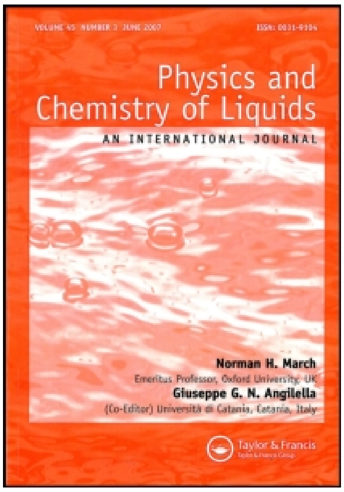

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CONDUCTOMETRIC INVESTIGATIONS ON AQUEOUS SOLUTIONS OF CALCIUM BUTYRATE IN PRESENCE OF ADDITIVES

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The conductance of the aqueous solutions of calcium butyrate in presence of added electrolytes (nitrates of aluminium, copper and ammonium) was measured at $40 \pm 0.05^\circ$C. The values of the critical micelle concentration (CMC), molecular conductance at infinite dilution, degree of dissociation, dissociation constant, free energy change for dissociation process and free energy change for micellization have been calculated in presence of these additives. The results suggest that the soap behaves as a weak electrolyte in these solutions below the critical micelle concentration.

KEY WORDS: Dissociation constant; free energy change.

INTRODUCTION

Multifarious industrial applications of the metal soaps[1–15] have been realized due to the structural features of their molecules. The colloidal soap can exist in the form of aggregates of their molecules or ions called micelle. The concentration at which micelles first appear in solution is termed the critical micelle concentration, CMC. The presence of counterions (cations) may affect micellization in the solutions of anionic surfactant. Previous study[16] was on the conductance behaviour of aqueous solutions of calcium butyrate with no additive. Therefore, the present investigation has been carried out with a view to study the change in behaviour of aqueous solutions of calcium butyrate in presence of counterions of varying valence (Al^{3+}, Cu^{2+} and NH_4^+).

EXPERIMENTAL

Anala R grade additives (nitrates of aluminium, copper and ammonium) and calcium oxide were used without further purification, and *n*-butyric acid (Sigma Chem. Co., U.S.A.) was purified by distillation under reduced pressure. The boiling point of purified *n*-butyric acid was 163.0°C. The calculated amount of metal oxide and butyric acid were suspended in water and heated upto 80°C with constant stirring. After the evolution of CO_2 ceased, the solution was evaporated to obtain the metal soap. The soap was recrystallized with alcohol, dried initially in an air oven (100-105°C) and finally under reduced pressure and stored over calcium chloride. The purity of the soap was checked by elemental analysis and the results agreed with the theoretically calculated value. The reproducibility of the results was checked by preparing two samples of the soap under similar conditions.

The conductance of the soap solutions in presence of additives (10^{-5}g. mole l^{-1}) was measured with a digital conductivity meter (Toshniwal CL 01.10A) and a dipping type conductivity cell with platinized electrodes (cell constant 0.90). All measurements were made at a constant temperature (40 ± 0.05°C). The specific and molecular conductances were expressed in mhos cm^{-1} and mhos cm^2/g. mole respectively.

RESULTS AND DISCUSSION

Specific Conductance, k

Since the molecular conductivity, μ is a measure of conducting power of both the simple ions and micelles; therefore, the specific conductance, k of aqueous solutions of calcium butyrate in presence of added electrolytes has been plotted as a function of the soap concentration, C (g. mole l^{-1}) to determine the critical micelle concentration, CMC. The specific conductance of the soap solution increases with the increase in soap concentration (Figures 1, 2) which may be due to the fact that calcium butyrate behaves as a simple electrolyte in dilute solutions and is considerably ionised into simple metal cation (Ca^{2+}) and fatty acid anion ($C_3H_7COO^-$). The increase of specific conductance with increasing soap concentration at higher soap concentrations may be due to the formation of ionic micelle of higher conducting power than the simple ions. The plots of specific conductance, k vs soap concentration, C (Figures 1, 2) exhibit two breaks. The first break occurs at a concentration, CMC (I) at which the anions begin to aggregate together to form ionic micelles. The second break observed at higher soap concentration, CMC (II) may be due to the probable formation of neutral colloid. The particle of neutral colloid are larger and have laminated structure of layers of undissociated molecules of soap and are charged as a result of attachment of ions just like an ordinary colloidal particle. At the same experimental temperature (40 ± 0.05°C), the values of CMC (I) and CMC (II), that are 0.051M and 0.30M respectively in pure aqueous solutions of calcium butyrate[16], are higher than their corresponding values (Table 1) for aqueous soap solutions in presence of counterions of varying valence. A change in counterion to one of greater valence leads to a decrease in the values of both the CMC_s (Table 1). Addition of electrolytes causes a reduction in the thickness of the ionic atmosphere surrounding the polar head groups and a consequent decreased repulsion between them.

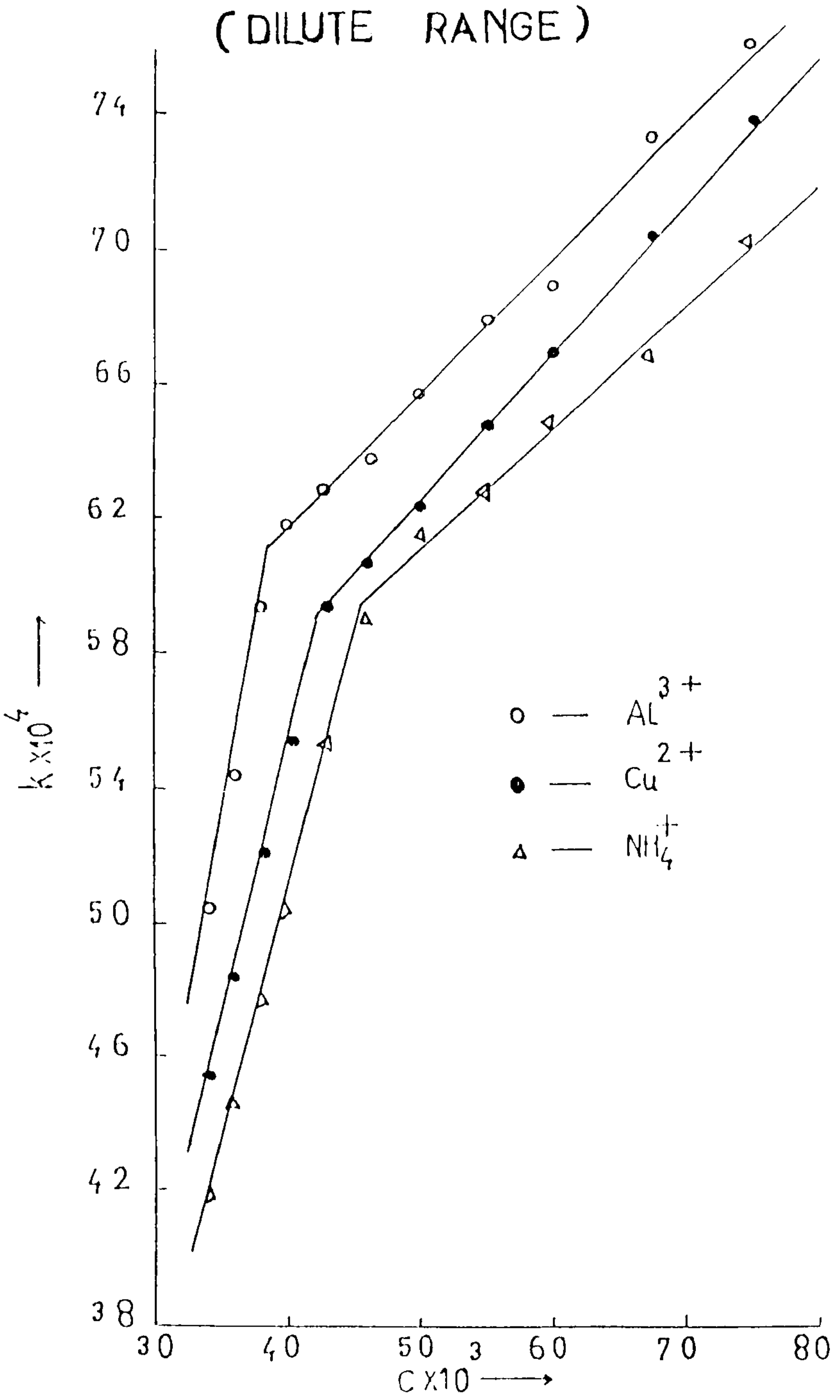

Figure 1 k vs. C (Dilute Range).

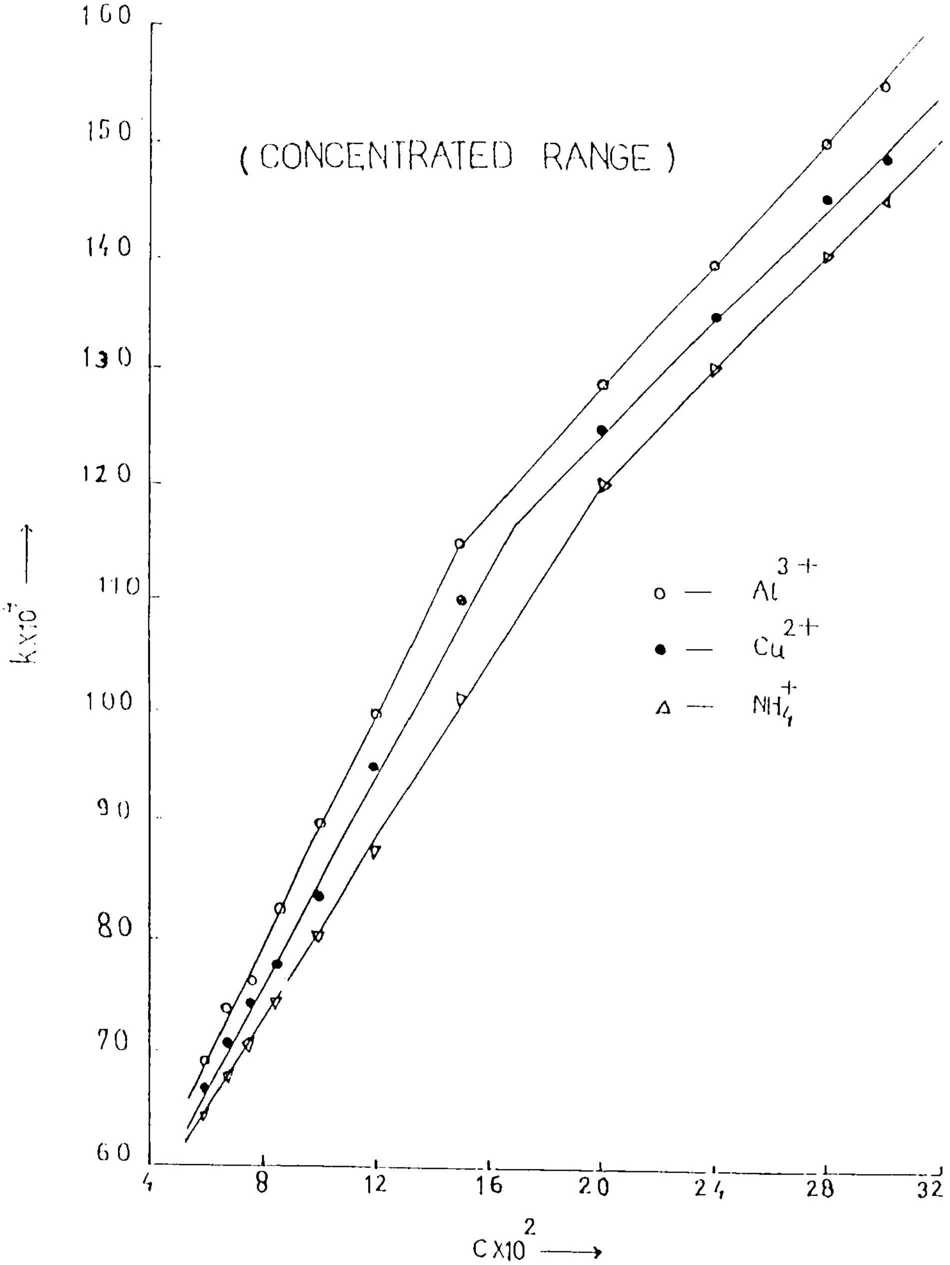

Figure 2 k vs. C (Concentrated Range).

Table 1 The values of CMC of aqueous solutions of calcium butyrate in presence of additives at 40°C.

Additives	*CMC (I)* × 10^2	*CMC (II)*
Al^{3+}	3.85	0.15
Cu^{2+}	4.30	0.17
NH_4^+	4.60	0.20

MOLECULAR CONDUCTANCE (μ) AND DISSOCIATION CONSTANT (K)

The values of molecular conductance, μ, of aqueous solutions of calcium butyrate in presence of these counterions (Al^{3+}, Cu^{2+} and NH_4^+) are low at higher soap concentrations and the same increase very rapidly in dilute solutions indicating that the soap behaves as a weak electrolyte in these solutions (Figure 3). The decrease in molecular conductance with the increasing soap concentration may be due to the combined effects of ionic atmosphere, solvation of ions and decrease of mobility and ionization with the formation of micelles. The plots (Figure 4) of log μ vs. log C are characterised by two breaks at concentrations which correspond to CMC (I) and CMC (II) (Table 1) of calcium butyrate. The behaviour of the soap solutions below the CMC (I) can be represented by the relationship:

$$\log \mu = A + B \log C \qquad \text{(i)}$$

where A and B are constants. The higher values of constant A and B (Table 2) for solutions below the CMC are probably due to an increase in micellar size with increasing soap concentration. The higher values of constant A below and above CMC (1.92 and 1.58 respectively) obtained for aqueous solutions of calcium butyrate in absence of counterions[16] than the value of constant A (Table 2) are indicative of higher aggregation number and reduction in CMC in presence of these counterions. In absence of counterions[16], constant B below the CMC (-0.13) is higher and above the CMC (-0.48) is lower than its corresponding values below and above the CMC (Table 2) in conformity with the previous result.

The nonlinear nature of the plots of μ vs. $C^{1/2}$ (Figure 3) invalidates the applicability of Debye-Hückel-Onsager's equation to aqueous solutions of calcium soap in presence of these counterions. Therefore, the values of the limiting molecular conductance, μ_0, for these solutions can not be obtained by usual extrapolation method. Since these dilute soap solutions behave as a weak electrolyte, Kraus and Bray type expression[17] for dissociation of calcium butyrate can be derived in the following manner.

$$\underset{C(1-\alpha)}{(C_3H_7COO)_2Ca} \rightleftharpoons \underset{C\alpha}{Ca^{2+}} + \underset{2C\alpha}{2C_3H_7COO^-}$$

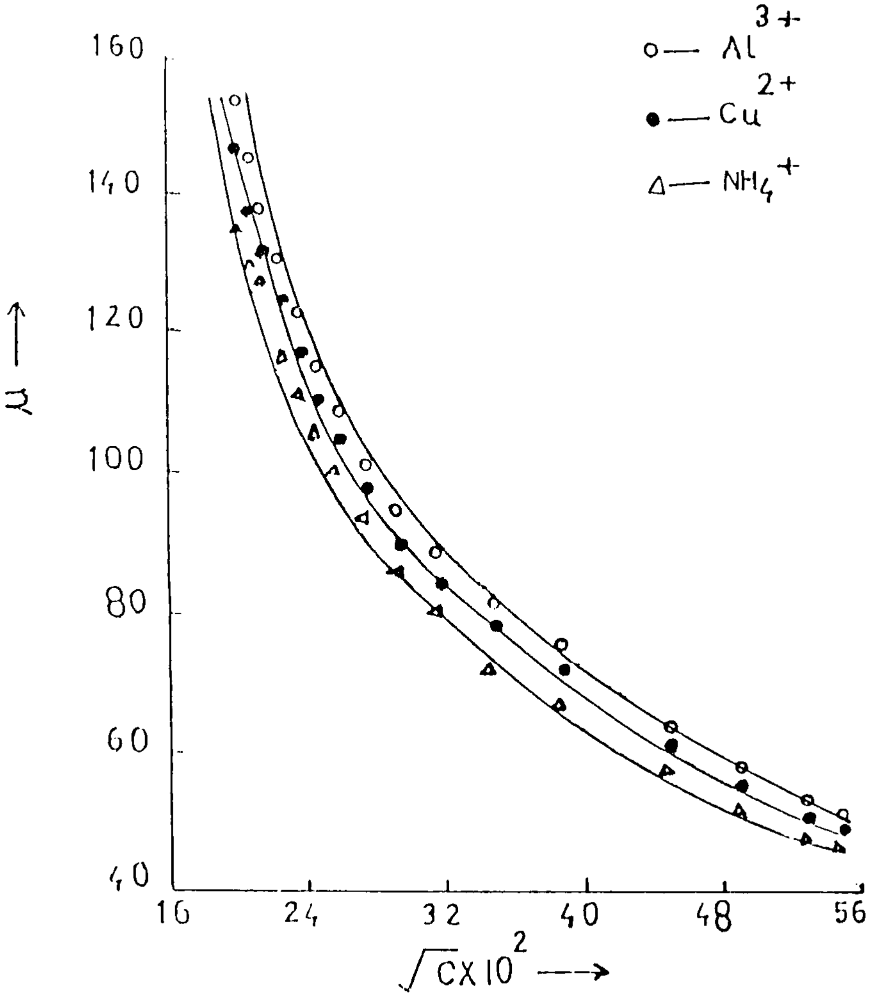

Figure 3 μ vs. $\sqrt{C}$.

The dissociation constant, K can be expressed as:

$$K = \frac{[Ca^{2+}][C_3H_7COO^-]^2}{[(C_3H_7COO)_2Ca]} = \frac{(C\alpha)(2C\alpha)^2}{C(1-\alpha)}$$

or,

$$K = \frac{4C^2\alpha^3}{1-\alpha} \tag{ii}$$

The degree of dissociation of calcium butyrate in dilute solutions is small and so the ionic concentrations are low and the interionic effects are almost negligible. Therefore, the dilute solutions do not deviate from ideal behaviour and so the activities of the

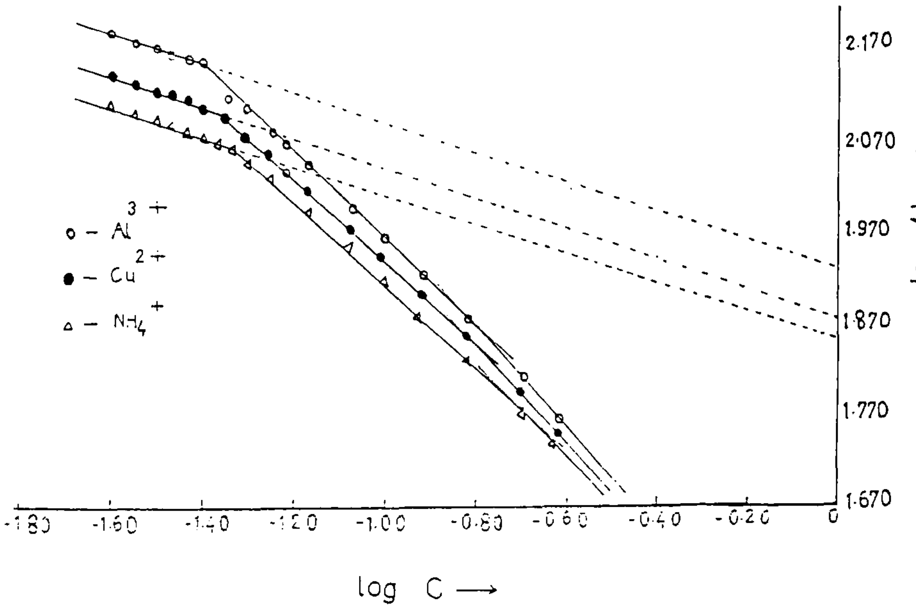

Figure 4 log μ vs. log C.

ions can be taken as almost equal to the concentrations. The degree of dissociation, α may be replaced by 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 value of α and rearranging, Eq. (ii) can be written as:

$$\mu^2C^2 = \frac{K\mu_0^3}{4\mu} - \frac{K\mu_0^2}{4} \tag{iii}$$

The values of dissociation constant, K and molecular conductance at infinite dilution, μ_0 can be obtained from the slope, $[K\mu_0^3/4]$ and intercept, $[-K\mu_0^2/4]$ of the linear plots of μ^2C^2 vs. $1/\mu$ (Figure 5) for dilute soap solutions. The values of $K(4.44 \times 10^{-4}$,

Table 2 The values of constant *A* and *B* (below CMC and above CMC) of aqueous solutions of calcium butyrate in presence of additives at 40°C.

Additives	*Below CMC*		*Above CMC*	
	A	$-B$	*A*	$-B$
Al^{3+}	1.91	0.15	1.52	0.47
Cu^{2+}	1.88	0.17	1.51	0.45
NH_4^+	1.86	0.18	1.49	0.44

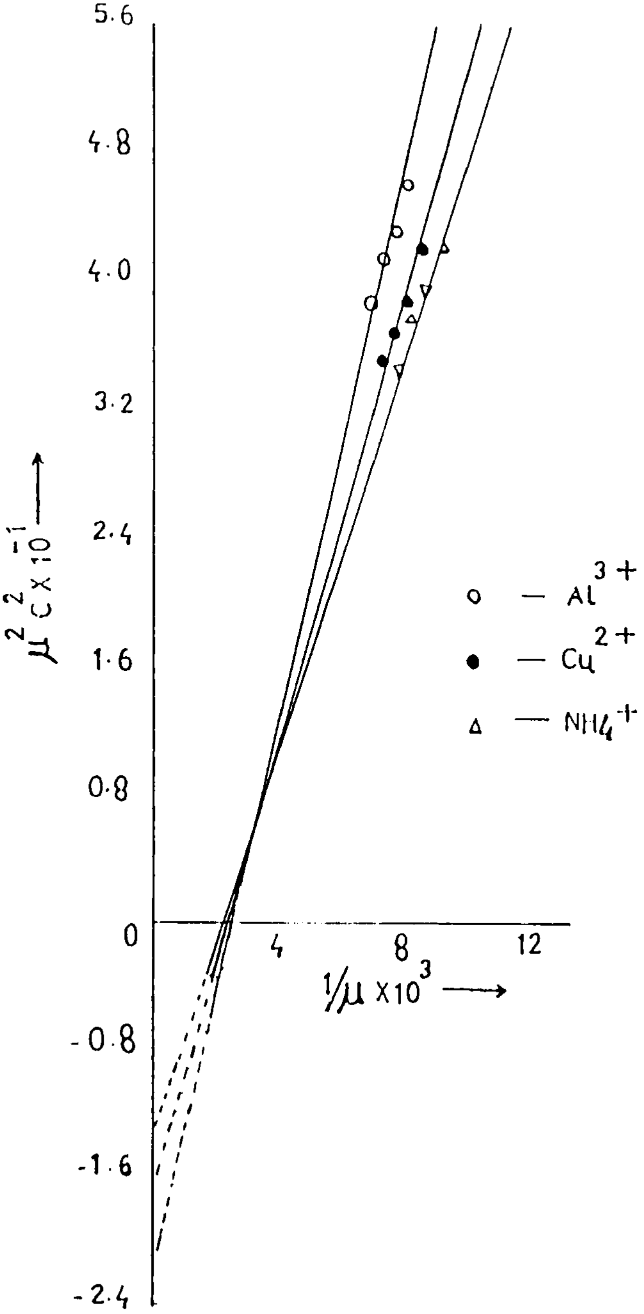

Figure 5 μ^2C^2 vs. $1/\mu$.

Table 3 The values of degree of dissociation, α and dissociation constant, K_D of aqueous solutions of calcium butyrate in presence of additives at 40°C.

Conc.	Al^{3+}		Cu^{2+}		NH_4^+	
$C \times 10^2$	α	$K_D \times 10^4$	α	$K_D \times 10^5$	α	$K_D \times 10^5$
3.4	0.366	3.46	0.164	2.40	0.112	0.70
3.6	0.362	3.46	0.163	2.70	0.110	0.70
3.8	0.360	3.44	0.163	2.96	0.106	0.75
4.0	0.356	3.44	0.162	3.55	0.104	0.80
4.3	0.337	3.45	0.161	3.60	0.101	0.92
4.6	0.320	3.45	0.155	3.60	0.101	0.93
5.0	0.303	3.50	0.146	3.64	0.097	0.94
5.5	0.286	3.55	0.138	3.70	0.090	0.94
6.0	0.266	3.60	0.131	3.75	0.085	0.94
6.7	0.253	3.65	0.123	3.81	0.079	0.98
7.5	0.234	3.70	0.116	3.90	0.074	0.99
8.6	0.222	4.16	0.106	3.94	0.068	1.03
10.0	0.207	4.47	0.098	4.17	0.063	1.07
12.0	0.192	5.05	0.092	4.94	0.057	1.13
15.0	0.177	5.30	0.086	6.26	0.056	1.36
20.0	0.148	6.09	0.073	6.68	0.047	1.74
24.0	0.134	6.40	0.066	6.97	0.043	1.86
28.0	0.124	6.83	0.061	7.10	0.040	2.09
30.0	0.120	7.07	0.058	7.46	0.038	2.28

9.00×10^{-5} and 2.60×10^{-5}), and μ_0 (433, 854 and 1269) have been obtained from these plots (Figure 5) in presence of counterions, Al^{3+}, Cu^{2+} and NH_4^+, respectively.

The values of the degree of dissociation, α at different soap concentrations (Table 3) have been calculated by assuming it as equal to the conductance ratio, μ/μ_0 and using the value of μ_0 obtained from the plots of u^2C^2 vs. $1/u$ (Figure 5). The plots of degree of dissociation, α vs. soap concentration, C show that the soap solutions behave as a weak electrolyte (Figure 6). The degree of dissociation of calcium butyrate decreases rapidly in dilute solutions with the increase in soap concentration, whereas it decreases slowly above the critical micelle concentration.

The values of dissociation constant, K of calcium butyrate (Table 3) have been calculated by using expression (ii) and assuming the degree of dissociation as equal to the conductance ratio, μ/μ_0. The values of the dissociation constant, K change slowly with the increase in the soap concentration in dilute solutions, but increase rapidly in concentrated solutions. The value of dissociation constant of aqueous soap solutions with no additive[16] was 10.59×10^{-4} which is higher than those recorded in Table 3. The decrease in values of the dissociation constant, K in presence of added electrolyte is due to the fact that the electrolyte causes a reduction in the thickness of the ionic atmosphere surrounding the polar head groups and reduced repulsion between them. Consequently, an increase in aggregation number and formation of larger micelle take place.

The plots of dissociation constant, K vs. soap concentration, C show a slight variation in dilute solutions but exhibit a drift with increasing soap concentration

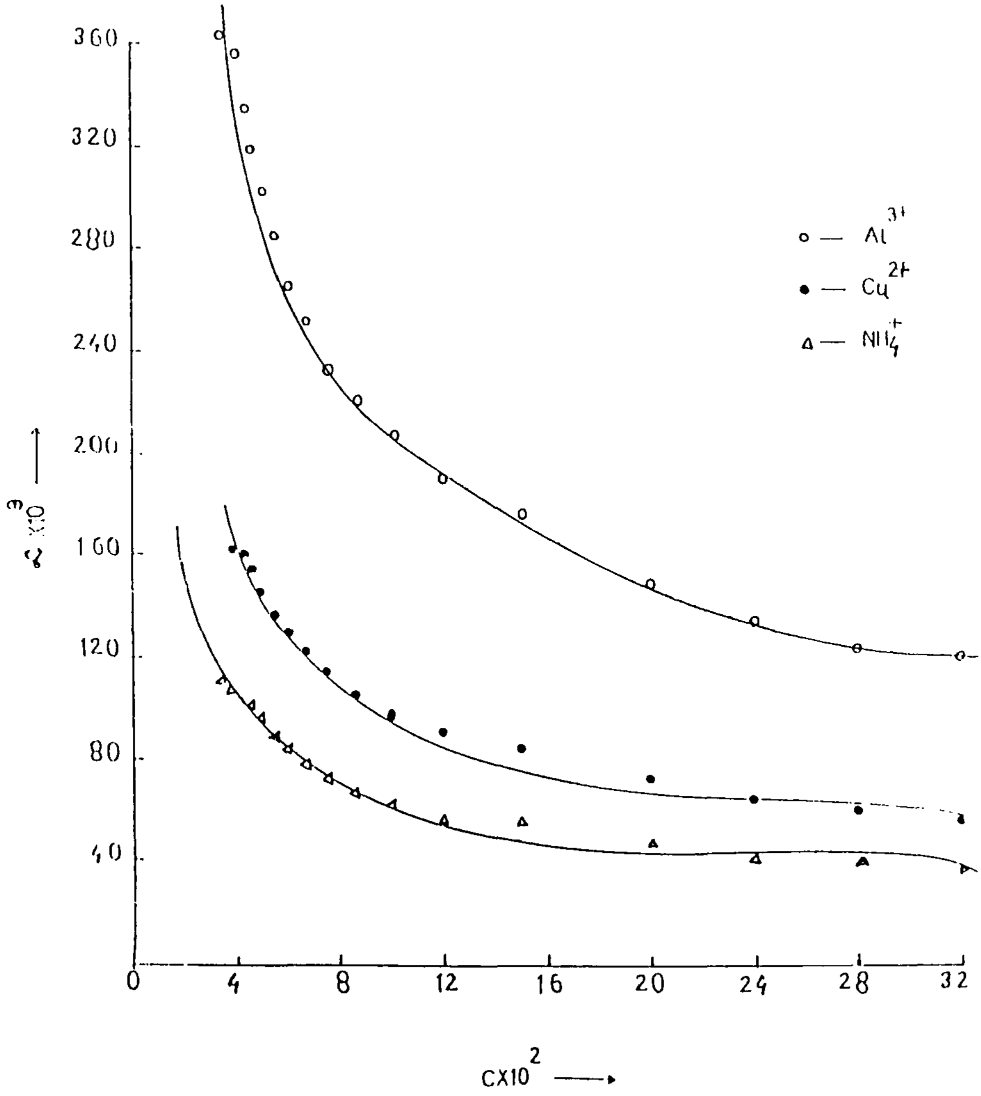

Figure 6 α vs. C.

indicating that the soap does not behave as very weak electrolyte (Figure 7). The drift in the values of dissociation constant with increasing soap concentration may be due partly to the fact that degree of dissociation, α is not exactly equal to the conductance ratio, μ/μ_0, but mainly because the activity coefficients of ions are not equal to unity. The deviations in the values of dissociation constant at higher concentrations may be due to the failure of simple Debye-Hückel's activity equation at higher concentrations.

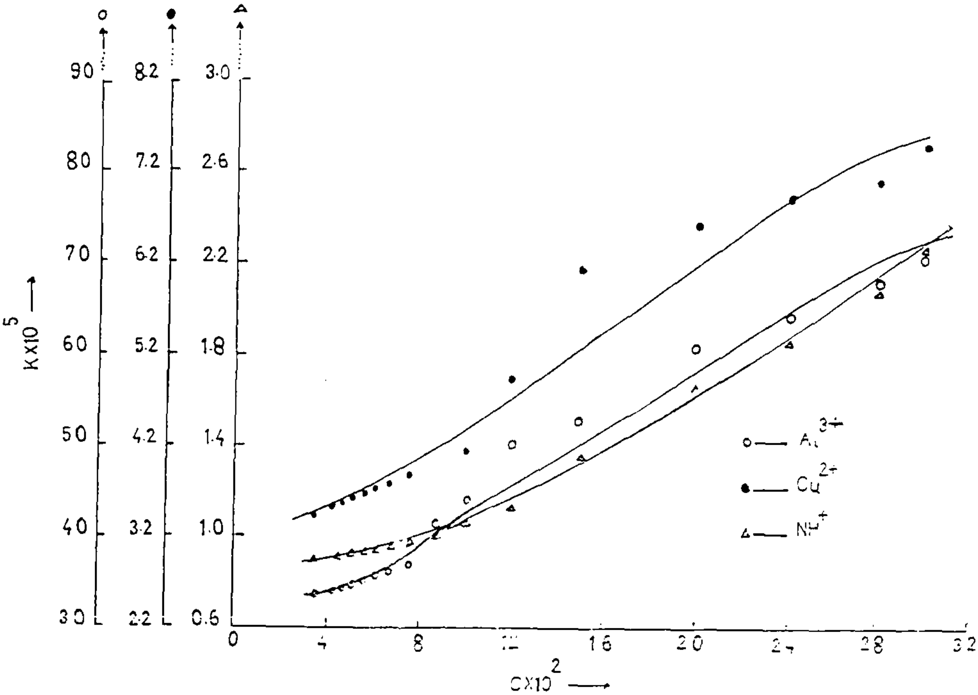

Figure 7 *K* vs. C.

The dissociation constant, K' of calcium butyrate when the activity coefficients of ions are not equal to unity, can be expressed as:

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

If the ionic strength is not too high, the activity coefficient of non ionized molecules of soap, i.e. f_{soap}, may be taken as unity. Using Debye-Hückel's limiting law for activity coefficients, K' can be expressed as:

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

The plots of log K vs. $(C\alpha)$ for dilute solutions of calcium butyrate are linear. The values of K' and A' (Table 4) have been calculated from the intercept, log K' and slope,

Table 4 Values of K' and A'.

Additives	K'	A'
Al^{3+}	3.00×10^4	3.0
Cu^{2+}	2.28×10^5	5.1
NH_4^+	6.60×10^6	6.2

Table 5 The values of free energy change for dissociation, ΔG°_{D} and free energy change for micellization, ΔG°_{m} of aqueous solutions of calcium butyrate in presence of additives at 40°C.

Additives	$-\Delta G^{\circ}_{D}(kJ\ \mathrm{mol}^{-1})$	$-\Delta G^{\circ}_{m}(kJ\ \mathrm{mol}^{-1})$
Al^{3+}	20.09	37.86
Cu^{2+}	24.24	37.29
NH_4^+	27.47	36.93

A' of the linear plots of log K vs. $\sqrt{(C\alpha)}$. The results show that the soap behaves as a weak electrolyte in dilute solutions below the CMC, and the conductance results can be explained on the basis of Ostwald's formula and Debye-Hückel's theory of weak electrolyte.

The free energy for the dissociation process, ΔG°_{D} was evaluated using the relationship:

$$\Delta G^{\circ}_{D} = -RT\ln K_A = RT\ln K_D$$

where K_A and K_D are the equilibrium constants for the association and dissociation process, respectively. The free energy values for dissociation (ΔG°_{D}) and micellization (ΔG°_{m}) have been calculated per mole of monomer and are tabulated (Table 5). The higher values of decrease in free energy for micellization process than dissociation process favours micellization.

For the aggregation process, when counterions are bound to micelle, the standard free energy of micellization (per mole of monomer) ΔG°_{A}, for the phase separation model[18,19] is given by the relationship:

$$\Delta G^{\circ}_{m} = 2\ RT\ln X_{\mathrm{CMC}}$$

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

$$X_{\mathrm{CMC}} = \frac{n_s}{n_s + n_0}$$

Since the number of moles of free surfactant, n_s is small as compared to the number of moles of solvent, n_0. Therefore,

$$X_{\mathrm{CMC}} = \frac{n_s}{n_0}.$$

The decrease in free energy for dissociation of aqueous calcium butyrate[16] in absence of additive (-17.18 KJ mol^{-1}) is lower than its corresponding value recorded in Table 5.

In conclusion to the present investigation, it may be pointed out that the soap behaves as a weak electrolyte in dilute solutions below the CMC, the conductance results can be explained on the basis of Ostwald's and Debye-Hückel's theory of weak electrolytes, and a change in counterion to one of greater valence leads to a decrease in the values of both the $\mathrm{CMC_S}$.

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