Dissociation and Micellization of Strontium Palmitate and Stearate in 70/30 Chloroform-Propylene Glycol Mixture.

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The conductance of the non-aqueous solutions of strontium palmitate and stearate was measured at different temperatures (35 to 50° C). The derived values (critical micellar concentration, molar conductance at infinite dilution, degree of dissociation, dissociation constant and free energy change for dissociation and micellization process) showed that (i) strontium palmitate and stearate behave as weak electrolytes in 70/30 chloroform - propylene glycol mixture below the CMC and (ii) micellization process is predominant over the dissociation process.

The study of metallic soaps is becoming increasingly important in industry, technology and allied sciences. It has been a subject of intense investigation in the recent past on account of its role in such diversified fields as detergents, softners, stabilizers, plasticizers, lubricants, catalysts, cosmetics, medicines, emulsifiers and water - proofing agents. However, technological applications of metallic soaps are mostly based on empirical knowhow and the selection of a soap is dependent largely on economic factors.

A survey of literature [1-11] reveals that the physico-chemical studies and micellar behaviour of alkaline earth metal soaps have not yet been studied systematically although these soaps are being widely used in many industries. The present work deals with the studies on the conductance and micellar behaviour of strontium soaps in a mixture of 70% chloroform and 30% propylene-glycol at different temperatures.

EXPERIMENTAL

Strontium bromide, palmitic acid and stearic acid of AnalaR grade were used without further purification. The chloroform and propylene glycol used were of EM/ BDH make and of AR grade. Strontium soaps were prepared by the direct metathesis of corresponding potassium soap with the required amount of aqueous solution of strontium bromide at 50-60° C under vigorous stirring. The precipitated soaps were washed with distilled water followed by acetone to remove the excess of strontium ions and unreacted palmitic/stearic acid. These soaps were recrystallised, dried under reduced pressure and stored over dry calcium chloride.

Elemental analysis of strontium soaps were found to be in good agreement with the theoretically calculated values. The absence of hydroxyl group was confirmed by IR spectra. The purified soaps have the following melting points.

Strontium palmitate : 240.0° C
Strontium stearate : 245.0° C

The conductance of the solutions was measured with a Systronics conductivity Bridge 305 (SR. No.993) and a dipping type conductivity cell with platinized electrodes (cell constant 1.6). All measurements were made at 35-50 C (± 0.05° C). The specific and molar conductance were calculated.

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RESULTS AND DISCUSSION

The specific conductance, k (mhos cm^{-1}) of strontium palmitate and stearate, at low concentration in 70% chloroform and 30% propylene glycol mixture, increases linearly (Fig. 1) with increasing soap concentration and temperature. This may be due to the fact that these soaps behave as simple electrolytes in dilute solutions and are ionised to a considerable extent into strontium cations and palmitic/stearic acid

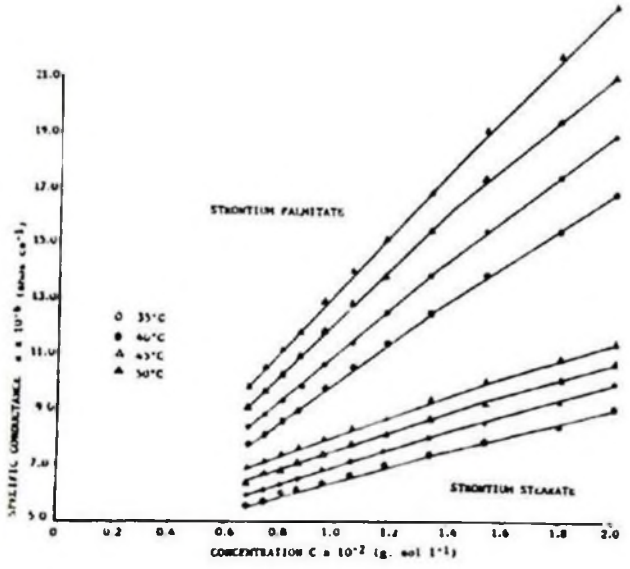


Fig 1. Specific Conductance *vs* Concentration Plots

Solvent: 70/30 chloroform/propylene glycol mixture

anions. The plots of specific conductance vs soap concentration (Fig. 1) show a break at higher concentration (CMC) indicating that the anionic species begin to associate together to produce ionic miscelles.

These results indicate that CMC also increases with the increase in temperature (Table 1). The process of micellization is assumed to occur when the energy released as a result of aggregation of the hydrocarbon chains of the monomer is sufficient to overcome and to balance the decrease in entropy accompanying aggregation. Since the kinetic energy of the monomer is higher at higher temperature, CMC is also higher.

Table 1

Critical Micellar Concentration (CMC in g mol. l^{-1}), Limiting Molar Conducatance, (in mhos cm^2/g mole) and Dissociation Constant, K_D of Strontium Palmitate and Strontium Stearate

Solvent: 70% Chloroform and 30% Propylene Gylcol Mixture (v/v).

Temp. (C)	35°	40°	45°	50°
Strontium Palmitate				
CMC x 10^{-2}	1.34	1.38	1.4	1.46
μ_o	1.36	1.42	1.51	1.58
K_D x 10^{3}	1.24	1.39	1.49	1.57
Strontium Stearate				
CMC x 10^{-2}	1.38	1.43	1.49	1.55
μ_o	1.03	1.10	1.15	1.25
K_D x 10^{4}	2.23	2.36	2.46	2.51

The molar conductance of the solutions (μ) decreases with the increase in soap concentration. This decrease may be due to the combined effects of (i) decreasing mobility due to ionic atmosphere and solvation of ions and (ii) also due to the formation of ionic micelles. The plots of molar conductance (μ) *vs* square root of soap concentration are not linear which indicates that the Debye-Huckel-Onsager equation is not applicable to these soap solutions; strontium palmitate/stearate behave as weak electrolytes in dilute solutions. The dissociation can be represented as [12]:

$$\underset{C(1-\alpha)}{Sr(COO)_2} \;\underset{}{<====>}\; \underset{C\alpha}{Sr^{2+}} + \underset{2C\alpha}{2RCOO^-} \quad .... (1)$$

Here C is the bulk concentration of the soap, α is the degree of dissociation. The dissociation constant (K_D) can be expressed as:

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

Since the values of degree of dissociation of strontium palmitate and stearate are small and the ionic concentrations are low, the interionic effects are almost negligible. Therefore, the dilute solutions may be assumed not to deviate appreciably from ideal behaviour and the activities of ions can be taken as almost equal to concentration. The degree of dissociation, α, has been calculated by the conductance ratio, μ/μ_o where μ is the molar conductance at finite concentration and μ_o is the limiting molar conductance at infinite dilution. Substituting $\alpha=\mu/\mu_o$ in eq (2) and rearranging, one obtains

$$\mu^2\ C^2 = \frac{K_D \mu_o^3}{4\ \mu} - \frac{K_D\ \mu_o^2}{4} \quad .....(3)$$

The values of dissociation constant and limiting molar conductance have been obtained from the slope and intercept of the plots of $\mu^2\ C^2$ *vs* $1/\mu$ and included in the Table 1. The increase in temperature brings about an increase in the limiting molar conducatance and dissociation constant.

The values of the dissociation constant are approximately constant in dilute solutions but drift with increasing soap concentrations. This drift in the values at higher concentrations may partly be due to the degree of dissociation being not exactly equal to the condutance ratio, but it is more due to the activity coefficients of ions not being equal to unity. Simple Debye - Huckel activity equation may fail at higher soap concentrations.

The dissociation constant K' is defined for cases having the activity coefficients of ions not equal to unity.

$$K' = \frac{4C^2\ \alpha^3}{(1-\alpha)} \cdot \frac{f_+\ f_-^2}{f_{soap}} \quad .... (4)$$

where f_+, f_- and f_{soap} refer to the activity coefficients of cation, anion and soap, respectively.

If the ionic strength is not too high, the activity coefficient of non ionised soap molecules (f_{soap}) may be taken as unity. Using Debye - Huckel's limiting law for activity coefficients, K_D, can be expressed as

$$\log K_D = \log K' + A' \sqrt{C\alpha} \quad .... (5)$$

The values of K' and A' have been obtained from the intercept and slope of the plots of $\log K_D$ *vs* $\sqrt{C\alpha}$. These values are recorded in Table 2.

Table 2

Values of constants K' and A' (obtained from the plots of $\log K_D$ *vs* $\sqrt{C\alpha}$

Temp. °C	Strontium Palmitate K' x 10^3	A'	Strontium Stearate K' x 10^4	A'
35	1.20	15.56	8.71	22.00
40	1.45	10.00	9.33	20.00
45	1.78	10.00	10.59	20.00
50	2.51	7.08	9.77	10.50

The heat of dissociation (ΔH°_D) is represented by the following expression

$$\log K_D = - \Delta H^\circ_D /(2.303RT) + C \quad .... (6)$$

The values of heat of dissociation (ΔH°_D) have been obtained from the slope of the linear plots of log K_D *vs* 1/T and are recorded in Table 3. The negative values of ΔH°_D indicate that the dissociation processs is exothermic in nature.

Table 3

Heat of Dissociation (ΔH°_D) and Micellization (ΔH_M) in kJ per mole of monomer

Electrolyte: Strontium Palmitate and Strontium Stearate

Solvent: 70% Chloroform and 30% Propylene-Glycol Mixture (v/v).

Soap	ΔH°_D	ΔH_M
Strontium Palmitate	-5.75	9.97
Strontium Stearate	-3.15	14.86

X_{CMC} is defined as the CMC expressed in terms of mole fraction and is explained on the basis of phase separation model [13 - 15] by the relationship

$$X_{CMC} = n_s/(n_s+n_o) \quad ..... (7)$$

where n_s and n_o are the number of moles of soap and solvent, respectively. Since the number of moles of free soap is small as compared to the number of moles of solvent, $n_s + n_o$ is nearly equal to n_o and X_{CMC} can be calculated as n_s/n_o. This has been calculated at different temperatures and presented in Table 4

Table 4

Values of $\ln X_{CMC}$ of Strontium Palmitate and Strontium Stearate.

Soap	< ——— $\ln X_{CMC}$ at ——— >			
	35° C	40° C	45° C	50° C
Strontium Palmitate	-6.864	-6.834	-6.806	-6.778
Strontium Stearate	-6.834	-6.799	-6.757	-6.718

The standard enthalpy change of micellization per mole of monomer ΔH°_M is given by the relationship

$$\ln X_{CMC} = \Delta H^\circ_M/(2RT) + C \quad ...(8)$$

The values of ΔH°_M of strontium palmitate and stearate have been obtained from the slope of linear plots of $\ln X_{CMC}$ *vs* 1/T (Fig.2) and are included in Table 3.

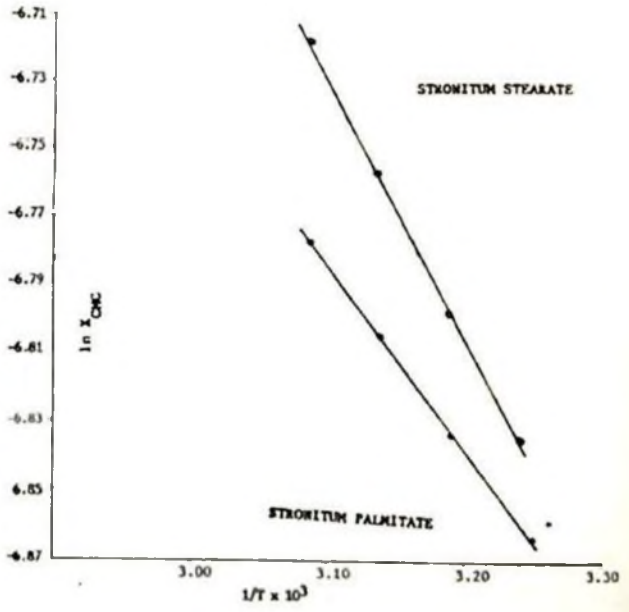


Fig 2 $\ln X_{CMC}$ *vs* 1/T plots

The values of change in free energy, ΔG°_{D}, and entropy ΔS°_{D} per mole for the process of dissociation have been calculated by using the relationship

$$\Delta G^{\circ}_{D} = -RT \ln K_{D} \quad \ldots\ldots (9)$$

and

$$\Delta S^{\circ}_{D} = (\Delta H^{\circ}_{D} - \Delta G^{\circ}_{D})/T \quad \ldots\ldots (10)$$

The calculated values of ΔG°_{D} and ΔS°_{D} are recorded in Table 5.

For the micellization process, the standard free energy of micellization per mole of monomer (ΔG°_{M}) is calculated by the following relationship:

$$\Delta G^{\circ}_{M} = 2RT \ln X_{CMC} \quad \ldots\ldots (11)$$

and included in the same Table.

Table 5

Free Energy (in kJ mol^{-1}) and entropy (in kJ mol^{-1} degree^{-1}) of dissociation and micellization processes

Electrolyte: Strontium Palmitate and Strontium Stearate

Solvent: 70% chloroform and 30% propyleneglycol mixture

Temp. °C	Dissociation Process ΔG°_{D}	ΔS°_{D}	Micellization Process ΔG°_{M}	ΔS°_{M}
Strontium Palmitate				
35	8.78	-4.72	-17.60	8.95
40	8.57	-4.58	-17.81	8.88
45	8.62	-4.52	-18.02	8.87
50	8.55	-4.43	-18.23	8.73
Strontium Stearate				
35	10.78	-4.52	-17.53	10.52
40	10.88	-4.48	-17.72	10.41
45	11.00	-4.45	-17.89	10.30
50	11.15	-4.43	-18.07	10.20

A careful scrutiny of thermodynamic parameters (Table 5) indicates that the micellization process is favoured over the dissociation process.

These results showed that the thermodynamics of dissociation and micellization can be explained satisfactorily in the light of phase separation model. These results also indicated that the strontium palmitate and stearate behave as weak electrolytes and micellization process is predominant over the dissociation process.

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