

Thermodynamics of Dissociation and Micellization of Manganese Caprylate and Laurate in 70/30 (v/v) Benzene-Methanol Mixture

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The conductivity results showed that manganese caprylate and laurate behave as weak electrolyte in dilute solutions and the micellization was found to be dominant over the dissociation process. The values of the critical micellar concentration of these soaps increase with an increase in temperature and the dissociation constant, degree of dissociation and limiting molar conductance were evaluated from conductivity measurements.

INTRODUCTION

Carboxylate of metals other than alkali metals are generally insoluble in water and are called *metallic soaps*. The metallic soaps are soluble in a wide variety of pure and mixed organic solvents and yield liquids, gels and dispersion with characteristic colloidal properties. The physical properties of the solutions of metal soaps in organic solvents can be interpreted in terms of the micellar theory. A micelle is an aggregate of three or more soap molecules existing in the liquid thermodynamically stable equilibrium. The main cause of micellization is the energy change due to dipole-dipole interaction between the polar head groups of the surfactant molecules. Several workers¹⁻¹² have measured the critical micellar concentration and colloidal behaviour and time effect in the supramolecular formation of cobalt and other transition metal soaps in non-aqueous medium. The studies on transition metal soaps have not yet been carried out systematically inspite of their large scale applications in different industries.

The present paper deals with the conductance behaviour of manganese caprylate and laurate in 70/30 benzene-methanol mixture (v/v) with a view to study the micellar phenomenon and to evaluate the various thermodynamic parameters both for the dissociation and micellization process.

EXPERIMENTAL

AnalaR-grade manganese acetate and fatty acids were used without further purification. The benzene and methanol used were AnalaR-grade (EM/BDH) chemicals. Manganese soaps were prepared by the metathesis of corresponding potassium soaps with the required amount of manganese acetate in water-alcohol medium at 50 to 60°C. The precipitated manganese soaps were washed with

distilled water, methanol and acetone two times to remove excess of metal contents and unreacted fatty acids. The elemental analysis and IR spectra give an idea about the purity of these soaps. The melting points of the purified manganese caprylate and laurate were found to be 92.6°C and 99.0°C. Two samples of the same soaps were prepared under similar conditions in order to check the reproducibility of the results.

The conductance of the soaps in 70/30 benzene-methanol mixture (v/v) was measured with a Systronics conductivity Bridge 305 (SR N.993) and a dipping type conductivity cell (cell constant 1.6) with platinized electrodes. All the measurements were made at 35–50°C ($\pm 0.05^\circ\text{C}$). The specific and molar conductance were expressed in mhos cm^{-1} and $\text{mhos cm}^2/\text{g mole}$, respectively.

RESULTS AND DISCUSSION

The increase in specific conductance of the non-aqueous solutions of manganese caprylate and laurate with an increase in soap concentration (Fig. 1) may be due to the fact that manganese soaps behave as simple electrolyte below the CMC and are considerably ionized into manganese cations Mn^{2+} and fatty acid anions. However, the increase in the specific conductance at higher soap concentration is probably due to the formation of ionic micelles. The values of CMC of these soaps are summarised in Table-1. It is apparent that the CMC increases with increasing temperature because the micellization is assumed to occur when the energy released as a results of aggregation of the hydrocarbon chains of the monomer is sufficient to overcome to the electrical repulsion between the ionic head groups and to balance the decrease in entropy accompanying aggregation. Therefore, increase in temperature would have been expected to increase the CMC values since the kinetic energy of the monomer would have been increased.

TABLE-1
CRITICAL MICELLAR CONCENTRATION (CMC), LIMITING MOLAR CONDUCTANCE, (μ_0) AND DISSOCIATION CONSTANT (K_D) OF MANGANESE SOAPS IN 70/30 BENZENE-METHANOL MIXTURE (V/V)

Manganese Caprylate	Temperature ($^\circ\text{C}$)			
	35	40	45	50
$\text{CMC} \times 10^{-3} (\text{g. mol l}^{-1})$	5.50	5.70	5.80	6.05
$\mu_0 (\text{mhos cm}^2/\text{g mole})$	3.90	4.33	4.91	5.50
$K_D \times 10^{-6}$	18.0	13.7	10.3	7.5
$\ln X_{\text{CMC}}$	-7.932	-7.896	-7.870	-7.837
Manganese Laurate	Temperature ($^\circ\text{C}$)			
	35	40	45	50
$\text{CMC} \times 10^{-3} (\text{g. mol l}^{-1})$	4.70	4.90	5.10	5.30
$\mu_0 (\text{mhos cm}^2/\text{g mole})$	3.50	4.15	4.62	5.21
$K_D \times 10^{-6}$	10.1	7.8	5.9	4.4
$\ln X_{\text{CMC}}$	-8.089	-8.048	-8.008	-7.969

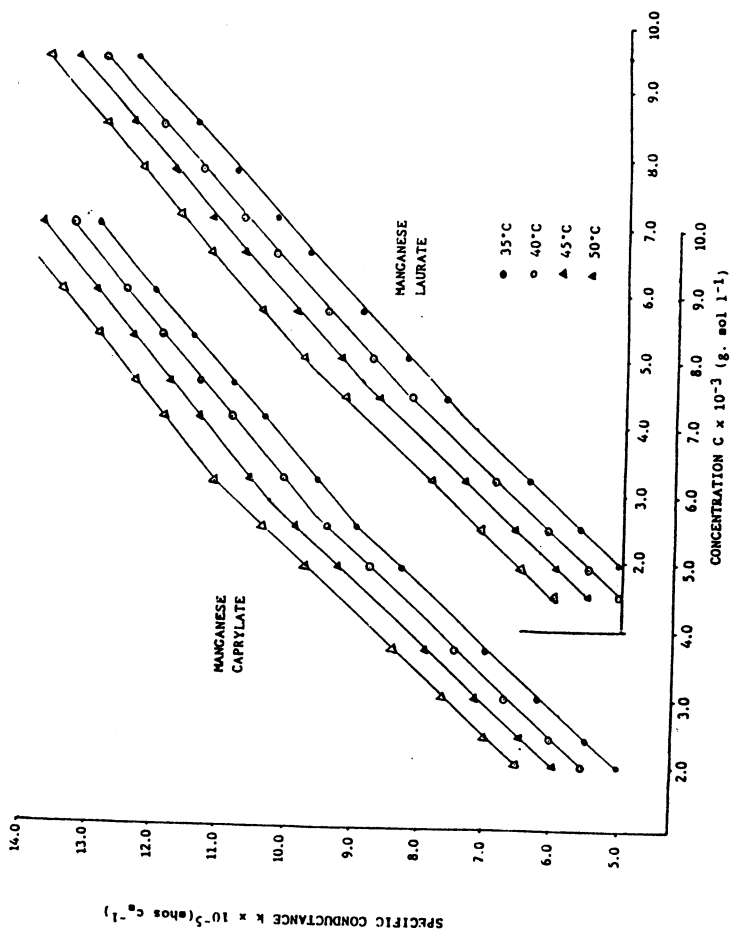


Fig. 1. Specific conductance vs concentration manganese caprylate and laurate in 70:30 benzene methanol mixture.

The molar conductance of the dilute solutions of manganese caprylate and laurate in 70/30 benzene-methanol mixture decrease with an increase in soap concentration. The values of critical micellar concentration can not be however, obtained due to the concave nature of the plots of molar conductance against square root of soap concentration. This indicates that manganese soaps behave as weak electrolyte in dilute solutions and Debye-Huckel Onsager's equation is not applicable to these soap solutions. Since these metal soaps behave as weak electrolyte in dilute solutions, the following expression¹³ for their dissociation may be derived.

$$\mu^2 C^2 = \frac{K_D \mu_0^3}{4\mu} - \frac{K_D \mu_0^2}{4} \quad (1)$$

The values of the dissociation constant K_D and the molar conductance at infinite dilution, μ_0 have been determined from the slope and intercept of the linear plots of $\mu^2 C^2$ vs $1/\mu$ for dilute soap solutions. The values of limiting molar conductance and dissociation constant K_D increase with the increase in temperature. The degree of dissociation, α at different temperatures and concentrations have been calculated by assuming it as equal to the ratio of molar conductance, μ/μ_0 . These results show that zinc soaps behave as weak electrolyte in 70/30 benzene-methanol (v/v) mixture. The values of degree of dissociation of manganese caprylate and laurate decrease rapidly in dilute solutions with increasing soap concentration whereas it decreases slowly above the CMC.

The values of dissociation constant are almost constant in very dilute solutions but exhibit a drift with increasing concentration which indicates that manganese soaps do not behave as very weak electrolyte in 70/30 benzene-methanol mixture. The drift in the values of dissociation constant with increasing concentration may be due to the fact that the degree of dissociation is not exactly equal to the ratio of molar conductance, μ/μ_0 but mainly due to the fact that the activity coefficients of ions are not equal to unity at higher soap concentrations.

The dissociation constant K' of manganese soaps in 70/30 benzene-methanol mixture when the activity coefficients of ions are not equal to unity can be expressed as:

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

Where f_+ , f_- and f_{soap} refer to activity coefficients of cations, anions and soaps, respectively. If the ionic strength is not too high the activity coefficients of non-ionised molecules of soap *i.e.* f_{soap} may be taken as unity and using Debye-Huckel's limiting law for activity coefficients, K' can be expressed as:

$$\log K = \log K' + A' \sqrt{C\alpha} \quad (3)$$

The values of K' and A' have been obtained from the intercept and slope of the $\log K$ vs $\sqrt{C\alpha}$ and are recorded in Table-2. The heat of dissociation ΔH_D and the standard enthalpy change of micellization ΔH_m per mole of monomer for the phase separation model¹⁴⁻¹⁶ have been calculated (Table-3) by the following relationships.

TABLE-2
VALUES OF CONSTANTS K' and A' obtained from the plots of $\log K_D$ Vs $\sqrt{C\alpha}$

Temperature (°C)	Manganese Caprylate		Manganese Laurate	
	K'	A'	K'	A'
35	1.20×10^{-5}	18.18	1.24×10^{-5}	5.00
40	1.12×10^{-5}	21.43	0.88×10^{-5}	7.50
45	0.93×10^{-5}	37.30	0.82×10^{-5}	12.50
50	0.75×10^{-5}	38.89	0.69×10^{-5}	16.17

TABLE-3
VALUES OF HEAT OF DISSOCIATION AND MICELLIZATION (PER MOLE OF MONOMER) OF MANGANESE CAPRYLATE AND LAURATE IN 70/30 BENZENE-METHANOL MIXTURE (V/V)

Soap	Heat of Dissociation ΔH_D KJ mol ⁻¹	Heat of Micellization ΔH_m KJ mol ⁻¹
Manganese Caprylate	- 80.35	11.65
Manganese Laurate	- 23.01	15.07

For dissociation process:

$$\frac{\partial(\log K_D)}{\partial T} = \frac{\Delta H_D}{RT^2}$$

or

$$\log K_D = -\frac{\Delta H_D}{2.303 RT} + C \quad (4)$$

For micellization process:

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

$$\ln X_{CMC} = \frac{\Delta H_m}{2RT} + C \quad (5)$$

Where X_{CMC} is the CMC expressed in terms of mole fraction (Table-1) and is explained by the relationship.

$$X_{CMC} = n_s/(n_s + n_o) \quad (6)$$

Where n_s and n_o are the number of moles of soap and solvent, respectively. Since the number of moles of free soap, n_s is very small as compared to the number of moles of solvent n_o , so the equation No. 6 can be written as:

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

The values of heat of dissociation, ΔH_D and micellization ΔH_m have been

obtained from the slope of the linear plots of $\log K_D$ vs $1/T$ and $\ln X_{CMC}$ vs $1/T$ for manganese caprylate and laurate in 70/30 benzene-methanol mixture are recorded in Table-3. The values of heat of dissociation and micellization indicate that the dissociation process is exothermic in nature while micellization was found to be endothermic.

The values of the change in free energy ΔG_D^0 and entropy, ΔS_D^0 per mole of monomer for the dissociation process have been calculated by using the following relationships.

$$\Delta G_D^0 = -RT \ln K_D \quad (8)$$

$$\Delta S_D^0 = (\Delta H_D - \Delta G_D)/T \quad (9)$$

The values of ΔG_D^0 and ΔS_D^0 of manganese caprylate and laurate at different temperatures are recorded in Table-4.

TABLE-4
THERMODYNAMIC PARAMETERS OF DISSOCIATION AND MICELLIZATION
PROCESS OF MANGANESE CAPRYLATE AND LAURATE IN 70/30 BENZENE-
METHANOL MIXTURE

Temperature (°C)	Dissociation Process		Micellization Process	
	ΔG_D KJ mol ⁻¹	$\Delta S_D \times 10^2$ KJ mol ⁻¹	G_m KJ mol ⁻¹	$\Delta S_m \times 10^2$ KJ mol ⁻¹
Manganese Caprylate				
35	14.00	- 30.00	- 20.34	10.38
40	14.58	- 30.33	- 20.58	10.29
45	15.21	- 30.05	- 20.84	10.21
50	15.86	- 29.79	- 21.08	10.06
Manganese Laurate				
35	14.74	- 12.26	- 20.74	11.63
40	15.33	- 12.25	- 20.97	11.51
45	15.95	- 12.25	- 21.20	11.41
50	16.57	- 12.25	- 21.43	11.30

The standard free energy ΔG_m^0 for the micellization process (per mole monomer) is calculated by the equation (Table-4).

$$\Delta G_m^0 = 2RT \ln X_{CMC} \quad (10)$$

The scrutiny of the thermodynamic parameters, calculated by above mentioned equations indicate that negative values of free energy of micellization, ΔG_m^0 and the positive values of entropy for micellization ΔS_m^0 (Table-4) and positive values of free energy for dissociation ΔG_D^0 and negative values of entropy for dissociation process ΔS_D^0 , the micellization process is dominant over the dissociation process.

It is, therefore, concluded that the values of the critical micellar concentration of manganese caprylate and laurate in 70/30 benzene-methanol mixture increase with increasing temperature and the micellization process was found to be

dominant over dissociation process. These results also indicated that the manganese soaps behave as weak electrolytes in non-aqueous medium.

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