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Micellization and Thermodynamic Behavior of Anionic Surfactant in Mixed Organic Solvent

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ABSTRACT:

The micellar behavior of anionic surfactants ie. zinc hexanoate and decanoate as zinc mono alkanoates and butanedioate and hexanedioate as dialkanoates in a mixture of benzene-methanol (50% v/v) have been determined by conductometric measurements at different temperatures. The results indicates that alkanoate solutions of zinc mono alkanoates behave as moderate electrolyte while, dialkanoates of zinc behave as weak electrolytes in dilute solution. The values of CMC decreases with increasing chain length of fatty acid component. The molar conductance, degree of ionization constant, ionization and various thermodynamic parameters have also been evaluated for both ionization and micellization process.

KEY WORDS: Anionic surfactants; micellization; moderate electrolyte; thermodynamic parameter.

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1. INTRODUCTION

Surface active agents are characterized by the possession of both polar and non-polar regions in the same molecule. This dual nature is responsible for the phenomenon of surface activity, and micellization and solublization. The dual nature of a surfactant is typified by metal alkanoates or alkanoates can be called association colloids, indicating their tendency to associate in solution, forming particles of colloidal dimensions.

During last decades considerable work have been reported on mono-carboxylic metal alkanoates of alkaline earth, transition metal and lanthanides, whereas the studies on dicarboxylic metal alkanoates have remained almost untouched with the result that only few references[1-5] are available in this relatively unexplored field. The studies on the nature and structure of these alkanoates are of great importance for their uses in industries and explaining their characteristics under different conditions. The application of metal alkanoates largely depends on their physico-chemical properties such as physical state, thermal stability, chemical reactivity and solubility in polar and non-polar solvents. Burrows et al[1] synthesized dicarboxylic acid metal alkanoates by metathesis and Ikhuoria et al[2] studied the effect of temperature on the stability of metal alkanoates of dicarboxylic acids. Liu et al[3] synthesized different metal dialkanoates such as calcium glutarate, zinc glutarate, calcium sebacate and zinc sebacate and discussed their use as thermal stabilizers for PVC material. Barbara and Lacz[4] studied the thermal decomposition of cadmium butanedioate dihydrate. Liu et al[5] synthesized different metal dialkanoates such as calcium glutarate, zinc glutarate, calcium sebacate and zinc sebacatand and discussed their use as thermal stabilizers for PVC material. A number of workers have used ultrasonic[6] measurements of metal alkanoates for the determination of ion-solvent interaction in organic solvents. Viscometric[7], conductometric[8-9] measurements and thermodynamic[9-10] parameters of the solution of lanthanide and transition metal alkanoates have been reported in different organic solvents.

In this paper, we have presented effect of temperature on CMC alongwith dissociation and association constants with the determination of various thermodynamic parameters of anionic surfactants ie. zinc mono-(hexanoate and decanoate) and di- (butanedioate and hexanedioate) alkanoates in mixed organic solvent of benzene and methanol (50% v/v) at different (20, 30 and 40±0.05ºC) temperature.

2. EXPERIMENTAL

All the chemicals used were of BDH/AR grade. Solvents benzene and methanol were purified by distillation under reduced pressure. Zinc mono- (hexanoate and decanoate) alkanoates were synthesized by direct metathesis of corresponding potassium alkanoates as mentioned in our earlier publications[6,9], while di-alkanoates of zinc were synthesized by metathesis[1-2] in alcohol solution. The zinc di-alkanoates (butanedioate and hexanedioate) was first prepared by dissolving the dicarboxylic acid in hot ethanol, followed by treatment with potassium hydroxide solution. To this mixture, solution of the metal salt was added slowly with continuous stirring. The precipitated soap of the dicarboxylic acid was filtered off, washed with hot water and air-dried. The alkanoates were purified by recrystallization with alcohol and dried under reduced pressure. The purity was checked by their melting points (hexanoate-130.0°C decanoate-92.0°C and butanedioate-310.0°C hexanedioate-263.0°C) and absence of hydroxylic group was confirmed by IR spectra. The reproducibility of the results was checked by preparing two samples of the same alkanoates under similar conditions.

The solutions of anionic surfactants of zinc were prepared by dissolving a known amount of alkanoates in a benzene-methanol mixture (50% v/v) and were kept for 2 hr in a thermostat at different (20, 30 and 40±0.05ºC) temperature. The zinc alkanoates do not possess high solubility in pure solvents thus measurements were conducted in benzene - methanol mixture. A digital conductivity meter (Toshniwal CL 01.10A) and a dipping type conductivity cell with platinized electrodes (cell constant 0.895) were used for measuring the conductance of solutions of zinc alkanoates in mixed organic solvent at different temperature.

3. RESULTS AND DISCUSSION

Specific conductance, k of the solutions of anionic surfactants of zinc in a mixture of benzene and methanol (50% v/v) increase with increase in concentration of soap concentration, C, as well as temperature (Fig.1-2). It may be due to the fact that anionic surfactant behave as moderate electrolyte in dilute solutions, and are considerably ionized into a simple metal cations, Zn^{2+} and fatty acid anions, $RCOO^-$ (where R is C_5H_{11} and C_9H_{19} for hexanoate and decanoate, respectively) and $R(COO^-)_2$ (where R is C_2H_4 and C_4H_8 for butanedioate and hexanedioate , respectively) in dilute solutions due to the formation of micelles at higher soap concentrations. The decrease in specific conductance, k with increase in chain length of fatty acid may be due to the increasing size and decreasing mobility of anions with increasing the number of carbon atoms in the zinc alkanoates. The values of critical micellar concentration, CMC (Table 1) of these mono- alkanoates have been determined by k-C plot (Fig.1).

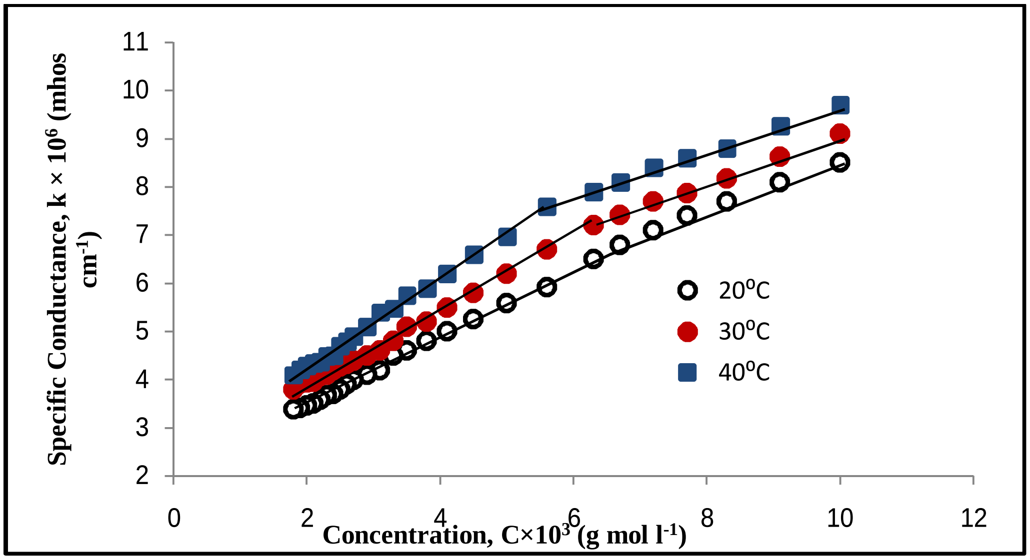

Fig. 1 Specific conductance vs concentration zinc hexanoate

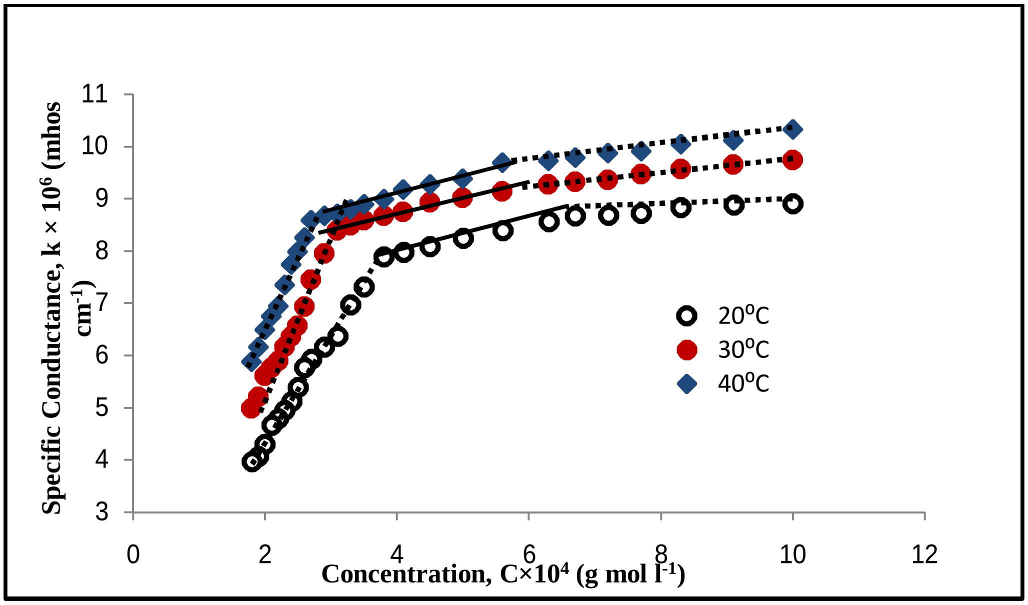

Fig.2 Specific conductance vs concentration zinc hexanedioate

The concentration at which micelles formation starts known as critical micellar concentration (CMC), beyond this concentration the bulk properties of the surfactant, such as osmotic pressure, turbidity, solublization, surface tension, viscosity, ultrasonic velocity and conductivity changes abruptly. If the micelles are formed in non-aqueous medium the aggregates are called “reversed micelles” in this case the polar head groups of the surfactant are oriented in the interior and the lyophilic groups extended outwards in to the solvent. It is suggested that the zinc mono alkanoates are considerably ionized in dilute solutions and the anions begin to aggregate to form micelles. These micelles are in thermodynamic equilibrium with the metal ions, Zn^{2+} mono alkanoate ions, $RCOO^-$ present in the solution. The increase in conductance above the CMC may be due to the liberation of some of attached counterions from the micelles. The values of CMC decrease with increase in temperature of solution as well as chain length of fatty acids constituent of zinc alkanoates molecule (Table 1).

Table 1: CMC(mol dm^{-3}) values of anionic surfactants of zinc

	Hexanoate	Decanoate	Butanedioate		Hexanedioate	
			CMC(I)	CMC(II)	CMC(I)	CMC(II)
20°C	6.7	6.5	3.8	6.7	3.5	6.5
30°C	6.3	5.6	3.1	6.3	2.9	6.1
40°C	5.6	5.0	2.8	5.8	2.6	5.4

The plots of k-C (Fig.2) of zinc dialkanoates have been characterized by two breaks at definite concentration which corresponds to the critical micellar concentration, CMC (I) and CMC (II) in organic solvent. The appearance of CMC (I) and CMC (II) can be explained on the basis of the formation of ionic and neutral micelles in the surfactant solution. It is indicated that the soap is considerably ionized in dilute solution and the anions begin to aggregate, to form ionic micelles at CMC (I). The dialkanoates are largely present in the form of ionic micelles at moderate concentration between CMC (I) and CMC (II) and there is an interesting formation of neutral micelles takes place at the CMC (II). The dipole-dipole interactions between the head groups of the surfactant molecules act as a deriving force for the formation of micelles. The decrease in CMC with increasing temperatures may be due to the reduction in the thickness of ionic atmosphere surrounding the polar head groups and consequent decreased repulsion between them[11].

The molar conductance, Λ of the solutions of anionic surfactant decreases with increasing soap concentration may be due to the combined effects of ionic atmosphere, solvation of ions, decrease of mobility of ion and ionization and formation of micelles. Since the molar conductance of the solutions of anionic surfactant of zinc does not vary linearly with the square root of soap concentration, the Debye-Huckel-Onsager’s equation[12] is not applicable to these solutions. Molar conductance results show that soap solutions of mono-alkanoates of zinc behave as moderate electrolyte while, zinc dialkanoates behave as weak electrolytes in dilute solutions and ionization of zinc alkanoates may be explained by Ostwald's manner.

If C, is the concentration and α is the degree of dissociation of zinc alkanoates, molar concentration may be represented as follows: For mono alkanoates

$$Zn(RCOO)_2 \rightleftharpoons Zn^{2+} + 2RCOO^-$$

$$C(1-\alpha) \qquad C\alpha \quad 2C$$

And for di-alkanoates-

$$Zn[R(COO)_2]_2 \rightleftharpoons Zn^{2+} + 2R(COO-)_2$$

$$C(1-\alpha) \qquad C\alpha \quad 2C$$

The dissociation constant, K_d, for this equilibrium may be expressed as follows:

for mono alkanoates-

$$K_d = [M^{2+}]\,[RCOO^-]^2/[M(RCOO)_2]$$

$$= 4C^2\,\alpha^3/(1-\alpha) \qquad (1)$$

For di-alkanoate -

$$K_d = [Zn^{2+}]\,[(R(COO)_2)^-]^2/[Zn(R(COO)_2)_2] \quad = 4C^2\,\alpha^3/(1-\alpha) \qquad (2)$$

Since, ionic concentration are low and inter-ionic effects are almost negligible in dilute solutions, the solution of zinc alkanoates do not deviate appreciably from ideal behavior, and the activities of ions can be taken as almost equal to the concentrations of anionic surfactant anionic surfactant solution. The degree of dissociation, α, may be replaced by the conductance ratio, Λ/Λ_∞, where Λ and Λ_∞($cm^2\ mol^{-1}$) are the molar conductance at finite and infinite dilution, respectively. By substituting the value of α and rearranging equation (1 and 2)

$$\Lambda^2C^2 = \frac{K_d\Lambda^3{}_\infty}{4\Lambda} - \frac{K_d\Lambda^2{}_\infty}{4} \qquad (3)$$

The values of dissociation constant, K_d , and limiting molar conductance, Λ_∞ (Table 2) were obtained from the slope, $K_d\Lambda^3{}_\infty/4\Lambda$ and intercept $-K_d\Lambda^2{}_\infty/4$ of the linear part of the plots of Λ^2C^2 vs $1/T$ below critical micellar concentration.

Table 2: Values of limiting molar conductance, Λ_∞ and dissociation constant, K_d at different temperatures

Zinc alkanoates	20^0C		30^0C		40^0C	
	Λ_∞	K_d	Λ_∞	K_d	Λ_∞	K_d
Hexanoate	1.91	12.28×10^{-5}	2.21	8.42×10^{-5}	2.32	6.61×10^{-5}
Decanoate	1.62	9.55×10^{-5}	1.90	6.20×10^{-5}	2.30	4.37×10^{-5}
Butanedioate	6.38	4.35×10^{-7}	6.78	3.35×10^{-7}	7.51	2.06×10^{-7}
Hexanedioate	1.73	7.61×10^{-7}	3.47	5.47×10^{-7}	4.25	4.10×10^{-7}

It is seen that dissociation constant, K_d decreases with an increase in the numbers of carbon atoms in soap molecules i.e., with increasing chain length of the mono-(hexanoate to decanoate) and di-(butanedioate to hexanedioate) alkanoates. However, the decrease in the values of dissociation constant with increasing temperature indicates the exothermic nature of the dissociation of zinc alkanoates in benzene-methanol mixture (50% v/v).

The heat of dissociation, $\Delta H^0{}_d$ for anionic surfactant is determined[9-10,13] with the following equation.

$$\frac{\partial(\log K_d)}{\partial T} = \frac{\Delta H^0{}_d}{RT^2} \tag{4}$$

$$\log K_d = -\frac{\Delta H^0{}_d}{2.303RT} + C \tag{5}$$

The values of heat of dissociation $\Delta H^0{}_d$ were obtained from the slope of the linear plots of $\log K_d$ vs $/T$ (Fig.3) and are recorded in Table 3. The negative values of heat of dissociation, ΔH_d, indicate that the dissociation process for anionic surfactant of zinc is exothermic in nature.

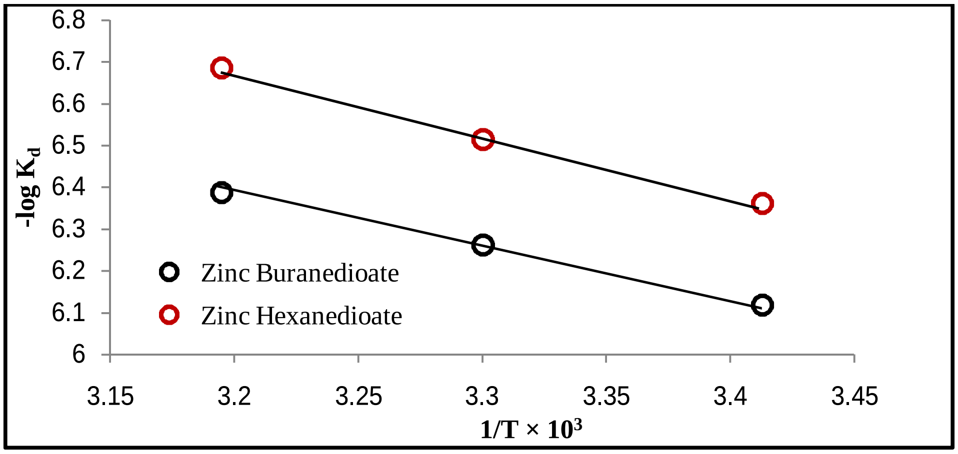

Fig. 3 -log K_d vs 1/T zinc dialkanoates

The values of standard free energy change, $\Delta G^0{}_d$ and standard entropy change, $\Delta S^0{}_d$ per mole for dissociation process are calculated[9-10, 13] by using the relationship

$$\Delta G^0{}_d = -RT \ln K \tag{6}$$

Where, K, is the equilibrium constant.

$$T\Delta S^0{}_d = \Delta H^0{}_d - \Delta G^0{}_d \tag{7}$$

The calculated values of, $\Delta G^0{}_d$ and $\Delta S^0{}_d$ are shown in Table 4. Careful scrutiny of thermodynamic parameters indicates that the positive values of $\Delta G^0{}_d$ and negative values of $\Delta S^0{}_d$ for the dissociation process (Table. 4) show that the dissociation process is a nonspontaneous process for mono-(hexanoate to decanoate) and di-(butanedioate to hexanedioate) alkanoates in benzene –methanol mixture (50% v/v).

For the micellization process, when counterions are bound to micelles, the standard free energy of micellization per mole of monomer, $\Delta G^0{}_a$ (Table 5), for the phase separation model[14-16] is given by relationship:

$$\Delta G^0{}_a = 2RT \ln X_{cmc} \tag{8}$$

Where X_{cmc} is the CMC expressed as a mole fraction and is defined by:

$$X_{cmc} = \frac{n_s}{n_s + n_0} \tag{9}$$

As the number of moles of free surfactant, n_s is small as compared to the number of moles of solvent, n_0 then

$$X_{cmc} = \frac{n_s}{n_0} \tag{10}$$

The standard enthalpy of micellization per mole of monomer, $\Delta H^0{}_a$ for the phase separation model is given by the relationship:

$$\frac{\partial(\ln X_{cmc})}{\partial T} = \frac{\Delta H^0{}_a}{2RT^2} \tag{11}$$

$$\ln X_{cmc} = \frac{\Delta H^0{}_a}{2RT} + C \qquad (12)$$

The values of $\Delta H^0{}_a$ were obtained from the slope of linear plots of $\ln X_{cmc}$ vs $/T$ (Fig.4) and are recorded in Table 3.

Table 3: Heat of dissociation, $\Delta H^0{}_d$ and Heat of association, $\Delta H^0{}_a$ of anionic surfactants

zinc alkanoates	$-\Delta H^0{}_d$ (kJ mol^{-1})	$-\Delta H^0{}_a$ (kJ mol^{-1})
Hexanoate	23.63×10^{-3}	13.67×10^{-3}
Decanoate	29.82×10^{-3}	18.82×10^{-3}
Butanedioate	28.50×10^{-3}	23.28×10^{-3}
Hexanedioate	23.59×10^{-3}	22.67×10^{-3}

The positive values of $\Delta H^0{}_a$ indicate that the micellization process of zinc alkanoates in benzene-methanol (50% v/v) is endothermic.

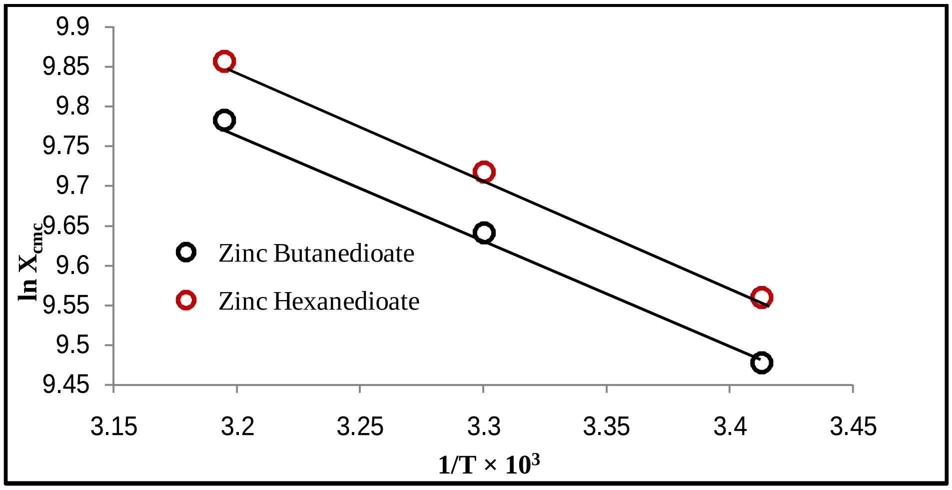

Fig. 4 ln X_{cmc} vs 1/T zinc dialkanoates

The standard entropy change per mole of monomer (Table. 5) is calculated by relationship:

$$T\Delta S^0{}_a = \Delta H^0{}_a - \Delta G^0{}_a \qquad (13)$$

The negative enthalpy change of dissociation (Table. 3) tends to make up for the unfavorable change in free energy and entropy of dissociation process (Table.4). On the other hand, the negative free energy and positive entropy (Table. 5) favor micellization and compansate for the unfavorable enthalpy change for the process (Table 3). The results show that the association process is dominant over the dissociation process.

Table 4: Free energy of dissociation, $\Delta G^0{}_d$, Entropy of dissociation, $\Delta S^0{}_d$, of anionic surfactants at different temperatures

	20^0C		30^0C		40^0C	
zinc alkanoates	$\Delta G^0{}_d$ (kJ mol^{-1})	$-T\Delta S^0{}_d$ (kJ mol^{-1})	$\Delta G^0{}_d$ (kJ mol^{-1})	$-T\Delta S^0{}_d$ (kJ mol^{-1})	$\Delta G^0{}_d$ (kJ mol^{-1})	$-T\Delta S^0{}_d$ (kJ mol^{-1})
Hexanoate	21.940	21.96	23.640	23.66	25.050	25.07
Decanoate	22.553	22.58	24.411	24.44	26.127	26.16
Butanedioate	35.689	35.72	37.565	37.53	40.070	40.10
Hexanedioate	34.326	34.35	36.330	36.31	38.279	38.26

Table 5: Free energy of association, $\Delta G^0{}_a$, Entropy of association, $\Delta S^0{}_a$, of anionic surfactants at different temperatures

zinc alkanoates	20^0C		30^0C		40^0C	
	$-\Delta G^0{}_a$ (kJ mol^{-1})	$T\Delta S^0{}_a$ (kJ mol^{-1})	$-\Delta G^0{}_a$ (kJ mol^{-1})	$T\Delta S^0{}_a$ (kJ mol^{-1})	$-\Delta G^0{}_a$ (kJ mol^{-1})	$T\Delta S^0{}_a$ (kJ mol^{-1})
Hexanoate	32.192	32.20	33.600	33.61	35.322	35.33
Decanoate	32.415	32.43	34.194	34.21	35.912	35.93
Butanedioate	46.173	46.19	48.774	48.79	50.914	50.93
Hexanedioate	46.573	46.59	49.110	49.13	51.299	51.31

It is therefore concluded that the thermodynamics of dissociation and association of anionic surfactant ie. zinc zinc mono-(hexanoate and decanoate) and di-(butanedioate and hexanedioate) alkanoates can be satisfactorily explained in the light of the phase separation model by conductivity measurements. The results showed that dissociation of anionic surfactant was found to be exothermic while the association process was endothermic in nature and critical micellar concenteration decreased with increase in tempertures as well as chainlength of fatty acid constituent of anionic surfactant.

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