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Thermodynamic and Micellar Studies on Iron and Cobalt Soap Solutions

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The investigations on the conductance of the solutions of iron and cobalt soaps in a mixture of benzene and methanol (50:50 v/v) have been made at different temperature to determine the critical micellization concentration, dissociation constant, molar conductance and thermodynamic parameters for dissociation and association process. The results show that the critical micellization concentration of these soaps increases with the increasing temperature. The values of enthalpy, free energy and entropy changes confirm the exothermic nature of dissociation process and decrease in free energy for association process shows that the micellization is favoured over dissociation process.

Key Words: Critical micellization concentration, Metal soaps, Conductivity.

INTRODUCTION

Metal soaps are used in almost all the sectors of the national economy owing either to the formation of micelles in solution or to high surface activity. The studies on the nature and structure of these soaps are of great importance for their use in various industries and for explaining their characteristics under different conditions. The method and preparation of potassium soaps and metal soaps were described by several workers[1-6]. The infrared spectra, X-ray diffraction and thermal analysis of manganese and zinc soaps were investigated by Upadhyaya *et al.*[7] Thermodynamics of dissociation of chromium soaps and copper dilaurate were described by Topellar *et al.*[8] and Kumar[9]. Preparation and characterization of aluminium stearate were made by Loncar *et al.*[10]. Sawada *et al.*[11] synthesized and characterized micro particles of zinc soaps. Verma *et al.*[12] carried out ultrasonic measurements of zirconium soaps. These transition metal soaps are used in various fields such as protection of crop, fungicidal activities, preservation of wood, lubrication, emulsification, waterproofing and repellency[13-16]. Imori *et al.*[17] used the complexes of molybdenum and cobalt soaps as adhesives for steel cord and rubber in radial tyres. The present work has been initiated with a view to determine the conductivity of iron and cobalt soaps at different temperatures in a mixture of benzene and methanol (50:50 v/v) to evaluate critical micelle concentration and various thermodynamic parameters.

EXPERIMENTAL

Preparation of soaps: The chemicals used were of AR/GR grade. Iron and cobalt soaps (caprate, laurate and myristate) were prepared by refluxing the corresponding potassium soaps with required amount of aqueous solution of iron and cobalt nitrate at 50-55ºC under vigorous stirring. The precipitated soaps were filtered off and washed several times with distilled water and acetone to remove excess of metal ions and unreacted fatty acid. The soaps were purified by recrystallization. The metal soaps thus obtained were first dried in an air oven at 50-60ºC and the final drying of the soaps was carried out under reduced pressure.

The purity of soaps was checked by IR spectra and by determination of their melting point. Iron caprate = 120ºC, iron laurate = 130ºC, iron myristate = 160ºC. cobalt caprate = 70ºC, cobalt laurate = 75ºC, cobalt myristate = 80ºC

The conductance of the solutions was measured with a digital conductivity meter (Toshniwal Model CL 01/01 10A) and a dipping conductivity cell (cell constant 0.90 cm^{-1}) with platinized electrode at different temperature (30, 40 and 50 ± 0.05ºC).

RESULTS AND DISCUSSION

Specific conductance (k) and molar conductance (μ): The specific conductance, k of the solutions of iron and cobalt soaps (caprate, laurate and myristate) in a mixture of benzene and methanol (50:50 v/v) increases with the increasing soap concentration (C) and temperature. The increase in the specific conductance with the increase in soap concentration may be due to the ionization of iron and cobalt soaps into simple metal cation M^{2+} and fatty acid anions $RCOO^-$ (where M is iron and cobalt 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 soap concentration. The plots of specific conductance *vs.* soap concentration are characterized by an intersection of two straight lines at a definite soap concentration which corresponds to the critical micellization concentration (CMC) of the soap indicating the formation of ionic micelles at this soap concentration The results show that the CMC increases with the increase in temperature as shown in (Table-1) but decreases with increasing chain length of fatty acid constituent of the soaps.

The molar conductance (μ) of the solutions of iron and cobalt soap decreases with increasing soap concentration but increases with increase in temperature (Tables 2-4). The decrease in molar conductance may be attributed to combined effects of ionic atmosphere, solvation of ions decrease in mobility and ionization with the formation of micelles. The

TABLE-1
CRITICAL MICELLE CONCENTRATION (CMC) (mol L^{-1}) OF IRON AND COBALT SOAPS AT DIFFERENT TEMPERATURES

Temp. (ºC)	CMC × 10^3					
	Iron			Cobalt		
	Caprate	Laurate	Myristate	Caprate	Laurate	Myristate
30	14.8	14.4	13.8	13.4	13.2	12.6
40	15.0	14.8	14.2	13.8	13.4	12.8
50	15.2	15.0	14.5	14.0	13.7	13.0

TABLE-2
MOLAR CONDUCTANCE (μ) (mhos cm^2 mol^{-1}) OF THE SOLUTIONS OF IRON AND COBALT SOAPS AT DIFFERENT TEMPERATURES

Concentration C × 10^3	Molar conductance (μ)					
	Iron caprate			Cobalt caprate		
	30ºC	40ºC	50ºC	30ºC	40ºC	50ºC
20.0	0.995	1.025	1.035	0.885	0.905	0.940
18.1	1.077	1.099	1.116	0.945	0.967	0.994
16.6	1.151	1.163	1.187	1.000	1.024	1.054
15.3	1.229	1.242	1.261	1.059	1.085	1.118
14.2	1.282	1.317	1.338	1.127	1.148	1.190
13.3	1.323	1.376	1.406	1.181	1.218	1.248
12.5	1.360	1.416	1.472	1.216	1.248	1.280
11.7	1.402	1.444	1.496	1.248	1.300	1.325
11.1	1.432	1.486	1.523	1.288	1.315	1.342
10.5	1.467	1.495	1.571	1.314	1.362	1.400
10.0	1.480	1.550	1.595	1.350	1.400	1.440
9.5	1.505	1.558	1.632	1.379	1.421	1.452
8.7	1.563	1.644	1.701	1.460	1.517	1.563
8.3	1.578	1.675	1.735	1.482	1.542	1.615
7.4	1.757	1.811	1.892	1.595	1.689	1.716
6.8	1.823	1.868	1.912	1.662	1.735	1.824
6.4	1.828	1.922	1.969	1.719	1.797	1.891
6.0	1.867	1.983	2.067	1.783	1.867	1.967
5.8	1.879	2.000	2.103	1.793	1.879	1.983
4.7	2.064	2.255	2.426	2.106	2.213	2.319

plots of molar conductance, μ against the square root of the soap concentration ($C^{½}$) are not linear which indicates that the soap behaves as a simple electrolyte in these solutions. The limiting molar conductance, μ_0 cannot be obtained by the usual extrapolation method as the Debye-Huckel Onsager's equation is not applicable to these soap solutions.

TABLE-3
MOLAR CONDUCTANCE (μ) (mhos cm^2 mol^{-1}) OF THE SOLUTIONS OF IRON AND COBALT SOAPS AT DIFFERENT TEMPERATURES

Concentration C × 10^3	Molar conductance (μ)					
	Iron laurate			Cobalt laurate		
	30ºC	40ºC	50ºC	30ºC	40ºC	50ºC
20.0	0.925	0.960	0.975	0.810	0.825	0.885
18.1	0.994	1.033	1.050	0.862	0.873	0.950
16.6	1.054	1.096	1.115	0.898	0.922	1.006
15.3	1.118	1.157	1.190	0.941	0.967	1.065
14.2	1.169	1.232	1.261	0.979	1.000	1.113
13.3	1.233	1.256	1.263	1.023	1.053	1.128
12.5	1.264	1.264	1.280	1.048	1.014	1.176
11.7	1.282	1.286	1.325	1.077	1.145	1.231
11.1	1.306	1.308	1.342	1.099	1.162	1.234
10.5	1.314	1.324	10.381	1.133	1.200	1.286
10.0	1.320	1.360	1.410	1.170	1.230	1.320
9.5	1.337	1.368	1.411	1.200	1.253	1.347
8.7	1.379	1.425	1.471	1.241	1.333	1.414
8.3	1.398	1.446	1.506	1.277	1.361	1.446
7.4	1.486	1.568	1.635	1.378	1.446	1.527
6.8	1.575	1.676	1.721	1.426	1.471	1.603
6.4	1.531	1.688	1.750	1.453	1.531	1.672
6.0	1.550	1.700	1.766	1.517	1.600	1.717
5.8	1.569	1.724	1.776	1.534	1.621	1.741
4.7	1.660	1.745	1.957	1.766	1.830	1.979

Assuming that the soaps are completely dissociated into M^{2+} and $RCOO^-$ ions. The dissociation of metal soaps may be represented as:

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

where M stands for iron and cobalt 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 soap.

The dissociation constant, K can be written as

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

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

TABLE-4
MOLAR CONDUCTANCE (μ) (mhos cm^2 mol^{-1}) OF THE SOLUTIONS OF IRON AND COBALT SOAPS AT DIFFERENT TEMPERATURES

Concentration $C \times 10^3$	Molar conductance (μ)					
	Iron myristate			Cobalt myristate		
	30ºC	40ºC	50ºC	30ºC	40ºC	50ºC
20.0	0.850	0.870	0.885	0.720	0.760	0.790
18.1	0.890	0.923	0.939	0.757	0.801	0.840
16.6	0.940	0.964	0.994	0.783	0.825	0.873
15.3	0.980	1.013	10.52	0.810	0.876	0.915
14.2	1.021	1.056	1.120	0.852	0.894	0.944
13.3	1.053	1.090	1.135	0.857	0.940	0.992
12.5	1.072	1.120	1.160	0.872	0.952	1.016
11.7	1.111	1.154	1.180	0.915	0.966	1.026
11.1	1.135	1.171	1.207	0.919	0.982	1.036
10.5	1.171	1.181	1.219	0.943	1.000	1.057
10.0	1.180	1.200	1.240	0.950	1.030	1.080
9.5	1.211	1.221	1.253	0.979	1.042	1.105
8.7	1.264	1.287	1.310	1.011	1.080	1.184
8.3	1.277	1.301	1.349	1.012	1.096	1.205
7.4	1.378	1.392	1.432	1.054	1.162	1.324
6.8	1.441	1.441	1.485	1.118	1.250	1.338
6.4	1.469	1.469	1.516	1.141	1.267	1.359
6.0	1.483	1.933	1.567	1.183	1.283	1.367
5.8	1.500	1.534	1.586	1.190	1.293	1.379
4.7	1.660	1.723	1.787	1.340	1.468	1.574

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

Assuming that the solutions do not deviate appreciably from ideal behavior and the activities of ions can be taken as almost equal to the concentration. Thus α may be replaced by the conductance ratio, μ/μ_0 where μ is the molar conductance at a finite concentration that is attributed to 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 eqn. 3 can be written as:

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

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.* $1/\mu$ below the CMC and are recorded in (Table-5). The results show that the values of limiting molar conductance increases while the dissociation constant decreases with increasing temperature.

TABLE-5
VALUE OF μ_0 OBTAINED FROM THE PLOT OF μ^2c^2 *vs.* $1/\mu$ OF THE SOLUTION OF IRON AND COBALT SOAP AT DIFFERENT TEMPERATURE (ºC)

Temp. (ºC)	Iron			Cobalt		
	Caprate	Laurate	Myristate	Caprate	Laurate	Myristate
30	4.20	6.55	7.32	3.90	5.50	6.50
40	5.22	7.40	8.45	4.50	6.00	7.00
50	6.23	8.33	9.02	5.60	6.70	7.40

The decrease in the values of dissociation constant with increasing temperature indicate the exothermic nature of the dissociation of iron and cobalt soaps in a mixture of benzene and methanol (50: 50 v/v).

The values of degree of dissociation (α) and dissociation constant (K) have been calculated at different concentration by using the value of μ_0 and eqn. 3. The plots of α *vs.* C show that the iron and cobalt soaps behaves as a weak electrolyte in these solutions. The values of dissociation constant remain almost constant in dilute solutions but show a drift at higher soap concentration, which may be due to the failure of Debye Huckel's activity equation at higher soap concentration.

The heat of dissociation is given by the relationship.

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

$$\log K = \frac{-\Delta H_D^0}{2.303RT} + \text{Constant} \qquad (5)$$

The values of the heat of dissociation ΔH_D^0 have been obtained from the slope of the linear plot of -log K *vs.* 1/T are recorded in (Table-6).

The negative values of heat of dissociation indicate the dissociation process is exothermic in nature.

The values of the change in free energy (ΔG_D^0) and entropy (ΔS_D^0) per mole for the dissociation process have been calculated (Table-7) using the relationship.

TABLE-6
VALUES OF THE HEAT OF DISSOCIATION (ΔH^0_D) (KJ mol^{-1}) FROM THE PLOT OF -log K *vs.* 1/T

Metal	Caprate	Laurate	Myristate
Iron	-227.27	-195.45	-172.41
Cobalt	-193.55	-166.67	-150.00

TABLE-7
THERMODYNAMIC PARAMETERS OF IRON AND COBALT SOAPS FOR DISSOCIATION PROCESS

Temp. (ºC)	Caprate		Laurate		Myristate	
	ΔG^0_D (KJ/mol)	$-S^0_D \times 10^2$ (KJ/mol K^{-1})	ΔG^0_D (KJ/mol)	$-S^0_D \times 10^2$ (KJ/mol K^{-1})	ΔG^0_D (KJ/mol)	$-S^0_D \times 10^2$ (KJ/mol K^{-1})
Iron soaps						
30	12.15	71.02	12.42	60.41	12.62	52.74
40	12.97	68.47	13.13	58.25	13.25	50.85
50	13.72	66.12	13.84	56.23	14.02	49.04
Cobalt soaps						
30	12.05	59.90	12.15	51.00	12.29	45.45
40	12.72	57.77	12.87	49.14	13.22	43.70
50	13.69	55.68	13.80	47.33	13.92	42.13

$$\Delta G^0_D = -RT \ln k_D \qquad (6)$$

$$\Delta S^0_D = \frac{[\Delta H^0_D - \Delta G^0_D]}{T} \qquad (7)$$

For the aggregation process, the standard free energy of micellization (per mole of monomer) ΔG^0_A for the phase separation model[18,19] (Table-8) is given by the relationship.

$$\Delta G^0_A = 2RT \ln X_{CMC} \qquad (8)$$

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-8
VALUES OF THE STANDARD FREE ENERGY OF MICELLIZATION ($KJ\ mol^{-1}$) OF IRON AND COBALT SOAPS FOR ASSOCIATION PROCESS

Temp. (ºC)	Caprate	Laurate	Myristate
Iron soaps			
30	-10.51	-10.57	-10.66
40	-10.82	-10.86	-10.95
50	-11.14	-11.17	-11.25
Cobalt soaps			
30	-10.72	-10.76	-10.86
40	-11.01	-11.08	-11.18
50	-11.33	-11.38	-11.50

The standard enthalpy change of micellization per mole of monomer for the phase separation model[20,21], ΔH_A^0 is given by the relationship.

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

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

The values of ΔH_A^0 of iron and cobalt soap have been calculated from the slope of the plots of- $\ln X_{CMC}$ *vs.* 1/T and the values are depicted in (Table-9).

TABLE-9
VALUES OF HEAT OF ASSOCIATION ($KJ\ mol^{-1}$) FROM THE PLOT OF $-\ln X_{CMC}$ *vs.* 1/T

Metal	Caprate	Laurate	Myristate
Iron	-5.15	-3.33	-2.55
Cobalt	-8.33	-6.38	-4.46

The values of ΔH_A^0 decreases as the CMC also decreases with increasing chain length of soap.

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 favoured over dissociation process.

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