $k\times10^3$ mhos cm^{-1}	Molar conductance (μ) mhos cm^2mol^{-1}	$1/\mu$	Degree of dissociation α
1.	20.0	19.7	0.985	1.015	0.365
2.	18.2	19.1	1.049	0.953	0.389
3.	16.6	18.6	1.121	0.892	0.415
4.	15.3	18.2	1.189	0.841	0.440
5.	14.2	17.8	1.254	0.797	0.464
6.	13.3	17.5	1.316	0.759	0.487
7.	12.5	17.3	1.373	0.728	0.509
8.	11.7	16.7	1.427	0.701	0.539
9.	11.1	16.3	1.455	0.687	0.539
10	10.5	15.7	1.495	0.669	0.554
11.	10.0	15.0	1.500	0.667	0.556
12.	9.5	14.6	1.537	0.651	0.569
13.	9.0	14.1	1.567	0.638	0.580
14.	8.6	13.8	1.605	0.623	0.594
15.	8.0	13.1	1.638	0.610	0.607
16.	7.4	12.6	1.703	0.587	0.631
17.	6.8	12.0	1.765	0.567	0.654
18.	6.4	11.4	1.781	0.561	0.659
19.	5.2	10.6	2.039	0.490	0.755
20.	4.8	9.8	2.042	0.489	0.756

Table 5. Conductivity measurements of Calcium myristate in 70% chloroform - 30% propylene glycol (v/v) at 30 ± 0.05^0C

S.No	Concentration $C\times10^3$ mol l^{-1}	Specific conductance $k\times10^3$ mhos cm^{-1}	Molar conductance (μ) mhos cm^2mol^{-1}	$1/\mu$	Degree of dissociation α
1.	20.0	21.3	1.065	0.938	0.344
2.	18.2	20.6	1.131	0.883	0.365
3.	16.6	20.0	1.204	0.830	0.388
4.	15.3	19.7	1.287	0.776	0.415
5.	14.2	19.3	1.359	0.735	0.438
6.	13.3	18.9	1.421	0.703	0.458
7.	12.5	18.6	1.476	0.677	0.476
8.	11.7	18.3	1.564	0.639	0.505
9.	11.1	18.1	1.616	0.618	0.521
10	10.5	17.4	1.657	0.603	0.535
11.	10.0	16.8	1.680	0.595	0.542
12.	9.5	16.3	1.715	0.582	0.553
13.	9.0	15.8	1.756	0.569	0.567
14.	8.6	15.1	1.756	0.569	0.567
15.	8.0	14.4	1.800	0.555	0.581
16.	7.4	13.8	1.860	0.536	0.600
17.	6.8	13.2	1.941	0.515	0.626
18.	6.4	12.6	1.968	0.507	0.635
19.	5.2	11.4	2.192	0.456	0.707
20.	4.8	10.6	2.208	0.452	0.712

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

Table 6. Conductivity measurements of Calcium palmitate in 70% chloroform - 30% propylene glycol (v/v) at 30±0.05^{0}C

S.N.	Concentration $C \times 10^3$ mol l^{-1}	Specific conductance $k \times 10^3$ mhos cm^{-1}	Molar conductance (μ) mhos $cm^2 mol^{-1}$	$1/\mu$	Degree of dissociation α
1.	20.0	22.0	1.100	0.909	0.333
2.	18.2	21.6	1.187	0.843	0.360
3.	16.6	21.0	1.265	0.791	0.383
4.	15.3	20.8	1.359	0.736	0.412
5.	14.2	20.5	1.444	0.693	0.438
6.	13.3	20.2	1.518	0.658	0.460
7.	12.5	20.0	1.587	0.630	0.481
8.	11.7	19.8	1.692	0.590	0.513
9.	11.1	19.6	1.750	0.571	0.530
10	10.5	19.4	1.847	0.541	0.559
11.	10.0	19.2	1.920	0.520	0.582
12.	9.5	18.4	1.936	0.516	0.587
13.	9.0	17.8	1.977	0.505	0.599
14.	8.6	17.2	2.000	0.508	0.600
15.	8.0	16.2	2.025	0493	0.614
16.	7.4	15.3	2.067	0.483	0.626
17.	6.8	14.6	2.147	0.465	0.651
18.	6.4	13.9	2.171	0.460	0.658
19.	5.2	12.5	2.403	0.416	0.728
20.	4.8	11.6	2.416	0.413	0.732

Table 7. Conductivity measurements of Calcium stearate in 70% chloroform - 30% propylene glycol (v/v) at 30±0.05^{0}C

S.N.	Concentration $C \times 10^3$ mol l^{-1}	Specific conductance $k \times 10^3$ mhos cm^{-1}	Molar conductance (μ) mhos $cm^2 mol^{-1}$	$1/\mu$	Degree of dissociation α
1.	20.0	22.8	1.140	0.877	0.317
2.	18.2	22.2	1.219	0.820	0.339
3.	16.6	21.7	1.301	0.769	0.361
4.	15.3	21.3	1.392	0.718	0.387
5.	14.2	21.0	1.478	0.677	0.411
6.	13.3	20.8	1.564	0.639	0.434
7.	12.5	20.5	1.626	0.610	0.452
8.	11.7	20.3	1.735	0.576	0.482
9.	11.1	20.1	1.794	0.557	0.499
10	10.5	20.0	1.904	0.525	0.529
11.	10.0	19.8	1.980	0.505	0.550
12.	9.5	19.6	2.063	0.484	0.573
13.	9.0	18.8	2.089	0.479	0.580
14.	8.6	18.2	2.116	0.472	0.588
15.	8.0	17.2	2.150	0.465	0.597
16.	7.4	16.3	2.203	0.454	0.612
17.	6.8	15.4	2.265	0.441	0.629
18.	6.4	14.7	2.297	0.435	0.638
19.	5.2	13.2	2.538	0.394	0.705
20.	4.8	12.3	2.563	0.390	0.712

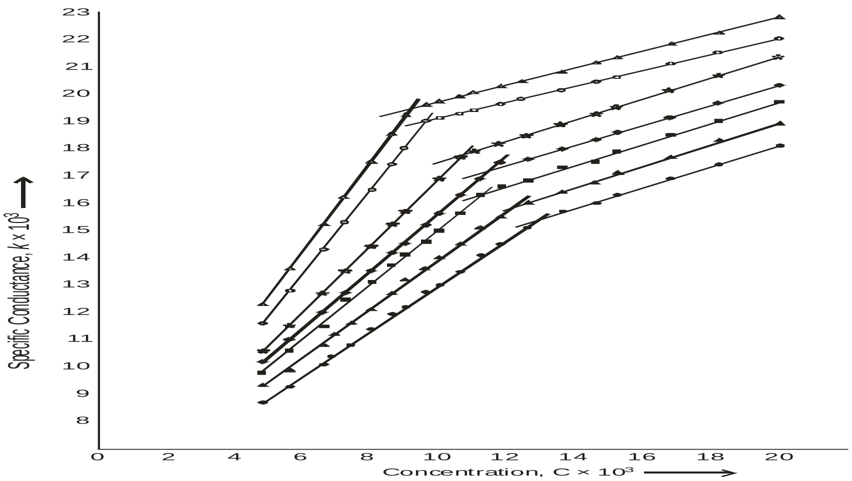

Fig. 1. : Specific Conductance vs Concentration for Calcium Carboxylates
(●) Caproate, (▲) Caprylate, (■) Caprate, (◆) Laurate, (☆) Myristate, (○) Palmitate, (△) Stearate

Table 8. CMC and values of various constants for Calcium carboxylates at 30±0.05^{0}C

Name of Carboxylates	CMC	μ_0	$K \times 10^6$
Caproate	0.0132	2.2	5.68
Caprylate	0.0128	2.4	5.25
Caprate	0.0120	2.7	5.00
Laurate	0.0116	2.9	4.84
Myristate	0.0110	3.1	4.17
Palmitate	0.0098	3.3	4.02
Stearate	0.0092	3.6	3.52

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 carboxylate solutions. Assuming that these carboxylates are completely associated in to M^{3+} and $RCOO^-$ ions. The dissociation of metal soap may be represented as:

$$\underset{C\,(1-\alpha)}{M[RCOO^-]_2} \rightleftharpoons \underset{C\alpha}{M^{2+}} + \underset{2C\alpha}{2\,RCOO^-} \qquad \dots (1)$$

Where M is Calcium and R is C_5H_{11}, C_7H_{15}, C_9H_{19}, $C_{11}H_{23}$, $C_{13}H_{27}$, $C_{15}H_{31}$ and $C_{17}H_{35}$ for caproate, caprylate, caprate, Laurate, myristate, palmitate and stearate respectively and α and C are the degree of dissociation and concentration.

The dissociation constant, K can be written as

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

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

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

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 carboxylates and μ_0 is the limiting molar conductance of these ions. On substituting the value of α and rearranging, equation (3) can be written as:

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

The values of K and μ_0 have been obtained from the slope and intercept of the linear plots of μ^2c^2 vs. $1/\mu$ below the CMC and are recorded in (Table-8). The results show that the values of limiting molar conductance increases while the dissociation constant decreases with increasing concentration. 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 (3). The plots of α vs. C show that these Calcium Carboxylates 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.

APPLICATIONS

Calcium Carboxylates 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.

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