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Thermodynamic and Micellar Studies on the Carboxylates of Strontium and Barium

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ABSTRACT

The investigations on the conductance of the solutions of Strontium and Barium carboxylates in a mixture of 70% chloroform and 30% Propylene glycol (v/v) have been made at different temperature in order to determine the CMC, dissociation constant, Molar Conductance and Thermodynamic parameters for dissociation and association Process. The results Shown that the CMC of these carboxylates decreases with increasing temperature. The values of enthalpy, free energy and entropy changes confirm the exothermic nature of dissociation process and the decrease in free energy for association process shows that the micellization in favored over dissociation process.

Keywords: Metal carboxylates, conductivity, micellization CMC value.

INTRODUCTION

The carboxylates of alkaline earth metal are being widely used in industry, technology and allied Sciences. These carboxylates have greatly attracted the attention of industries and are finding increasing applications in many fields. The studies on the nature and structure of these carboxylates are of great importance for their uses in industries and for explaining their characteristics under different conditions. The Survey of literature[1-12] reveals that the physicochemical properties and structure of transition, lanthanide and Actinide carboxylates are thoroughly investigated but alkaline earth metal carboxylates have not been thoroughly investigated. The present work has been initiated with a view of determine the conductivity of Strontium and Barium carboxylates at different Temperature in a mixture of 70% chloroform and 30% propylene glycol (v/v) to evaluate critical micelle concentration and various Thermodynamic Parameters.

MATERIALS AND METHODS

Preparation of Carboxylates : The chemicals used were of AR/GR grade. Strontium and Barium carboxylates (Carprate, Laurate and Myristate) were prepared by direct metathesis of the corresponding potassium carboxylates with slight excess of aqueous solutions of strontium and Barium 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 potassium carboxylates. The carboxylates were purified by recrystallisation, dried in an air oven at

50-60ºC and the final drying of the carboxylates was carried out under reduced pressure. The purity of these carboxylates was checked by elemental analysis, IR spectra and by determination of their melting point.

Name of the metal	Caprate	Laurate	Myristate
Strontium	200ºC	218ºC	222ºC
Barium	296ºC	300ºC	310ºC

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 0.90 cm^{-1}) with plantinized electrode at different temperatures. [30, 40 and 50 ± 0.05ºC].

RESULTS AND DISCUSSION

Specific conductance, k and molar conductance: The specific conductance, k of the solutions of Strontium and Barium carboxylates [Caprate, Laurate and Myristate] in a mixture of 70% chloroform and 30% propylene glycol (V/V) increases with the increasing carboxylates concentration, C and temperature. The increase in the specific conductance with the increase in carboxylates concentration may be due to ionization of Strontium and Barium carboxylates into simple metal cation M^{2+} and fatty acids Anions $RCOO^{-}$ [where M is Strontium, Barium and R is C_9H_{19}, $C_{11}H_{23}$ and $C_{13}H_{27}$ for Caprate, Laurate and Myristate, respectively] in solutions and also due to the formation of micelles at higher carboxylates concentration. The plots of specific conductance Vs carboxylates concentration (Fig. 1) are characterized by an intersection of two straight lines at a definite carboxylates concentration which corresponds to the CMC of the carboxylates indicating the formation of ionic micelles at this carboxylates concentration. The results show that the CMC increases with the increase in temperature but decreases with increasing chain length of fatty acid constituent of the carboxylates (Table 1).

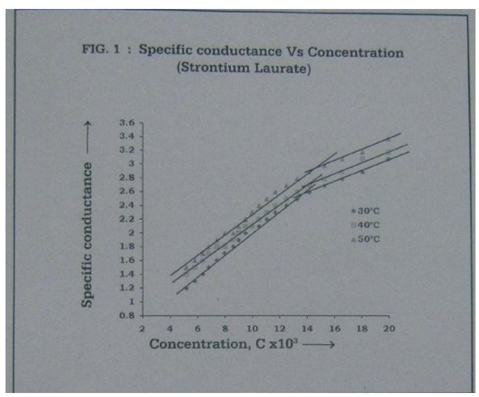

Fig. 1 Plot of specific conductance Vs carboxylates concentration

Table 1. Critical Micelle Concentration, CMC (Mol l^{-1}) of Strontium and Barium carboxylates at different temperatures

S. No.	Temperature (^{0}C)	CMC x 10^3					
		Strontium			Barium		
		Caprate	Laurate	Myristate	Caprate	Laurate	Myristate
1.	30	14.3	13.8	13.3	13.2	12.8	12.4
2.	40	15.0	14.2	13.8	14.2	13.6	13.0
3.	50	15.6	14.6	14.4	14.8	14.0	13.4

The molar conductance, μ of the solutions of Strontium and Barium carboxylates decreases with increasing carboxylates concentration but increases with increase in temperature (Table 2a,b,c). 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(a) : Molar conductance, μ (Mhos cm^2 mol^{-1}) of the solutions of Strontium Caprate and Barium Caprate at different temperatures

S. No.	Concentration ($Cx10^3$)	Molar Conductance μ					
		Strontium			Barium		
		30°C	40°C	50ºC	30ºC	40ºC	50ºC
1.	20.0	140	145	155	125	130	145
2.	18.1	149	160	166	127	138	149
3.	16.6	157	169	181	133	145	157
4.	15.3	169	176	189	137	150	163
5.	14.2	176	183	191	141	155	169
6.	13.3	180	187	195	143	158	173
7.	12.5	176	184	200	144	160	176
8.	11.7	179	189	205	145	162	180
9.	11.1	180	198	207	144	162	180
10.	10.5	190	200	209	143	162	181
11.	10.0	190	210	210	150	160	181
12.	9.5	189	200	221	147	168	179
13.	9.0	189	211	222	144	167	178
14.	8.6	198	209	232	140	163	186
15.	8.0	200	212	237	150	163	188
16.	7.4	203	216	243	149	162	189
17.	6.8	205	220	250	148	177	191
18.	6.4	203	234	250	141	172	188
19.	5.8	207	241	259	138	172	207
20.	5.2	212	230	260	135	173	212

Table 2(b). Molar conductance, μ (Mhos cm^2 mol^{-1}) of the solutions of Strontium Laurate and Barium Laurate at different temperatures

S. No.	Concentration ($Cx10^3$)	Molar Conductance μ					
		Strontium			Barium		
		30°C	40°C	50ºC	30ºC	40ºC	50ºC
1.	20.0	155	160	170	140	160	165
2.	18.1	160	171	177	144	160	171
3.	16.6	169	175	187	151	169	181
4.	15.3	176	183	196	157	177	190
5.	14.2	183	190	204	162	183	197
6.	13.3	187	196	211	165	181	196

7.	12.5	192	200	216	168	184	200
8.	11.7	196	205	222	170	188	205
9.	11.1	198	207	225	171	189	207
10.	10.5	200	210	229	171	191	210
11.	10.0	210	210	230	170	190	210
12.	9.5	210	211	232	168	190	211
13.	9.0	211	222	233	167	189	211
14.	8.6	209	220	233	186	186	209
15.	8.0	212	225	250	175	188	213
16.	7.4	216	243	257	176	189	216
17.	6.8	220	250	265	177	191	235
18.	6.4	219	250	266	172	188	234
19.	5.8	224	259	276	172	190	241
20.	5.2	230	269	288	173	192	250

Table–2(c): Molar conductance, μ (Mhos cm^2 mol^{-1}) of the solutions of Strontium Myristate and Barium Myristate at different temperatures

S. No.	Concentration ($Cx10^3$)	Molar Conductance μ					
		Strontium			Barium		
		30°C	40°C	50°C	30°C	40°C	50°C
1.	20.0	180	190	200	145	165	175
2.	18.1	187	193	216	155	177	188
3.	16.6	192	205	229	168	181	199
4.	15.3	202	216	242	170	190	209
5.	14.2	204	225	254	176	204	218
6.	13.3	210	233	263	181	211	226
7.	12.5	216	232	256	184	216	232
8.	11.7	217	239	261	188	214	231
9.	11.1	216	243	267	180	216	234
10.	10.5	219	248	270	190	219	238
11.	10.0	220	250	263	190	220	240
12.	9.5	221	253	267	190	221	242
13.	9.0	222	256	267	189	222	244
14.	8.6	221	256	275	198	221	244
15.	8.0	225	263	284	200	225	250
16.	7.4	229	270	284	203	230	257
17.	6.8	235	279	294	206	235	265
18.	6.4	234	281	297	203	234	266
19.	5.8	241	293	310	207	241	276
20.	5.2	250	308	327	212	250	289

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

Assuming that the carboxylates are completely associated in to M^{2+} and $RCOO^-$ ions. The dissociation of metal carboxylatess may be represented as :

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

where M stands for Strontium and Barium and R is C_9H_{19}, $C_{11}H_{23}$ and $C_{13}H_{27}$ for Caprate, Laurate and Myristate respectively α and c are the degree of dissociation and concentration of carboxylates.

The dissociation constant, K can be written as

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

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

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

Assuming that the solutions do not deviate appreciably from ideal behavior 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 :

$$\mu^2 c^2 = \frac{K\mu_0^3}{4\mu} - \frac{\mu_0^2 K}{4} \quad \ldots.(4)$$

The values of dissociation constant, K and limiting molar conductance, 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 temperature. The decrease in the values of dissociation constant with increasing temperature indicate the exothermic nature of the dissociation of Strontium and Barium carboxylates in a mixture of 70% chloroform and 30% propylene glycol (V/V).

Table 3 . Values of μ_0 obtained from the plot μ^2c^2 vs $1/\mu$ of the solution of Strontium and Barium carboxylates at different temperature (°C**)**

S.No.	Temperature (ºC)	Strontium			Barium		
		Caprate	Laurate	Myristate	Caprate	Laurate	Myristate
1	30	250.00	333.00	500.00	167.67	200.00	333.33
2	40	270.00	625.00	909.00	178.57	243.70	416.67
3	50	451.00	833.33	1250.00	357.14	434.78	909.00

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 plot of α vs C show that the Strontium and Barium carboxylates behave as a weak electrolyte in these solutions. The values of dissociation constant remain almost constant in dilute solutions but show a drift at higher carboxylates concentration which may be due to the failure of Debye-Huckel's activity equation at higher carboxylates concentration.

$$\frac{\partial lnK}{\partial T} = \frac{\Delta H_D^0}{RT^2}$$

Or $$\log K = -\frac{\Delta H_D^0}{2.303RT} + constant \quad \ldots(5)$$

The values of the heat of dissociation, ΔH^o_D have been obtained from the slope of the linear plot of logK vs 1/T (Fig.2) and are recorded in (Table 4).

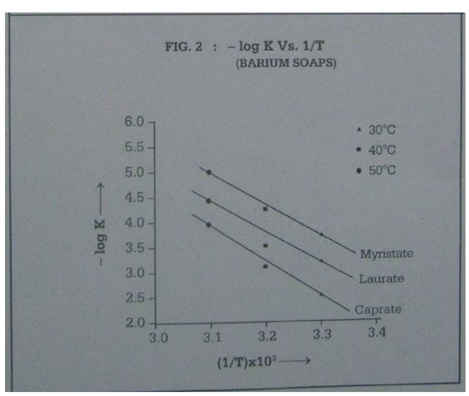

Fig.2 Linear plot of logK vs 1/T

Table 4 . The values of the heat of dissociation, ΔH_D^0(KJ mole^{-1}) from the plot of –logK vs 1/T.

S.No.	Metal	Caprate	Laurate	Myristate
1.	Strontium	–191.40	–153.12	–127.60
2.	Barium	–159.49	–127.60	–119.63

The negative values of heat of dissociation indicate that the dissociation process is exothermic in nature.
The values of the change in free energy, ΔG^o_D and entropy ΔS^o_D, per mole for the dissociation process have been calculated (Table-5) using the relationship.

$$\Delta G_D^0 = -RT \ln K_D \quad \ldots(6)$$

$$\Delta S_D^0 = \frac{[\Delta H_D^0 - \Delta G_D^0]}{T} \quad \ldots(7)$$

Table 5. Thermodynamic parameters of Strontium and Barium carboxylates for dissociation process

S. No.	Temperature (ºC)	Caprate		Laurate		Myristate	
		ΔG_D^0 KJ/mol	$-\Delta S_D^0$x10^2 KJ/mol K	ΔG_D^0 KJ/mol	$-\Delta S_D^0$x10^2 KJ/mol K	ΔG_D^0 KJ/mol	$-\Delta S_D^0$x10^2 KJ/mol K
Strontium							
1	30	15.32	68.82	22.39	57.93	26.05	50.71
2	40	22.25	68.26	27.91	57.84	31.16	50.72
3	50	27.38	67.73	32.63	57.51	35.17	50.39
Barium							
1	30	14.49	47.85	19.14	35.58	21.23	32.48
2	40	18.63	44.85	21.56	33.88	25.52	30.07
3	50	24.73	41.69	27.20	31.08	31.46	27.30

For the aggregation process. The standard free energy of micellization (per mole of monomer) ΔG_A^0 for the phase seperation model[13,14] (Table 6) is given by the relationship.

$$\Delta G_A^0 = 2\,RT \ln X_{CMC} \quad \ldots(8)$$

Where X_{CMC} is the CMC expressed as a mole fraction and defined as :

$$X_{CMC} = \frac{n_s}{n_s+n_0}$$

Since the number of moles of free surfactant, n_s is small as compared to the number of moles of solvent, n_0.

$$X_{CMC} = \frac{n_s}{n_0}$$

Table 6 . Values of the standard free energy of micellization ΔG_A^0 (KJ mol^{-1}) of Strontium and Barium carboxylates for association process

S.No.	Temperature (ºC)	Caprate	Laurate	Myristate
Strontium				
1	30	–23.07	–23.24	–23.43
2	40	–23.58	–23.86	–24.01
3	50	–24.12	–24.48	–24.55
Barium				
1	30	–23.47	–23.63	–23.78
2	40	–23.86	–24.09	–24.32
3	50	–24.40	–24.70	–24.94

The standard enthalpy change of micellization per mole of monomer for the phase separation model[15,16]. ΔH_A^0 is given by the relationship.

$$\frac{\partial(\ln X_{CMC})}{\partial T} = \frac{\Delta H_A^0}{2RT^2}$$

$$\ln X_{CMC} = \frac{\Delta H_A^0}{2RT} + \text{Constant} \qquad \ldots(9)$$

The value of ΔH_A^0 of Strontium and Barium carboxylates have been calculated from the slope of the plots of –lnX_{CMC} vs 1/T and the values are depicted in Table 7.

Table 7 . The values of the heat of association, ΔH_A^0 (KJ mole^{-1}) from the plot of –ln XCMC vs 1/T.

S.No.	Metal	Caprate	Laurate	Myristate
1.	Strontium	–6.65	–4.99	–3.33
2.	Barium	–9.98	–8.31	–5.82

The value of ΔH_A^0 decreases as the CMC also decreases with increasing the chain length carboxylates.The values of enthalpy, free energy and entropy changes ($\Delta H_D^0 < 0$, $\Delta G_D^0 > 0$, $\Delta S_D^0 < 0$, $\Delta H_A^0 < 0$,) confirm the exothermic nature of dissociation process and the decrease in free energy for association process shows that the micellization is favored over dissociation process.

APPLICATIONS

These studies are applicable to evaluate critical micelle concentration and various Thermodynamic Parameters.

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REFERENCES

[1] Matsumoto, Norichika, Jpn.Kokai, Tokkyo, Koho, Jp **2002**, 38, 198, (C1, C11 D13/02) 6 Feb (2002) April 2000/22, 603, 24 July (2000).
[2] Matsumoto, Norichika, Jpn. Kokai, Tokkyo, Koho, Jp. **2002**, 317, 199 (Cl, Cll, D13/00) 31 Oct. (2002), April 2001/122, 673, 2, 20 April (2001) Japan.
[3] Mehmet Gonen, Serdar Oztarki, Devrin Balkose, Salih Okur and Semra, Ind. Eng. Chem. Res., **2010,** 49(4), 1732-1736.
[4] F.Z.Soolurez, A.H. Anakilen R.K.Robuts *J. Phase Dig. & Thermo*, **2008,** 107, 213-217.
[5] P.Verghese, Suleman , F.M Prasad, *J. Ind. Chem. Soc*., **2008,** 85, 252-256.
[6] H.W.Lawureck, K.A.Samurai, *J. Appl. Prob*. **2008,** 76, 401-407.
[7] S.K.Upadhyaya, R.K. Shukla, G.Sharma, *J. Ind. Chem. Soc*. **2007,** 84, 149-157.
[8] R.P.Verma, S. Kumar, A.J.Verma, *Sandi Chemical Soc*., **2007,** 5(2), 225-230.
[9] W.Robert, *Corkery, Phys. Chem. Phys*., **2004,** 6, 1534-46.
[10] Kouhei Sawada and Miki Kenaka, *J. of Oleo Science*, **2004,** 53(12), 627-40.
[11] Singh Chitra, S.K.Upadhyaya., *Asian J. Chem.* **2001**, 13(3), 977-982.
[12] R.P.Verma, H.C.Goel, *Tenside Surft. Deterg.*, **2001,** 38(3), 183-185.
[13] B.W.Borry, G.F.J. Russel., *J. Colloid Interface, Sci.* **1972**, 40, 174.
[14] P.G.T.Fogg, R.C.Pink., *J. Chem. Soc*. **1959**, 1935.
[15] R.P.Verma, R.Dayal, *J. Am. Oil Chem. Soc*. **1976,** 53(1), 39-41.
[16] R.P.Verma, P.K.Jain., *Indian J. Chem*. **1980,** 54(3), 561-66.