

Conference Paper

Thermodynamics of Dissociation and Micellization of Sodium Surfactant Solutions in Formamide

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Abstract

Electrical conductivity and surface tension measurement of sodium surfactants, such as sodium caprylate, sodium laurate, sodium palmitate and sodium stearate, in formamide has been determined at different temperatures. The methods show that micelles are formed in formamide solution. Critical micelle concentration (CMC) has been determined for each of the sodium surfactants. The result show that these surfactants behave as a weak electrolyte in dilute solution of formamide below the critical micellar concentration, and the conductance result can be explained on the basis of Ostwald's formula and Debye-Huckel's theory of weak electrolytes. The dissociation constant and thermodynamic parameters for dissociation and micellization processes of these surfactants are also evaluated. The micellization process has been found to be predominant over the dissociation process.

Keywords: Critical Micelle Concentration (CMC), Micellization, Conductivity, Dissociation, Thermodynamics, Surface Tension

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1. Introduction

The study of metallic soaps is becoming increasingly important in technological and academic fields. It has been a subject of intense investigations in the recent past on account of its role in such diversified fields as detergents, softeners, stabilizers, plasticizer, lubricants, cosmetics, medicines, emulsifier, insecticides and water-proofing agents [1–9].

Several researchers [10–19] have prepared transition metallic soaps by treating the fatty acid with the requisite amount of metal oxide or hydroxide in the presence of aqueous to non-aqueous solutions. The critical micelle concentration (CMC) of these soap solutions, both in aqueous and in non-aqueous or in mixture of these solvents at different temperatures were determined using conductometrically and by ultrasonic

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velocity measurements. Few researchers [19, 20] studied the thermodynamics of dissociation and micellization of metallic soaps in mixed organic solvents to determine physicochemical properties and structures.

The present work deals with the evaluation of CMC values, degree of dissociation (α), dissociation constants (K_d), of sodium surfactants (caprylate, laurate, palmitate and stearate) in formamide by conductivity and surface tension measurements at different temperatures. These two methods are used to check the reliability and reproducibility of CMC values. The various aspects of the interaction of these surfactants in formamide during micelle formations are also discussed. Molar conductance at infinite dilution and the determination of thermodynamic parameters for sodium surfactants in formamide by conductivity measurements at different temperatures were also determined. Formamide, a non-aqueous solvent was chosen, because of its relative permittivity of 109.5 and surface tension of 58.5 mNm^{-1} at 25°C , has sufficient cohesive force to favor adsorption and micellar aggregation, while its dielectric properties ensure that solutions of ionic surfactants have electrolyte properties closely resembling those of aqueous solutions [9]. Some of the physical properties of water and formamide which influence micelle formation are given in table I [21, 22].

TABLE 1: A comparison of some of the physical properties of formamide and water.

Property	Formamide ²⁰	Water ²¹
Dipole moment, D	3.37	1.87
Dielectric constant	109.5 (20°C)	78.45 (25°C)
Surface tension, Nm^{-1}	58.35 (20°C)	62.60 (80°C)
Viscosity, cp	3.764 (20°C)	0.3547 (80°C)
Specific conductance, Scm^{-1}	2×10^{-7} (20°C)	10^{-6} (25°C)

2. Experimental

Formamide was obtained from FLUKA (purity >99%), specific conductance of the formamide at 22°C was found to be $2 \times 10^{-7} \text{ S cm}^{-1}$. For quality assurance purposes, the surface tensions of surfactant solutions are determined using a stalagmometer (TRAUB'S STALAGMOMETER Model 4855). The instrument consists of a straight tube which widens out in the upper part to form a bulb and narrows to a capillary tube in lower part, the open of which is ground smooth. The instrument is calibrated using water and formamide.

All the surfactants used in the present work obtained from FLUKA (purity > 99%), and were used without further purification. Specific conductivities of the solutions

were measured at a different temperature using a CRISON Model 225 CONDUCTMETER and a dipping cell with platinum electrodes (cell constant = 0.12 cm^{-1}). The reproducibility of the instruments was better than 0.1%, and accuracy was better than 0.2%.

3. Results and Discussion

Molar conductance, Λ , of sodium surfactant solutions in formamide decreased with increasing concentration and chain length of the surfactants are reported in table II. For each of the surfactant a drop in the molar conductivity is observed at a concentration, to determine the CMC as described elsewhere [23–27]. The decrease in molar conductivity is attributed to the combined effects of ionic atmosphere, solvation of ions, and decrease of mobility and ionization with the formation of micelles. Similar behavior was observed in using surface tension method (table II). For calculating CMC, tangents are drawn on the two portions (pre-micellar and post micellar regions) of the plots. Points of intersection of these tangents give the CMC [23–27]. The CMC values by these methods are reported in Table III which shows that micelle formations take places at a define soap concentration. It may be noted from Table III that the CMC values, obtained from surface tension measurements, are, in general, appreciably lower than those obtained from the conductance being presumably due to the difference in precision obtained in two methods.

TABLE 2: Molar conductance and surface tension of sodium (caprylate, laurate, palmitate and stearate) in formamide at $25^\circ\text{C} \pm 0.2^\circ\text{C}$.

$c \times 10^4 / \text{mol L}^{-1}$	Caprylate		Laurate		Palmitate		Stearate	
	$\Lambda / S \text{ cm}^2 \text{ mol}^{-1}$	γ / Nm^{-1}	$\Lambda / S \text{ cm}^2 \text{ mol}^{-1}$	γ / Nm^{-1}	$\Lambda / S \text{ cm}^2 \text{ mol}^{-1}$	γ / Nm^{-1}	$\Lambda / S \text{ cm}^2 \text{ mol}^{-1}$	γ / Nm^{-1}
0	2.300	0.032	2.240	0.030	2.200	0.028	2.140	0.026
3.0	2.140	0.029	2.100	0.027	2.060	0.026	2.020	0.025
4.0	2.080	0.027	2.000	0.026	1.960	0.025	1.920	0.024
5.0	1.920	0.025	1.900	0.024	1.840	0.023	1.800	0.022
6.0	1.780	0.024	1.720	0.023	1.700	0.022	1.760	0.021
7.0	1.700	0.022	1.680	0.021	1.640	0.020	1.620	0.019
8.0	1.600	0.020	1.580	0.019	1.560	0.018	1.520	0.016
9.0	1.540	0.019	1.540	0.018	1.520	0.017	1.500	0.015
10.0	1.500	0.018	1.480	0.017	1.460	0.016	1.420	0.014

This behavior suggests that the surfactants form micelle in formamide. It was also observed that the higher the chain length of the surfactant, the lower the solubility of

TABLE 3: Critical micelle concentration (CMC) of sodium surfactants in formamide at 25°C ± 0.2 °C.

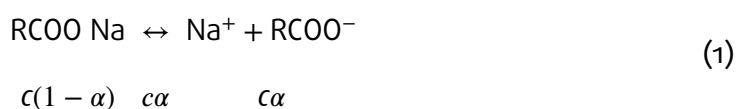
surfactant	C _n	CMC x 10 ⁴ .molL ⁻¹	
		A ^a	B ^b
Sodium caprylate	C ₈	8.6	8.0
Sodium laurate	C ₁₂	7.6	7.4
Sodium palmitate	C ₁₆	6.8	6.5
Sodium stearate	C ₁₈	6.2	6.1

^aConductivity method; ^bSurface tension method

the surfactant in formamide. Similar behavior has been reported for these surfactants in aqueous solution^{28–32}.

CMC for these surfactants in formamide is lower than in water at 22°C^{28–32}. As mentioned earlier, the dielectric constant of water is lower than the dielectric constant of formamide, and the dipole moment of formamide is twice that of water. It seems that dielectric constant plays a more dominant role in CMC formation than dipole moment. The ionization of the surfactants in formamide is higher than in water because formamide has a higher dielectric constant. Therefore, there is tendency of forming micelle at a lower concentration. The CMC for these surfactants in formamide shows that sodium surfactants behave as weak electrolytes in dilute solutions, and the extended Debye–Huckel–Onsager equation is not applicable to these surfactant solutions.

The probable mode of dissociation of surfactants in formamide can be represented as follows:



Where α is a degree of dissociation of surfactants. The dissociation constant K_d can be written as:

$$K_d = \frac{[\text{Na}^+][\text{RCOO}^-]}{[\text{RCOONa}]} = \frac{c\alpha^2}{(1 - \alpha)} \quad (2)$$

Since ionic concentrations are low and interionic effects are almost negligible in dilute solutions, the solutions of surfactants do not deviate appreciably from ideal behavior, and the activities of ions can be taken as almost equal to concentrations. The degree of dissociation, α , may be replaced conductance ratio Λ/Λ_{∞} , where Λ is the molar conductance at finite concentration and Λ_{∞} is the limiting molar conductance at infinite dilution.

By substituting the value of α and rearranging equation (1) can be written as follows

$$c\Lambda = \frac{K_d\Lambda_0}{\Lambda} - K_d\Lambda_0 \tag{3}$$

The values of K_d from table V were calculated from the slope ($K_d\Lambda_0^2$) and intercept ($-K_d\Lambda_0$) of the linear portion of the plots of $c\Lambda$ vs. $1/\Lambda$ below the CMC (table IV and figure I. It is seen that the values of K_d decreased with an increase in the numbers of carbon atoms in the surfactant molecules, i.e. with increasing chain length of the surfactant.

TABLE 4: The values of Λ_c and $1/\Lambda$ for sodium surfactants in formamide at $25^\circ\text{C} \pm 0.2^\circ\text{C}$.

Caprylate		Laureate		Palmitate		Stearate	
$\Lambda_c \times 10^7 / \text{Scm}^2\text{L}^{-1}$	$1/\Lambda / \text{S}^{-1}\text{cm}^{-2}\text{mol}$	$\Lambda_c \times 10^7 / \text{Scm}^2\text{L}^{-1}$	$1/\Lambda / \text{S}^{-1}\text{cm}^{-2}\text{mol}$	$\Lambda_c \times 10^7 / \text{Scm}^2\text{L}^{-1}$	$1/\Lambda / \text{S}^{-1}\text{cm}^{-2}\text{mol}$	$\Lambda_c \times 10^7 / \text{Scm}^2\text{L}^{-1}$	$1/\Lambda / \text{S}^{-1}\text{cm}^{-2}\text{mol}$
5.70	0.435	5.48	0.446	5.40	0.455	4.28	0.467
6.88	0.467	6.46	0.476	6.18	0.485	5.56	0.495
7.82	0.481	8.00	0.500	6.76	0.510	6.92	0.521
9.50	0.521	8.60	0.526	8.20	0.543	8.10	0.556
10.70	0.562	10.60	0.581	10.20	0.588	9.11	0.568
11.90	0.588	11.80	0.595	11.50	0.610	10.30	0.617
13.10	0.625	12.85	0.633	12.50	0.641	12.20	0.658
14.00	0.641	13.90	0.649	13.70	0.658	13.00	0.667
15.00	0.667	14.80	0.676	14.60	0.684	14.20	0.704

TABLE 5: Values of Λ_0 and K_d as obtained from the plot of Λ_c vs. $1/\Lambda$ for sodium surfactants in formamide at various temperatures.

Surfactants	298 K		303 K		308 K		313 K	
	$\Lambda_0 / \text{Scm}^2\text{mol}^{-1}$	$K_d \times 10^4$	$\Lambda_0 / \text{Scm}^2\text{mol}^{-1}$	$K_d \times 10^4$	$\Lambda_0 / \text{Scm}^2\text{mol}^{-1}$	$K_d \times 10^4$	$\Lambda_0 / \text{Scm}^2\text{mol}^{-1}$	$K_d \times 10^4$
Sodium caprylate	8.540	0.953	8.685	0.944	8.830	0.929	8.922	0.914
Sodium laurate	8.143	1.372	8.286	1.356	8.424	1.333	8.510	1.310
Sodium palmitate	8.019	1.424	8.156	1.406	8.294	1.380	8.378	1.356
Sodium stearate	7.987	1.576	8.124	1.552	8.262	1.526	8.342	1.498

However, the decrease in the values of dissociation constant with increasing temperature indicates the exothermic nature of the dissociation of sodium surfactants in formamide.

The heat of dissociation, ΔH_d , for sodium surfactants is determined with the following equation

$$\frac{\partial(\log K_d)}{\partial T} = \frac{\Delta H_d}{RT^2} \tag{4}$$

TABLE 6: Values of Thermodynamic Parameters G_m^o , H_m^o and S_m^o for sodium surfactants in formamide at $25^\circ\text{C} \pm 0.2^\circ\text{C}$.

Surfactants	C_n	$\Delta G_m^o / \text{kJmol}^{-1}$	$H_m^o / \text{kJmol}^{-1}$	$S_m^o / \text{Jmol}^{-1}\text{K}^{-1}$
Sodium Caprylate	C_8	-25.31	-4.89	68.5
Sodium Laurate	C_{12}	-25.56	-6.64	63.5
Sodium palmitate	C_{16}	-25.86	-7.02	63.2
Sodium Stearate	C_{18}	-26.18	-7.43	62.6

$$\log K_d = -\frac{\Delta H_d}{2.303RT} + C \tag{5}$$

The values of heat of dissociation, ΔH_d , were obtained from the slopes of the linear plots of $\log K_d$ vs. $1/T$ (Figure 2), and are shown in table VI. The negative values of heat of dissociation, ΔH_d , indicate that the dissociation process for sodium surfactants is exothermic in nature.

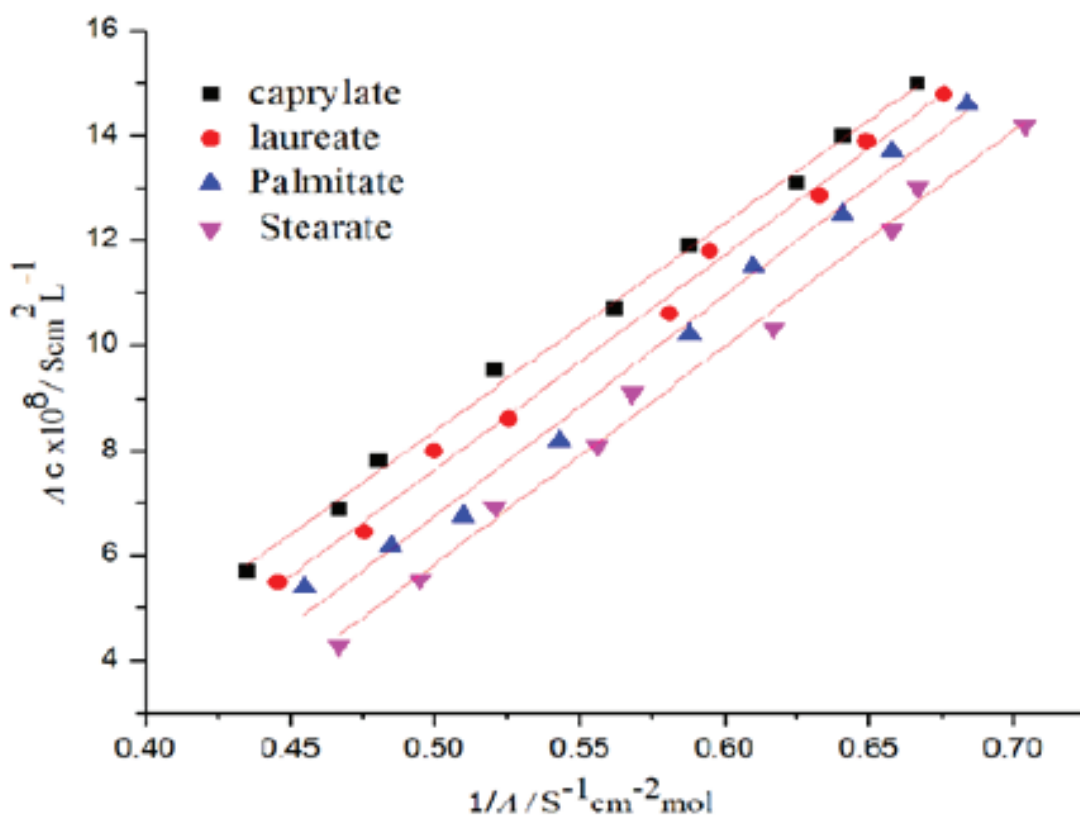


Figure 1: The plot of ΔG vs. $1/\Delta$ for sodium surfactants in formamide at $25^\circ\text{C} \pm 0.2^\circ\text{C}$.

The values of change in free energy, ΔG_d and entropy, ΔS_d per mole for the dissociation process are calculated by using the relationships:

$$\Delta G_d = -RT \ln K_d \tag{6}$$

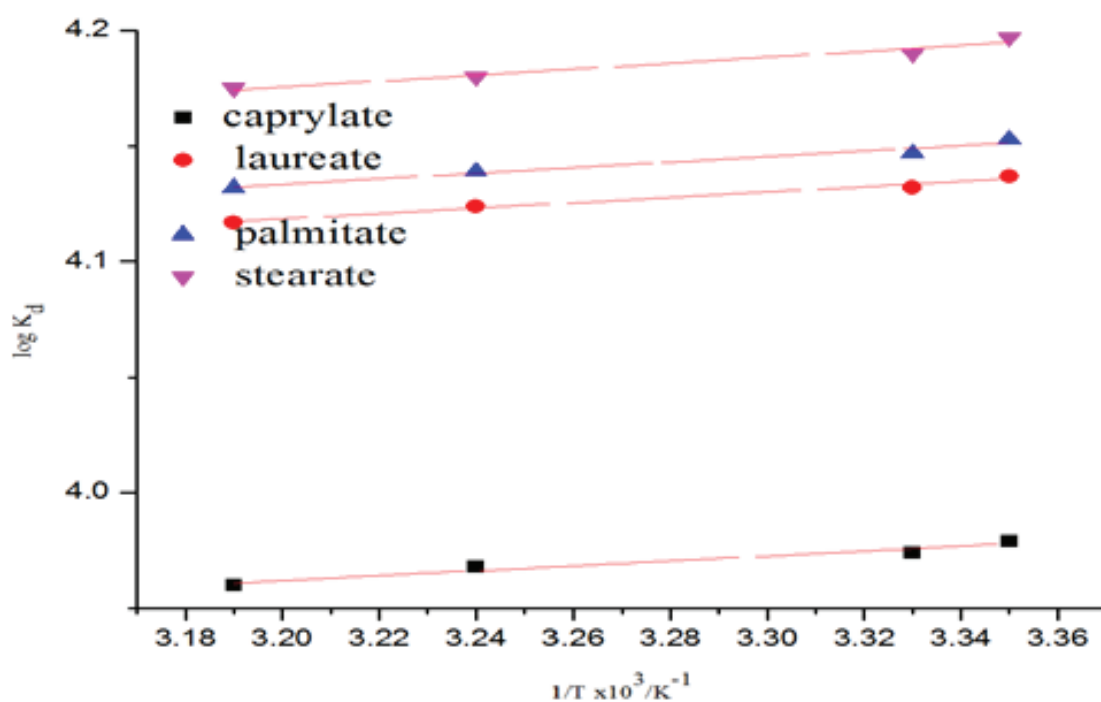


Figure 2: The plot of $\log K_d$ vs. $1/T$ for sodium surfactants in formamide at $25^\circ\text{C} \pm 0.2^\circ\text{C}$.

$$S_d = \frac{\Delta H_d - \Delta G_d}{T} \quad (7)$$

The calculated values of ΔG_d and ΔS_d are shown in Table VI. The thermodynamic parameters indicates that the negative values of ΔG_d , and positive values of ΔS_d for the dissociation process (Table VI) show that the dissociation process is a non-spontaneous occurrence physicochemically for sodium surfactants (caprylate, laurate, palmitate and stearate) in formamide.

However, as can be seen in table VI, the values of change in free energy, ΔG_d increased with increasing temperature whereas the values of entropy, ΔS_d decreased. Since the solute ions are aggregated to form the colloidal particles as micelles near the CMC value and after the CMC the micellization process is replaced the dissociation process, the negative changes of entropy may be obtained below the CMC value.

According to our previous work [23–27], the parameters for the thermodynamics of dissociation and micellization of sodium surfactants in formamide indicates that the negative values of ΔG_m and positive values of ΔS_m for the micellization process and positive values of ΔG_d and negative values of ΔS_d for the dissociation process show that the micellization process is favored over the dissociation process and the micellization is spontaneous occurrence but the dissociation is non spontaneous.

4. Conclusion

The results of conductivity and surface tension show that sodium surfactants in formamide behave as weak electrolytes in dilute solutions below CMC. The results also confirm that there is a significant interaction between surfactant and solvent molecules. The conductivity results show that the thermodynamics of dissociation and association can satisfactorily be explained in the light of phase separation model. The results showed that the micellization process is predominant over the dissociation process and sodium surfactants behaved as weak electrolyte in organic solvent.

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