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Micellar Studies of Calcium Soaps Using Ion-Selective Electrode

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ABSTRACT

Calcium soaps of caproic and caprylic acids were prepared and a cell was set up for the measurement of EMF of the cell containing referred soap solutions in methanol water solvent system with the aid of Ion-Selective Electrode. The Critical Micelle Concentration of soap solutions was determined by plotting the electromotive force of the cell against soap concentration. The Critical Micelle Concentration of these soap solutions varies with increase in chain length of the fatty acids in the soap. The energetic studies of the system have been carried out from the electromotive force values of the cell containing soap solution to ascertain the chain length compatibility and agglomeration profile. The values of free energy change are negative indicating the spontaneity of cell reaction and decreases with increasing soap concentration while increases with the increase methanol concentration in solvent mixture.

Keywords : Ion-Selective Electrode, Micellization, EMF, Hydrophilic Oleomicelle, Lipophilic Hydromicelle

INTRODUCTION

Literature survey reveals that alkaline earth metal soaps are widely used in industries as detergents, softeners, plasticizer greases, lubricants, anti-corrosion agent [1-8]. The micelles formed by soaps in solutions have become useful entities for the synthesis and stabilization of nanoparticles. Reactions involving nanoparticles in micellar solutions thus become a newer field of modern research [9-14]. The colloid chemical behavior of calcium soaps is important as the larger anionic part of these macromolecules shows the micellar effects on the surface phenomenon. Because of Ion-Selective Electrode (ISE) has become one of the most useful tools for rapid analysis and its ability to measure the concentration at low range (10^{-4}-10^{-6}M) with high selectivity. It influenced us to use them for systematic micellar studies of calcium soaps by the electrometric method.

EXPERIMENTAL

The present work has been started by preparing calcium soaps according to the methods reported earlier [15-16]. The information about the nature and structure of calcium soaps in a solid-state was carried out by elemental and infrared spectral analysis. The results obtained were in good agreement with previous workers [17-22]. The micellization and aggregation of referred soaps were studied in methanol-water solvent mixtures of varying compositions. The Critical Micelle Concentration (CMC) of soaps have been determined by electrometrically method using ISE.

PREPARATION AND PURIFICATION

Purification is done (n-caproic and n-caprylic acids) by keeping over anhydrous sodium sulphate for a week and then distilling under reduced pressure. Calcium soaps were prepared by the direct metathesis of the corresponding sodium soap prepared in laboratory with slight excess of the required amount of the calcium acetate solution at 50-55^{0}C under vigorous stirring. The precipitate thus obtained was filtered and washed several times with hot distilled water and finally with methanol to remove the free precipitant and acid respectively. The soaps were purified by recrystallization with ethyl alcohol and then dried under reduced pressure. The soap solutions of different soap concentration from 0.005M to 0.050M and 0.001M to 0.005M for calcium caproate and calcium caprylate respectively in the varying composition of the methanol-water solvent mixture were prepared. Since agglomeration of caproate soap molecules takes place at higher concentrations while it is at a lower concentration for caprylate soap, therefore different concentrations for caproate and caprylate were taken.

EMF Measurement

The electrometric studies have been carried out by constructing a cell using an ion-selective electrode, reference electrode and soap solution.

Thus the cell can be represented as the pattern suggested by previous workers [23-26].

Hg | Hg_2Cl_2 | Sat. KCl | Soap solution | Membrane | Sat. Soln. | AgCl | Ag

← Reference Electode → ← ISE →

The Electro-Motive Force (EMF) of the cell was measured potentiometrically.

Result and Discussion

EMF

The EMF values of the cell containing calcium caproate and calcium caprylate soap solutions of varying compositions are plotted concerning the logarithm of soap concentration (Fig. 1 & 2) respectively. It is observed from Figs. that the EMF value of the cell increases with an increase in soap concentration. The result can be explained based on a well-known electrode equation [27].

$$E = E_0 \pm \frac{RT}{Z_1F} \ln \left[a_1 + \sum_{i=2}^{n} K_{1i}^{Pot} (a_i)^{z_1/z_i} \right] \qquad \text{---------} (1)$$

Where :

	n	-	number of ions present in test solution
	'+'	-	sign holding for cations
	'-'	-	sign holding for anions
	z	-	charge on cation

K_{li}^{Pot} - selectivity coefficient

a_1 - activity of cation

a_i - activity of interfering ions

The electrode equation shows that when other ions are absent in soap solution than the term $\sum_{i=2}^{n} K_{li}^{Pot} (a_i)^{z_1/z_i}$ will remain constant and the EMF of the cell will depend only on the activity of the calcium ions (a_1) present in the soap solution. Since soap usually behaves as a weak electrolyte [28] the activity of calcium ions is given by the following equation:

$$\underset{\text{Calcium soap}}{Ca(COOR)_2} \rightleftharpoons Ca^{2+} + \underset{\text{Carboxylate anion}}{2RCOO^-} \quad \text{--------- (2)}$$

where : $R = CH_3\text{-}(CH_2)_4\text{-}$ for caproate

$R = CH_3\text{-}(CH_2)_6\text{-}$ for caprylate

TABLE – 1

EMF VALUES (in mV) OF THE CELL CONTAINING CALCIUM CAPROATE SOLUTIONS IN METHANOL-WATER SOLVENT MIXTURE

Concentration of soap (in mol. dm^{-3})	VOLUME PERCENT OF METHANOL IN THE SOLVENT MIXTURE								
	10%	**20%**	**30%**	**40%**	**50%**	**60%**	**70%**	**80%**	**90%**
0.005	81.52	80.63	79.13	78.92	78.13	77.58	76.25	74.62	73.14
0.010	85.01	84.26	83.41	81.83	80.56	79.08	77.64	76.18	75.08
0.015	90.18	88.14	86.29	85.02	83.12	81.67	79.92	78.24	77.19
0.020	94.62	92.31	89.85	87.73	85.57	84.3	82.15	80.11	79.08
0.025	99.54	96.01	93.18	90.62	88.16	86.09	84.13	82.35	80.96
0.030	103.66	99.76	96.54	93.17	90.02	88.11	86.44	83.92	82.04
0.035	104.38	100.51	97.12	94.67	91.14	89.22	86.78	84.79	83.36
0.040	105.92	102.07	99.15	95.03	92.56	90.07	87.62	85.55	84.17
0.045	107.02	103.01	100.17	96.62	93.88	90.87	88.63	86.34	84.68
0.050	108.14	104.19	101.07	97.5	94.06	91.69	89.87	87.77	85.03

TABLE - 2

EMF VALUES (in mV) OF THE CELL CONTAINING CALCIUM CAPRYLATE SOLUTIONS IN methanol-water solvent mixture

Concentration of soap (in mol. dm^{-3})	Volume percent of methanol in the solvent mixture								
	10%	20%	30%	40%	50%	60%	70%	80%	90%
0.0010	58.23	57.54	56.04	55.01	54.26	53.31	52.74	51.05	50.15
0.0015	65.07	63.11	61.84	59.77	58.22	57.36	55.92	54.66	53.61
0.0020	71.44	68.79	66.49	64.66	62.75	60.77	59.13	57.24	56.84
0.0025	77.57	74.06	71.83	69.21	66.29	64.07	62.57	61.47	60.08
0.0030	84.04	79.64	76.69	74.18	70.23	68.11	66.35	64.16	62.66
0.0035	90.14	84.92	81.26	77.59	74.43	71.44	69.86	67.54	66.01
0.0040	91.43	85.52	82.07	78.15	75.08	72.49	70.17	68.34	65.8
0.0045	92.22	86.62	83.13	79.26	75.96	72.84	70.78	69.21	66.45
0.0050	93.35	87.59	83.46	79.95	76.28	73.08	71.11	69.8	67.14

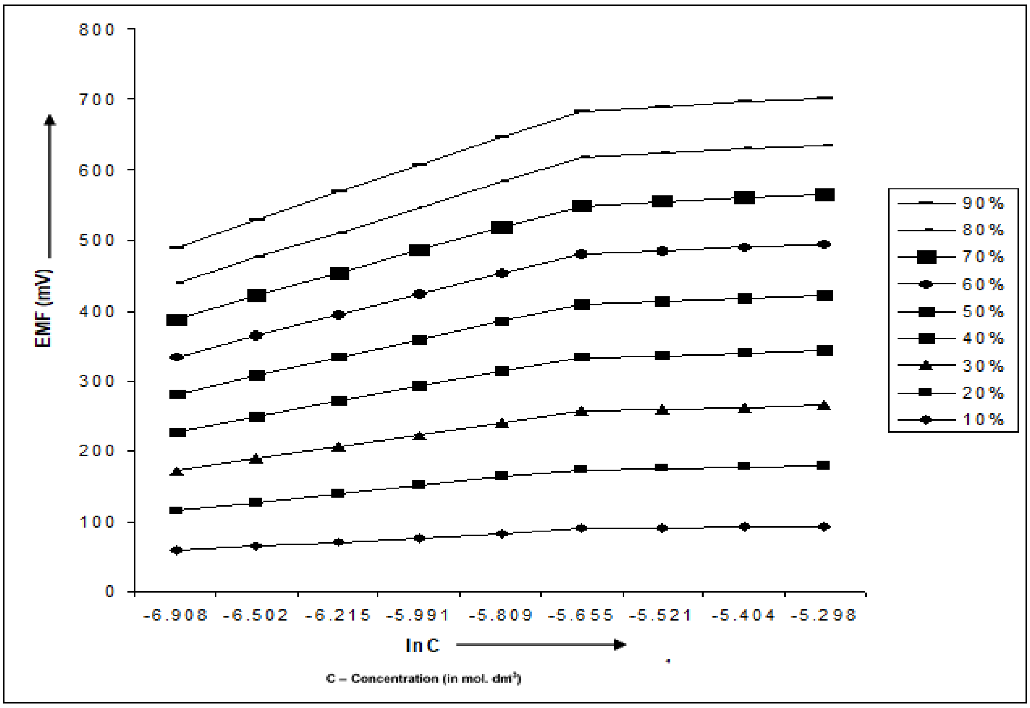

Fig. 1 Plot of EMF of the cell containing calcium caproate solutions against logarithms of soap concentration in methanol-water solvent

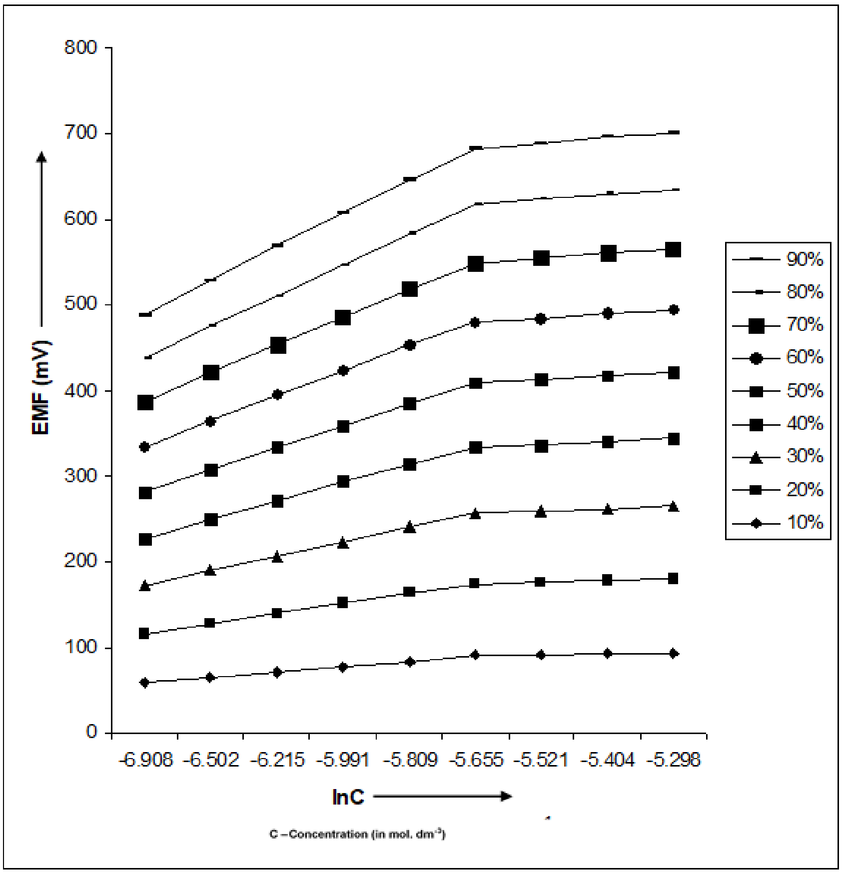

Fig. 2 Plot of EMF of the cell containing calcium caprylate solutions against logarithms of soap concentration in the methanol-water solvent

The above equation expresses that the activity of cation increases with the increase in soap concentration and thus the EMF of the cell for soap solution also increases. The perusal of the EMF data (Fig. 1 & 2) shows that the EMF value increases with an increase in soap concentration but decreases with the increase in methanol concentration in solvent mixtures. This may be due to the combination of two opposing factors. The first factor has an increasing effect on EMF because of a decrease in the degree of aggregation of ions and also in the hydration of micelles with the increase of methanol concentration which results in increasing the activity of cation and the EMF value of the cell. Whereas the second factor has a decreasing effect on EMF, since with the increase in methanol concentration in solvent composition the dielectric constant of the solution decreases. It is therefore logical to expect that the difference between these two effects and predominance of dielectric constant, the EMF of the cell decreases with the increase in methanol concentration in the system.

The plots of EMF against the logarithm of soap concentration (log C) of the soap solution are characterized by an intersection of two straight lines at a definite soap concentration, which corresponds to the critical micelle concentration (Fig. 1 & 2). It is clear from the plots that the EMF value at first increases rapidly and then gradually, which is because of the agglomeration of soap molecules since the soap deviates slightly from the ideal behavior in dilute solution, i.e. below CMC. It is thus apparent that soap behaves as a moderately strong electrolyte and with an increase in soap concentration, the activity of calcium ion increases which results in increasing the EMF value of the cell for referred soap solution as is shown by a straight line below CMC.
However, at concentration ranges above the CMC, the behavior of soap is non-ideal for micellization and an increase in soap concentration does not result in increasing the activity of cation too much. Therefore, above

the CMC, the activity of cation almost remains constant and so does the EMF of the cell, which is characterized by a second straight line after CMC.

It is also clear from the plots that the intersection of two straight lines that appears at the same concentration (i.e. CMC) is the same for all methanol-water solvent mixtures of varying compositions. This shows that the CMC of soap does not depend on methanol concentration in the solution. The above result is in good agreement with that obtained by conductivity measurement [29].

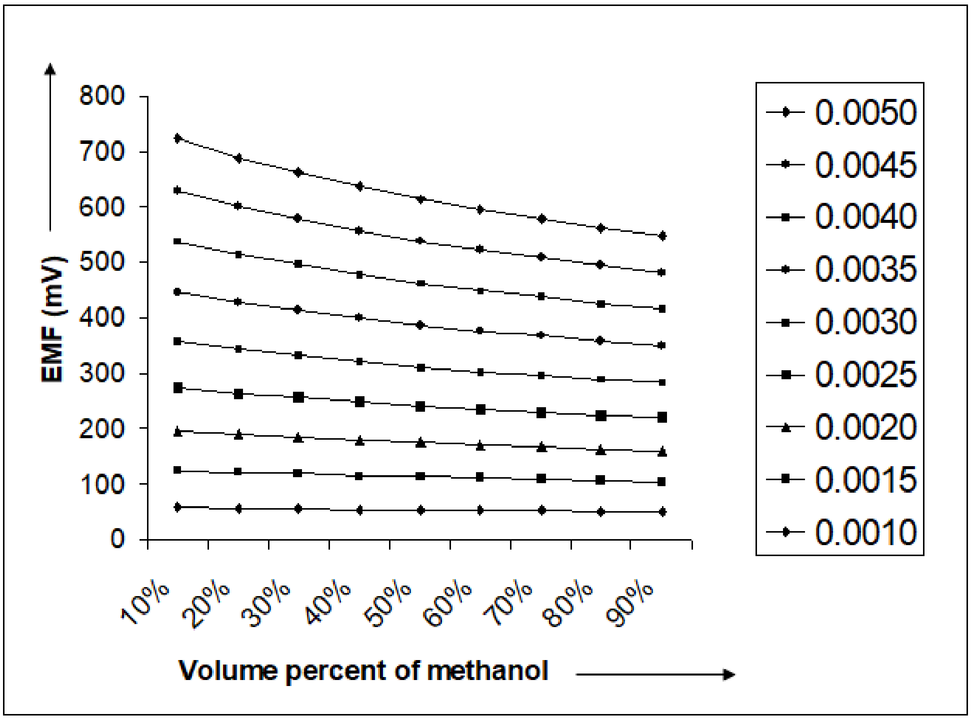

Fig. 3 Plot of EMF of the cell containing magnesium caproate solutions versus volume percent of methanol.

The plots of EMF against volume percent of methanol (Fig. 3) show that EMF at first decreases rapidly as the concentration of methanol increases from 10% to 50% composition and then decreases linearly with further increase in methanol concentration. This may be due to the change in the nature of micelles from hydrophilic oleomicelles to lipophilic hydro micelles [28].

The results are in fair agreement with the result reported earlier by the measurement of p^H and conductivity [31-33].

Free Energy Change

The free energy change (ΔG) of cell reaction for calcium soap solutions has been tested by using following thermodynamic equation:

$$(\Delta G) = -nEF \qquad \text{---------} \ (3)$$

It is apparent from the table values of ΔG are negative, showing the spontaneity of cell reaction. ΔG values first decrease rapidly with an increase in soap concentration and decrease linearly at higher soap concentration. The decrease in free energy is attributed to the fact that molecules of soap in dilute solutions are considerably ionized into metal cations and fatty acid anions. These ions are surrounded by a layer of solvent molecules that are firmly bounded and oriented towards the ions. The orientation of solvent molecules around the ions is attributed to the influences of their electrostatic fields and the internal pressure which results in the lowering of free energy [34].

The decrease in free energy at higher soap concentration may be explained by the predomination of ionic head groups in the micelles, resulting in increasing the ionic repulsion [35]. The decrease in free energy change is also due to the loss of translational and rotational degrees of freedom, which helps in the solubilization process. Besides that, the electrostatic head group repulsion term is reduced after solubilization, which helps in lowering the free energy of solubilized aggregates [36].

It is also clear from the ΔG values increase with the increase in methanol concentration in the solvent mixture. This may be because of a decrease in dielectric constant by a further increase in methanol concentration.

TABLE – 3
THE CALCULATED VALUES OF ΔG (IN CALORIES) FOR CALCIUM CAPROATE SOLUTIONS IN METHANOL-WATER SOLVENT MIXTURE

Concentration of soap (in mol. dm^{-3})	Volume percent of methanol in the solvent mixture								
	10%	20%	30%	40%	50%	60%	70%	80%	90%
0.005	-3763.96	-3722.87	-3653.61	-3643.91	-3607.44	-3582.04	-3520.63	-3445.37	-3377.04
0.010	-3925.10	-3890.47	-3851.23	-3778.28	-3719.64	-3651.30	-3584.81	-3517.40	-3466.61
0.015	-4163.81	-4069.62	-3984.20	-3925.56	-3837.84	-3770.89	-3690.09	-3612.52	-3564.04
0.020	-4368.82	-4262.16	-4148.58	-4050.69	-3950.96	-3892.32	-3793.05	-3698.86	-3651.30
0.025	-4595.99	-4433.00	-4302.33	-4184.13	-4070.55	-3974.97	-3884.47	-3802.28	-3738.11
0.030	-4786.22	-4606.14	-4457.47	-4301.87	-4156.43	-4068.24	-3991.13	-3874.78	-3787.97
0.035	-4819.46	-4640.77	-4484.25	-4371.13	-4208.14	-4119.49	-4006.83	-3914.94	-3848.92
0.040	-4890.56	-4712.80	-4577.98	-4387.75	-4273.70	-4158.73	-4045.61	-3950.04	-3886.32
0.045	-4941.35	-4756.20	-4625.07	-4461.16	-4334.65	-4195.67	-4092.25	-3986.51	-3909.87
0.050	-4993.07	-4810.69	-4666.63	-4501.79	-4342.96	-4233.53	-4149.50	-4052.54	-3926.03

TABLE - 4

THE CALCULATED VALUES OF ΔG (IN CALORIES) FOR CALCIUM CAPRYLATE SOLUTIONS IN METHANOL-WATER SOLVENT MIXTURE

Concentration of soap (in mol. dm^{-3})	Volume percent of methanol in the solvent mixture								
	10%	20%	30%	40%	50%	60%	70%	80%	90%
0.0010	-2688.61	-2656.75	-2587.49	-2539.94	-2505.31	-2461.44	-2435.12	-2357.09	-2315.54
0.0015	-3004.43	-2913.93	-2855.29	-2759.72	-2688.15	-2648.44	-2581.95	-2523.78	-2475.29
0.0020	-3298.55	-3176.19	-3069.99	-2985.50	-2897.31	-2805.89	-2730.17	-2642.90	-2624.43
0.0025	-3581.58	-3419.52	-3316.55	-3195.58	-3060.76	-2958.26	-2889.00	-2838.21	-2774.03
0.0030	-3880.32	-3677.16	-3540.95	-3425.06	-3242.68	-3144.79	-3063.53	-2962.41	-2893.15
0.0035	-4161.97	-3920.95	-3751.96	-3582.50	-3436.60	-3298.55	-3225.59	-3118.47	-3047.83
0.0040	-4221.53	-3948.65	-3789.36	-3608.36	-3466.61	-3347.03	-3239.91	-3155.41	-3038.13
0.0045	-4258.00	-3999.44	-3838.30	-3659.61	-3507.24	-3363.19	-3268.07	-3195.58	-3068.15
0.0050	-4310.18	-4044.23	-3853.54	-3691.47	-3522.02	-3374.27	-3283.31	-3222.82	-3100.00

Comparative Profile

A comparative profile of structural insight of calcium soaps has been made under the following subheads:

Solubility

The results show that the solubility of the soaps in the methanol-water mixture decreases with the increase in the chain length of acid in the soaps. It has been suggested that mixed films of soap and alcohol are formed and the alcohol takes the same position, as does the soap molecule in the palisade layers of the soap micelles. Therefore, the amount required for the saturation of the palisade layer decreases with the increase in the number of carbon atoms in the soap. The result is in close agreement with that reported earlier by Bhargava [37-40]. The solubility of soaps follows the order:

Caproate soap > Caprylate soap

EMF Values

The EMF values show a decreasing trend with an increase in the number of carbon atoms in the chain length of the soaps. Thus the values of EMF are greater for caproate than for caprylate.

CMC Values

The results show that there is a decrease in CMC values with an increase in the number of carbon atoms in the hydrophobic chain of soap anions, furthermore, the CMC of caproate is greater than caprylate. The order of CMC for caproate and caprylate is:

Calcium caproate > calcium caprylate

ΔG Values

The ΔG values for caproate are greater than caprylate since solubility for caproate is greater than caprylate

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