Research Paper :

Dissociation/association behaviour of alkaline earth metal laurates at different temperatures

ANIL KUMAR, DEEPTI TYAGI, SIMMI TYAGI AND DEEPIKA SHUKLA

See end of the article for authors' affiliations

Correspondence to:

ANIL KUMAR
Department of Chemistry,
D.A.V. (P.G) College,
MUZAFFARNAGAR (U.P.)
INDIA

ABSTRACT

The specific conductance, k (mS cm^{-1}) of alkaline earth metal (Mg/Ca/Sr/Ba) laurates in mixed solvent (50% methanol +50% chloroform) has been measured (30-50^{0}C) in order to look into the dissociation / association behaviour of these surfactant systems. The data for critical micelle concentration (c.m.c) help characterising their micellar behaviour. The significant parameters viz. degree of dissociation (α), dissociation constant(K_D) and limiting equivalent conductance at infinite dilution (μ_0) have been deduced for pre-micellar region (dilute range).Thermodynamic parameters *viz.*, enthalpy, free energy and entropy changes for both dissociation and association processes have also been computed.

Key words : Metal laurates, Conductance, Dissociation, Association, Critical micelle concentration (c.m.c), Thermodynamic parameters

Studies involving both nature and structure of the surfactant compounds have been a great help to their possible uses in industries. Alkaline earth metal soaps have found application to dispersants (Verma and Bahadur, 1974), lubricants (Sokoloova,1971; Nakonechaya, 1973 and Bouman, 1950), catalysts (Lower,1947 and Bapyatov and Polstyanoi, 1962), stabilizers (Lehmanm, 1951)and corrosion inhibiting agents (Mayne and Rooyen, 1954 and Johnson, 1959).The latest publications (Cook *et al.*, 2001, Leigh t and Li, 2002 and Owens *et al.*, 2003) by W.L. Leigh and co-workers underlined the significance of organometallics to the wide surfactant domain. However, so many national/ international publications (Hepler, 1969; Jalicoeur and Philip, 1975; Franks *et al.*, 1968; Sharma *et al.,* 1986 and Kumar,1994)have also appeared to signify studies on different physical properties of various surfactants. The present investigation has been initiated with a view to look into the dissociation/association behaviour of alkaline earth metal laurates in mixed solvent (50% methanol+50% chloroform) at different temperatures (30-50^{0}C). Various thermodynamic

parameters have also been evaluated to strengthen the conclusions made.

MATERIALS AND METHODS

Anala R-grade chemicals (lauric acid, methanol, chloroform, carbonates of magnesium /calcium/ strontium and barium) were obtained from Glaxo Labs Mumbai (India). The conductivity water was prepared by twice redistilling good quality distilled water over alkaline KMnO$_4$.

Alkaline earth metal laurates were prepared by direct metathesis. The aqueous solution containing stoichiometric amount of respective metal carbonate and potassium laurate were mixed at nearly 80^{0}C under constant stirring. As evolution of CO$_2$ ceased and metathetic displacement reaction completed (phenolphthalein indicator rendered colourless from pink), the desired compound was separated from mother liquor by vacuum filtration. The product was washed several times with benzene and oven dried. All the four compounds so prepared were further purified by recrystallization from methanol-chloroform

Surfactants	% Carbon		% Hydrogen		% Oxygen		%alkaline earth metal	
	Theoretical	Practical	Theoretical	Practical	Theoretical	Practical	Theoretical	Practical
Mg laurate	68.25	67.75	10.90	10.10	15.16	14.85	5.69	5.05
Ca laurate	65.75	65.30	10.50	9.90	14.61	13.90	9.13	8.69
Sr laurate	59.30	57.95	9.47	9.05	13.18	12.75	18.04	17.78
Ba laurate	53.80	53.10	8.59	7.85	11.95	11.20	25.65	25.05

Table 1: Percentage of elements in Alkaline earth metal laurates (Elements)

solvent mixture. The pure and well dried compounds (white amorphous solids) were then stored over calcium chloride. The recrystallized pure compounds are found to decompose between 200-220^{0}C. The preparation and quality of these compounds were checked by IR and elemental analyses (Table 1).

A digital conductivity meter (Elico Pvt. Ltd. Hyderabad, India Type 032, No.1455) and a dipping type conductivity cell with platinized electrodes were used for measuring the conductance of alkaline earth metal laurates in mixed solvent (50% methanol+50%chloroform). All the measurements were made at constant temperatures in a thermostat ($\pm$0.01^{0}C).

RESULTS AND DISCUSSION

The increase in specific conductance of alkaline earth metal laurates in solvent mixture (50% methanol+50% chloroform) with increasing surfactant concentration may be ascribed to their ionic dissociation in dilute solutions. The compounds undergo ionization forming a metal cation (Mg^{2+} / Ca^{2+} /Sr^{2+} /Ba^{2+}) and a laurate anion. $CH_3(CH_2)_{10}COO^-$. The increase in specific conductance at higher concentrations (Fig.1) may, however, be due to the formation of ionic micelles. The plots (Fig. 1) suggest considerable inflection at the critical micelle concentration (c.m.c) whereupon the anions $CH_3(CH_2)_{10}COO^-$ begin

to aggregate to form ionic micelles. The c.m.c. data for these solutions are recorded in Table 2. It is evident (Table 2) that c.m.c is found to decrease with increasing temperature and vary with different metal cations as:

Magnesium> Calcium> Strontium >Barium

Molar conductance of dilute surfactant systems under study is however found to decrease with increasing

Table 2 : c.m.c (mol dm^{-3}) data for alkaline earth metal laurates in mixed solvent (50% methanol+ 50% chloroform) at different temperatures (30-50^{0}C)

Surfactant	c.m.cx10^4				
	30^{0}C	35^{0}C	40^{0}C	35^{0}C	50^{0}C
Mg laurate	16.2	15.4	14.0	12.2	11.4
Ca laurate	16.0	14.2	13.8	12.1	11.3
Sr laurate	15.8	14.1	13.6	12.0	11.2
Ba laurate	14.4	10.8	10.4	10.0	9.4

surfactant concentration (Fig. 2). The plots of μ versus C$^{1/2}$ (Fig.2) are concave in nature suggesting that these compounds behave as weak electrolytes in dilute solutions and hence Debye-Huckel- Onsager's equation is not applicable to these solutions. As these compounds behave like weak electrolytes in dilute solutions, the expression (Kraus *et al.*,1913) for their dissociation can be derived as follows:
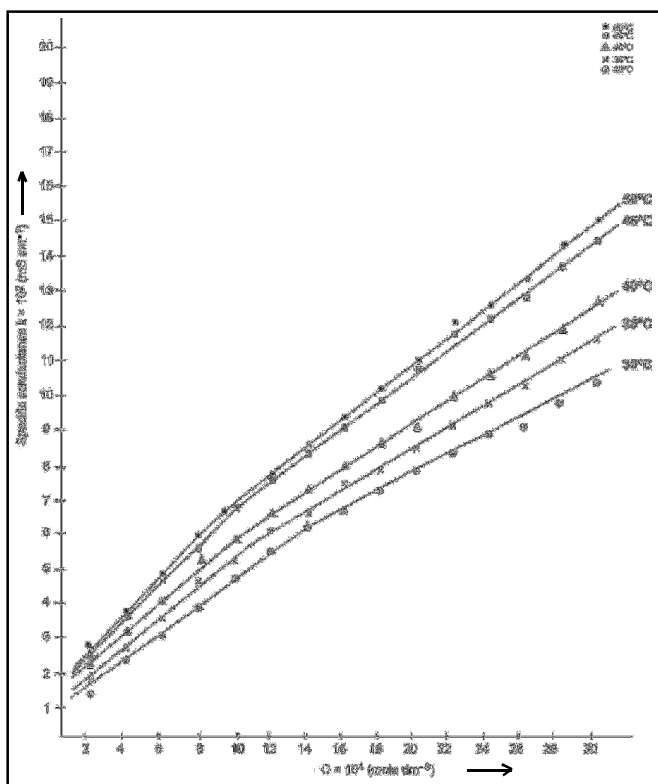

Fig. 1 :   The plots of specific conductance (k) vs concentration (c) for Ba-Laurate at different temperature (30-50^{0}C)
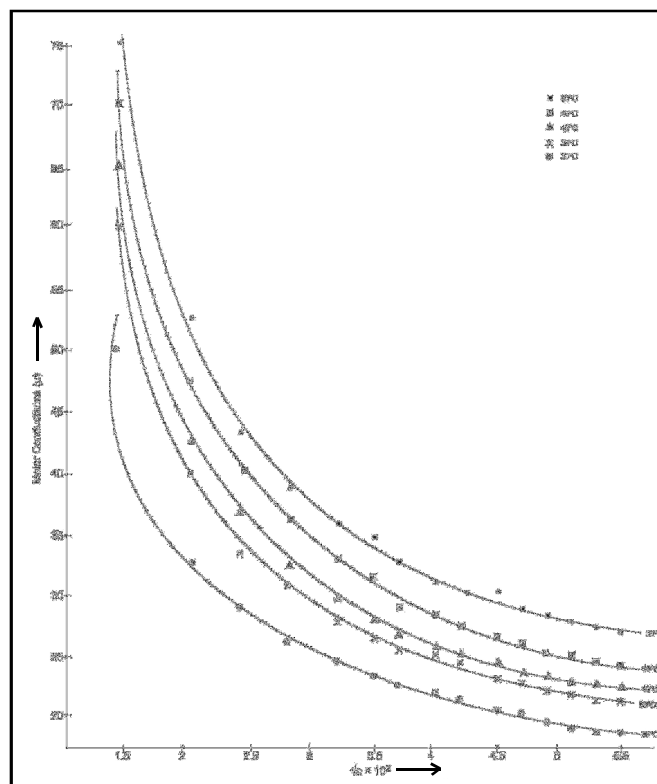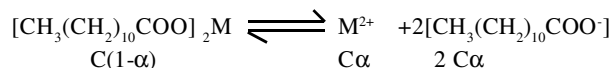

Fig. 2 :   The plots of molar conductance (μ) vs. (c)^{½} for Mg laurate at different temperature (30-50^{0}C)

Let C be the surfactant concentration and 'α' its degree of dissociation, the equivalent concentration of different species may then be expressed as:

$$[CH_3(CH_2)_{10}COO]_2M \;\rightleftharpoons\; M^{2+} + 2[CH_3(CH_2)_{10}COO^-]$$
$$\quad C(1-\alpha) \qquad\qquad\qquad\; C\alpha \qquad 2\,C\alpha$$

where 'M' represents magnesium/calcium/strontium/ barium. Dissociation constant, K_D may then be expressd as:

$$K_D = \frac{[M^{2+}][CH_3(CH_2)_{10}COO^-]^2}{[\{CH_3(CH_2)_{10}COO\}_2M]} = \frac{C\alpha\,(2C\alpha)^2}{C(1-\alpha)} = \frac{4\,C^2\alpha^3}{1-\alpha} \quad (1)$$

As degree of dissociation, 'α', for dilute surfactant solutions is small; the ionic concentration would be low and the interionic effects almost negligible. Hence, the dilute solution would not deviate from ideal behaviour and the activities of the ions as such could be taken as almost equal to the concentration. The degree of dissociation, 'α', may be replaced by the conductance ratio, μ/μ_0 where μ is the limiting conductance at finite concentration and μ_0 is the limiting conductance at infinite dilution. On substituting the values of α and rearranging, equation (1) becomes:
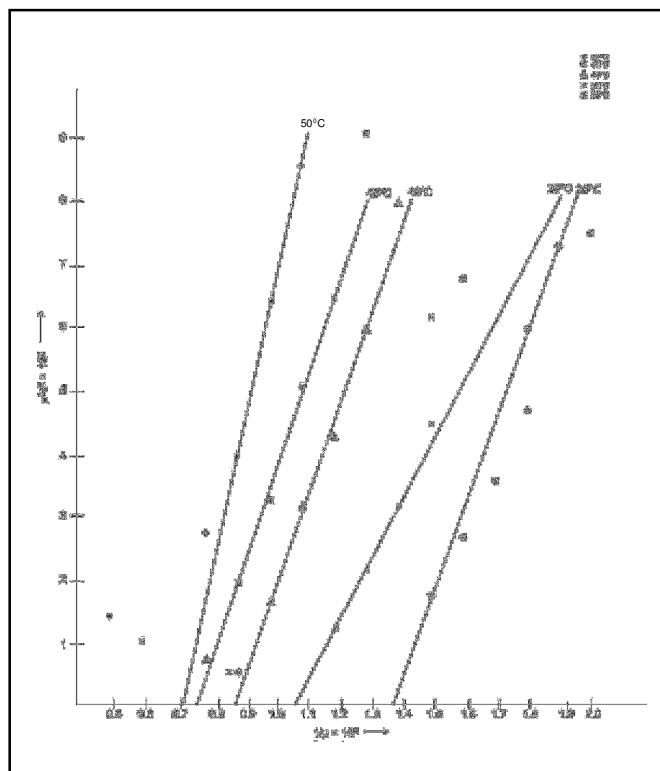

Fig. 2 : The plots of μ^2C^2 vs. $1/\mu$ for calcium laurate at different temperatures (30-50^{0}C) in pre-micellar region

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

The plots of μ^2c^2 verses $1/\mu$ are linear below the c.m.c. only (Fig. 3). The values of the dissociation constant, K_D, and limiting molar conductance at infinite dilution, μ_0, (Table 3) have been obtained 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 versus $1/\mu$ for dilute surfactant solutions, *i.e.* below the c.m.c lt is observed (Table 3) that with increase in temperature the limiting conductance at infinite dilution (μ_0) for these compounds increases whereas their dissociation constant (K_D) decreases suggesting that the dissociation of these compounds in the chosen solvent at the elevated temperatures. K_D is however found to vary with the metal as:
Mg>Sr>Ca>Ba

The degree of dissociation, 'α', at different surfactant concentration may be evaluated by assuming it to be equal to the conductance ratio, μ/μ_0 and using the value of μ_0 (Table 3) as observed from the plot of μ^2C^2 versus $1/\mu$. The variation of 'α' with metal follows as:
Mg>Sr>Ca>Ba

The heat of dissociation, ΔH^0_D for alkaline earth metal laurates in the chosen solvent is obtained from the slope of the linear plots of log K_D versus $1/T$ and recorded in (Table 4).

The negative enthalpy change for dissociation, ΔH^0_D (Table 4) suggests exothermic character of dissociation process (Table 4). The standard free energy change

Table 4 : Heat of dissociation, ΔH^0_D and heat of association, ΔH^0_A of alkaline earth metal laurates		
Surfactant	$-\Delta H^0_D \times 10^{-3}$ (kJmole^{-1})	$\Delta H^0_A \times 10^{-3}$ (kJmole^{-1})
Mg laurate	191.47	10.00
Ca laurate	76.59	4.02
Sr laurate	134.03	7.00
Ba laurate	124.46	6.50

($\Delta G^0_D = -$ RT log K_D, where K_D is the equilibrium constant for dissociation process)and standard entropy Change ($T\Delta S^0_D = \Delta H^0_D - \Delta G^0_D$)are evaluated for the dissociation process (Table 5).

For the micellization process' when counterions are bound to micelles the standard free energy of micellization per mole of monomer ΔG^0_A (Table6),

(Barry and Russel,1972; Robins and Thomas 1968 and Attwood and Florence, 1983) is given by the relationship;

$$\frac{\partial(\ln X_{c.m.c.})}{\partial T} = -\frac{\Delta H^0_A}{2RT^2}$$

$$\partial(\ln X_{c.m.c.}) = -\frac{\Delta H^0_A}{2RT} + C$$

The values of ΔH^0_A have been obtained from the slope of the linear plots of ln $X_{c.m.c}$ versus 1/T and are recorded in Table 4, The positive values of ΔH^0_A indicates that the association of alkaline earth metal laurates in solvent mixture (50%methanol + 50%chloroform) is endothermic. The standard entropy change per mole of monomer (Table 6) is then calculated as T $\Delta S^0_A = \Delta H^0_A - \Delta G^0_A$. The micellization of the surfactants (Table 4 and

Temp. (^{0}C)	Mg laurate		Ca laurate		Sr laurate		Ba laurate	
	$\Delta G^0_D \times 10^{-3}$ (kJmole^{-1})	$-T\Delta S^0_D \times 10^{-3}$ (kJmole^{-1})	$\Delta G^0_D \times 10^{-3}$ (kJmole^{-1})	$-T\Delta S^0_D \times 10^{-3}$ (kJmole^{-1})	$\Delta G^0_D \times 10^{-3}$ (kJmole^{-1})	$-T\Delta S^0_D \times 10^{-3}$ (kJmole^{-1})	$\Delta G^0_D \times 10^{-3}$ (kJmole^{-1})	$-T\Delta S^0_D \times 10^{-3}$ (kJmole^{-1})
30	23.99	215.46	29.49	106.08	28.35	162.38	31.78	156.24
35	27.46	218.94	34.89	111.48	30.79	164.82	35.12	158.59
40	28.35	219.82	36.79	113.38	32.28	166.31	39.25	163.71
45	36.32	227.79	38.64	115.23	36.00	170.03	39.52	163.98
50	37.61	229.08	38.93	115.52	46.02	180.05	42.59	167.15

Total 5 : Free energy of dissociation (ΔG^0_D) and entropy of dissociation(ΔS^0_D) of alkaline earth metal laurates in mixed solvent (50% methanol + 50% Chloroform) at different temperatures (30 - 50^0 C)

Temp. (^{0}C)	Mg laurate		Ca laurate		Sr laurate		Ba laurate	
	$-\Delta G^0_A \times 10^{-3}$ (kJmole^{-1})	$T\Delta S^0_A \times 10^{-3}$ (kJmole^{-1})	$-\Delta G^0_A \times 10^{-3}$ (kJmol^{-1})	$T\Delta S^0_A \times 10^{-3}$ (kJmol^{-1})	$-\Delta G^0_A \times 10^{-3}$ (kJmol^{-1})	$T\Delta S^0_A \times 10^{-3}$ (kJmol^{-1})	$-\Delta G^0_A \times 10^{-3}$ (kJmol^{-1})	T? $S^0_A \times 10^{-3}$ (jJmol^{-1})
30	29.44	39.44	29.50	33.50	29.56	36.56	30.03	36.53
35	30.18	40.18	30.60	34.60	30.63	37.64	32.00	38.50
40	31.17	41.17	31.25	35.25	31.32	38.32	32.71	39.22
45	32.40	42.40	32.44	36.44	32.48	39.48	33.45	39.95
50	33.27	43.27	33.31	37.31	33.36	40.36	34.30	40.80

Table 6 : Free energy of association (ΔG^0_A) and entropy of association (ΔS^0_A) of alkaline earth metal laurates in mixed solvent (50% methanol+50% chloroform) at different temperatures (30 - 50^0 C)

for the phase separation model (1921)is given by the relationship : $\Delta G^0_A = 2RT$ ln $X_{c.m.c}$ where, $X_{c.m.c}$ is the c.m.c expressed as a mole fraction and is defined by

$$X_{c.m.c.} = \frac{n_s}{n_s + n_0}$$

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

$$X_{c.m.c.} = \frac{n_s}{n_0}$$

The standard enthalpy change of micellization per mole of monomer, ΔH^0_A for the phase separation model

6) in the solvent mixture is consistent with $\Delta H^0_A > 0$, $\Delta G^0_A < 0$, $T\Delta S^0_A > 0$. On the other hand, the dissociation of the solvent mixed alkaline earth metel laurates (Table 4 and 5) is consistent with $\Delta H^0_D < 0$, $\Delta G^0_D > 0$, $T\Delta S^0_D < 0$ The negative enthalpy change of dissociation (Table 4) tends to make up for unfavourable change in free energy and entropy of the dissociation process (Table 5). On the other hand, the negative free energy and positive entropy (Table 6) favour micellization and compensate for the unfavourable enthalpy change for the association process (Table 4) It is thus concluded that micellization process is a highly favoured process in the present case.

Authors' affiliations:

DEEPTI TYAGI AND DEEPIKA SHUKLA, Department of Chemistry, D.A.V. (P.G.) College, MUZAFFARNAGAR (U.P.) INDIA

SIMMI TYAGI, Central Building Research Institute, CBRI (A Constitutent Establishment of CSIR), Ministry of Science and Technology (Government of India), ROORKEE (UTTARAKHAND) INDIA

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