Micellization and Dissociation Behaviour of Zinc Stearate in Methanol-*p*-Xylene Mixtures by Conductance Measurements

G.H. SONAWANE†, B.B. PATIL‡, H.A. PATIL** and V.S. SHRIVASTAVA*

Department of PG Studies and Research in Chemisry, G.T.P. College
Nandurbar-425 412, India
E-mail: clayminerals@yahoo.com

The critical micellar concentration of zinc stearate in a mixtures of methanol-*p*-xylene of varying compositions was determined at different temperatures (308.15, 313.15, 318.15, 323.15 K) by conductance measurement. The value of CMC increases with increase in temperature. The dissociation constant, degree of dissociation and limiting molar conductance were evaluated from conductivity measurements. The results show that this soap behaves as weak electrolyte in dilute solutions and the micellization process was dominant over the dissociation process.

Key Words : Zinc soap, Conductance, Micellization.

INTRODUCTION

The importance of metal soaps has already been realized owing to their proven utility as corrosion inhibiting agents, drier, catalyst stabilizers, lubricant dispersants and fungicides[1–6]. The soaps are useful for specific purposes on account of their various fundamental properties. A survey of literature[7–10] on transition metal soaps revealed that the studies on zinc soaps have not been thoroughly investigated despite their numerous applications in various industries[11, 12].

The present work deals with the study of micellization and dissociation behaviour of the solutions of zinc stearate in a mixture of methanol-*p*-xylene (70 : 30, 50 : 50, 30 : 70 v/v) at different temperatures by conductivity measurements. The various thermodynamic parameters for dissociation and micellization process have also been evaluated.

EXPERIMENTAL

All the chemicals were used of AR grade. Stearic ʌcid (50 g) was dissolved in 160 mL of alcohol at 65°C and neutralized with 2N solution of carbonate-free

†Kisan Arts, Commerce & Science College, Parola, Dist. Jalgaon-425 111, India.
‡Nutan Junior Science College, Dondaicha, Tal. Shindkheda, Dist. Dhule-425 408, India.
**Jai Hind Arts, Commerce and Science College, Dhule, Dist. Dhule-424 002, India.

potassium hydroxide. The resulting gel was liquefied by heating and the solution added slowly with vigorous stirring to a warm solution of zinc acetate in 50% alcohol. The zinc acetate was slightly in excess of that required for complete reaction. The precipitated soap was washed free of soluble impurities with double distilled water and to remove unreacted fatty acid or potassium soap by alcohol and acetone. After passing out the solvent, the soap was oven-dried at about 60°C and finally powdered and stored in a glass-stoppered bottle. Solutions of varying concentrations of this soap were prepared by dissolving known amount of soap in a mixture of methanol-*p*-xylene (v/v) and were kept for 2 h in a thermostat at the desired constant temperature.

A digital Equiptronics conductivity meter model EQ-664 was used for conductance measurements of soap solutions. The measurements were made at 308.15–313.15 (±0.05) K. The specific and molar conductances are expressed in mhos cm^{-1} and mhos cm^2/g-mol respectively.

RESULTS AND DISCUSSION

The results achieved during the course of the present investigation are given in Tables 1–4 and Fig. 1. The increase in specific conductance of the solutions of zinc stearate in methanol-*p*-xylene mixture with an increase in soap concentration and with increasing amount of methanol is presented in Fig. 1. This may be due to the fact that zinc stearate behaves as a weak electrolyte in dilute

TABLE-1

CRITICAL MICELLAR CONCENTRATION (CMC), LIMITING MOLAR
CONDUCTANCE (μ_0) AND DISSOCIATION CONSTANT (K_D) OF
ZINC STEARATE IN METHANOL-*p*-XYLENE MIXTURES

Temperature (°C)	35	40	45	50
70 : 30 Methanol-*p*-xylene Mixture				
CMC × 10^{-3} (g mol L^{-1})	6.90	7.01	7.24	7.46
μ_0	44.97	51.29	59.53	63.09
K_D × 10^{-4}	2.129	1.443	1.195	0.934
50 : 50 Methanol-*p*-xylene Mixture				
CMC × 10^{-3} (g mol L^{-1})	5.81	5.92	5.98	6.02
μ_0	24.16	24.62	25.87	26.35
K_D × 10^{-4}	2.030	1.801	1.449	1.334
30 : 70 Methanol-*p*-xylene Mixture				
CMC × 10^{-3} (g mol L^{-1})	4.07	4.83	5.27	5.69
μ_0	19.13	19.87	20.45	21.32
K_D × 10^{-4}	2.453	1.652	1.204	1.019

solutions and is considerably ionized into a zinc cation (Zn^{2+}) and fatty acid ($C_{18}H_{35}COO^-$). However, the increase in specific conductance at higher soap concentration is probably due to the formation of ionic micelles. The values of critical micellar concentration of zinc stearate in mixture of methanol-p-xylene are tabulated in Table-1. The CMC increases with increasing temperature because the micellization is assumed to occur when energy is released as a result of aggregation of hydrocarbon chain. The monomer is sufficient to overcome the electrical repulsion between the ionic head group and to balance the decrease in entropy accompanying aggregation. Therefore, increase in temperature would have been expected to increase the CMC value since the kinetic energy of the monomer would have been increased.
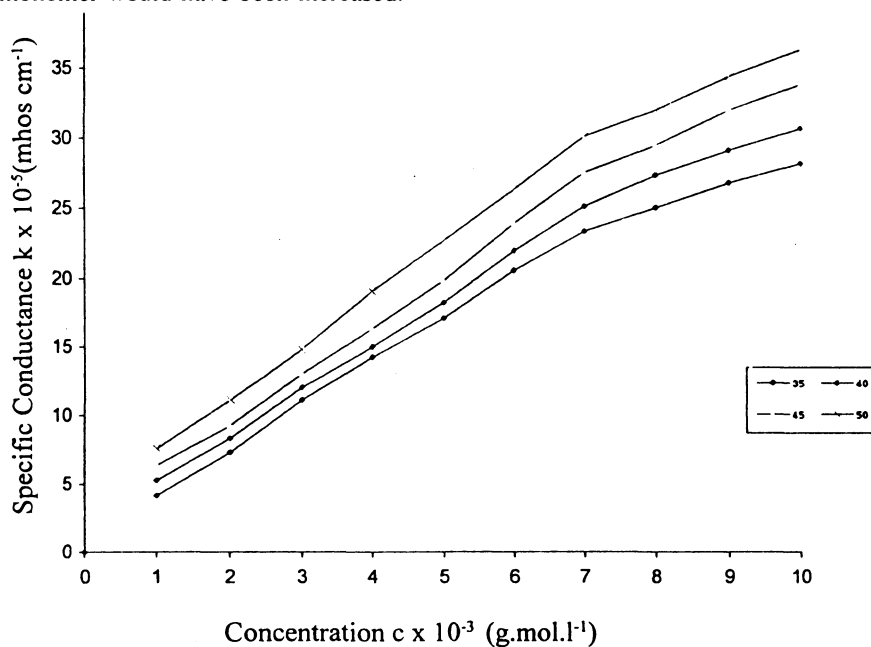

Fig. 1. Specific conductance *vs.* concentration of zinc stearate in 70/30 methanol-p-xylene mixtures at different temperatures

TABLE-2
HEAT OF DISSOCIATION AND MICELLIZATION (PER MOLE
OF MONOMER) OF ZINC STEARATE IN
METHANOL-p-XYLENE MIXTURES

Methanol	Heat of dissociation (ΔH_D kJ mol^{-1})	Heat of micellization (ΔH_m kJ mol^{-1})
70%	−44.25	11.10
50%	−23.11	5.77
30%	−14.20	4.45

TABLE-3

VALUE OF ln X_{CMC} ZINC STEARATE IN
METHANOL-*p*-XYLENE MIXTURES

Temperature	ln X_{CMC}		+
	70 : 30	50 : 50	30 : 70
	Methanol-*p*-xylene mixtures		
35	−5.64	−5.63	−5.76
40	−5.62	−5.60	−5.59
45	−5.59	−5.59	−5.49
50	−5.55	−5.58	−5.41

TABLE-4

THERMODYNAMIC PARAMETERS OF DISSOCIATION AND MICELLIZATION PROCESS OF ZINC STEARATE IN METHANOL-*p*-XYLENE MIXTURES

Temperature (°C)	Dissociation process		Micellization process	
	ΔG_D^o (kJ mol^{-1})	$\Delta S_D^o \times 10^2$ (kJ mol^{-1})	ΔG_m^o (kJ mol^{-1})	$\Delta S_m^o \times 10^2$ (kJ mol^{-1})
70 : 30 Methanol-*p*-xylene				
35	21.66	−21.39	−28.91	5.77
40	23.02	−21.48	−29.28	5.80
45	23.88	−21.41	−29.57	5.81
50	24.93	−21.40	−29.85	5.79
50 : 50 Methanol-*p*-xylene				
35	21.78	−14.56	−28.86	7.49
40	22.45	−14.54	−29.20	7.48
45	23.38	−14.61	−29.59	7.48
50	23.97	−14.57	−30.02	7.50
30 : 70 Methanol-*p*-xylene				
35	21.84	−11.69	−29.54	8.14
40	23.18	−11.93	−29.10	7.87
45	23.45	−11.83	−29.08	7.74
50	24.04	−11.83	−29.10	7.63

The decrease in molar conductance μ of zinc stearate solution with increase in soap concentration is due to the combined effect of ionic atmosphere decrease in mobility, solvation and formation of ionic micelles. The critical micellar concentration, *i.e.*, CMC however cannot be determined from the plots of μ *vs.* $\sqrt{c}$ which are concave upwards with increasing slopes, indicating that zinc stearate behaves as weak electrolyte in dilute solutions, so that Debye-Huckel-Onsager's equation is not applicable for these soap solutions. Since these metal soaps behave as weak electrolytes in dilute solutions, the following expression (1) for their dissociation can be derived:

$$\mu^2 c^2 = \frac{K_D \mu_0^3}{4\mu} - \frac{K_D \mu_0^2}{4} \tag{1}$$

The values of the dissociation constant K_D and limiting molar conducatnce μ_0 have been determined from the slope, $[K_D\mu_0^3]/4$ and the intercept $[K_D\mu_0^2]/4$ of the linear plots of μ^2c^2 vs. $1/\mu$ for dilute soap solutions. The results show that the value of molar conductance at infinite dilution and dissociation constant K_D increases with increasing temperature. The values of dissociation, α, for different concentrations and temperatures have been determined by assuming it as equal to conductance ratio μ/μ_0. The values of molar conductance were found to decrease with decrease in amount of methanol.

The value of degree of dissociation of soap decreases 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 zinc stearate does not behave as a very weak electrolyte in methanol-p-xylene 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 conductance ratio μ/μ_0 but mainly due to the fact that the activity coefficient of ions is not equal to unity at higher soap concentrations.

The heat of dissociation ΔH_D° for zinc stearate has been calculated by using the following expression:

$$\frac{\partial(\log K)}{\partial T} = \frac{\Delta H_D}{RT^2} \quad \text{or} \quad \log K = -\frac{\Delta H_D}{2.303RT} + C \tag{2}$$

The values of heat of dissociation ΔH_D° which have been evaluated (Table-2) from the slope of linear plots of log K vs. $1/T$ are -44.25, -23.11 and -14.20 kJ mol^{-1} for zinc stearate in 70%, 50% and 30% methanol respectively.

The values of the change in free energy ΔG_D° and change in entropy ΔS_D° per mole of monomer for the dissociation process have been calculated by using the following relationship:

$$\Delta G_D^\circ = -RT \ln K_D \tag{3}$$

$$\Delta S_D = (\Delta H_D - \Delta G_D)/T \tag{4}$$

The values of ΔG° and ΔS° at different temperatures for dissociation and micellization process are recorded in Table-4. The standard free energy ΔG_m° per mole of monomer for the phase separation model[13-15] is calculated by the relationship

$$\Delta G_m = 2RT \ln X_{CMC} \tag{5}$$

where X_{CMC} is the CMC expressed in terms of mole fraction (Table-3) and is represented by the relationship:

$$X_{CMC} = \frac{n_s}{(n_s + n_0)} \tag{6}$$

where n_s and n_0 are the number of moles of soap and solvent, respectively, since the number of moles of free soap, n_s, is small as compared to the number of moles of solvent n_0; hence equation (6) can be written as

$$X_{CMC} = n_s/n_0 \tag{7}$$

The standard enthalpy change of micellization per mole of monomer for the phase separation model[13-15] ΔH_m is given by the relationship

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

$$\ln X_{CMC} = \frac{\Delta H_{in}}{2RT} + C \tag{8}$$

The values of ΔH_m° of zinc stearate have been determined from the slope of linear plot of $\ln X_{CMS}$ *vs.* $1/T$ which are presented in Table-2. The positive values of ΔH_m° indicate that micellization is endothermic in nature.

A careful scrutiny of the thermodynamic parameters indicates that negative values of ΔG_m°, positives values of ΔS_m° for the micellization process (Table-4), positive values of ΔG_D° and negative values of ΔS_D° for the association process are favoured over the dissociation process.

It is, therefore, concluded that zinc stearate behaves as a weak electrolyte in methanol-*p*-xylene mixtures. The values of the critical micellar concentration increase with increasing temperature and the micellization process is predominant over dissociation process.

ACKNOWLEDGEMENTS

REFERENCES

1. V.A. Tulupov and M.I. Gagarina, *Zh. Fiz. Khim.*, **38**, 1695 (1964).
2. J.W. Larsen and L.W. Chang, *J. Org. Chem.*, **41**, 3382 (1976).
3. M.D. Goff, R.L. Shumack, K.L. Tilt and A.K. Hagan, *J. Arboricult.*, **22**, 201 (1996).
4. S.K. Upadhyaya and P.S. Sharma, *Indian J. Chem.*, **34A**, 220 (1995).
5. K.N. Mehrotra, K. Tandon and M.K. Rawat, *Bull. Electrochem.*, **7**, 237 (1991).
6. T.G. Sokolove, L.Yu. Ishchuk, N.S. Goshko, V.A. Vrol and V.V. Sinitsyn, *Kolloidu Zh.*, **33**, 859 (1971).
7. R.P. Varma and S. Shukla, *Tenside Surfactant Detergents*, **20**, 192 (1983).
8. K.N. Mehrotra, V.P. Mehta and T.N. Nagar, *J. Prolet Chem.*, **545**, 312 (1970).
9. K.N. Mehrotra, S. Singh and A. Kumar, *Indian J. Chem.*, **31A**, 756 (1992).
10. S.K. Upadhyaya and P.S. Sharma, *Asian J. Chem.*, **6**, 871 (1994).
11. K N. Mehrotra and D. Pooranchand, *Tenside Surfactant Detergent*, **25**, 180 (1988).
12. K.N. Mehrotra and R. Kachhwaha, *Bull. Inst. Politch. Lasi Sec.*, **224**, 45 (1978).
13. B.C. Barry and G.F.J. Russel, *J. Colloid. Interface Sci.*, **40**, 174 (1972).
14. D.C. Robins and I.L. Thomas, *J. Colloid. Interface Sci.*, **26**, 407 (1968).
15. D. Attwood and A.T. Florence, Surfactant System, Chapman & Hall, London, p. 100 (1983).
16. V.P. Mehta, P.R. Talesara and R. Sharma, *Indian J. Chem.*, **40A**, 399 (2001).