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Physico-Chemical Studies of Calcium Caproate after Addition of Amide Additive Using Ion-Selective Electrode

Dushyant Pareek*, Narendra Nirwan, Chandresh Pareek
Department of Chemistry, S.D. Govt. College, Beawar, Rajasthan, India
e-mail: pareekd08@gmail.com

ABSTRACT

EMF of the cell containing calcium caproate-soap solution in methanol-water solvent system was measured with the aid of ion-selective electrode. The Critical Micelle Concentration of soap solutions was determined by graphical method. The effect of amide additives on CMC values of referred soap solution has been studied by using electrometric method with the aid of ion selective electrode. 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 : Hydrophilic Oleomicelle, Ion-Selective Electrode, Lipophilic Hydromicelle, Ice-Berg, Palisade Layers

I. INTRODUCTION

By the study of many literatures it reveals that calcium soaps are widely used in industries as detergents, softeners, plasticizer greases, lubricants, anti-corrosion agent [1-8]. The micelles formed by soaps in solutions are very useful entities for 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 particularly important as the larger anionic part of these macromolecules shows the micellar effects on the surface phenomenon. Because of Ion-Selective Electrode (ISE) have become one of the most useful tool for rapid analysis and its ability to measure the concentration in very low range (10^{-4}-10^{-6}M) with a high selectivity. It influenced us to use them for systematic micellar studies of calcium soaps by electrometric method.

II. EXPERIMENTAL

Purification of caproic acid is done 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 method is similar as reported earlier [15-16]. The information about the nature and structure of calcium soaps in solid state were carried out by elemental and infrared spectral analysis. The results obtained were in good agreement with pervious 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 electrometrically method using ISE. In the present work the effect of various organic amide additives on

CMC values of referred soaps has been studied by using electrometric method with the aid of ion selective electrode and the work has been initiated with a view to find out the nature of micelles formed in soap solutions under different conditions. The measurement of the EMF of the cell containing soap solutions have been carried out by using ISE's after the addition of 2 mg of each additive in test solutions. All the measurements were made at a constant temperature.

The soap solutions of different soap concentration from 0.005M to 0.035M for calcium caproate in varying composition of methanol-water solvent mixture were prepared.

EMF Measurement

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

Thus the cell can be represented as the pattern suggested by previous workers [24-26].

$$Hg \mid Hg_2Cl_2 \mid \text{Sat. KCl} \mid \text{Soap solution} \mid \text{Membrane} \mid \text{Sat. Soln.} \mid AgCl \mid Ag$$

$\longleftarrow$ Reference Electrode $\longrightarrow$ $\longleftarrow$ ISE $\longrightarrow$

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

III. RESULT AND DISCUSSION

SOLUBILIZATION

The solubility of urea, acetamide and benzamide in pure water and referred soap solutions of varying compositions are presented in Table – 1. It is pointed out from the Table that the solubility, of these amides are much higher in pure water than in the soap solutions in methanol – water solvent mixtures. This may be due to the fact that these compounds are incapable to replace methanol from the palisade layers of the micelles and so the layers get saturated with small amount of these compounds. It is also observed from the Table – 1 that the solubility of these amides decreases with increase in methanol concentration in solvent mixtures of varying compositions. This is probably due to the fact that the amount of these compounds, required for the saturation of palisade layers, is less in presence of higher concentration of methanol than for lower concentration of methanol.

TABLE – 1 SOLUBILITY OF AMIDE COMPOUNDS (in g. mol. l^{-1}) IN PURE WATER AND IN CALCIUM CAPROATE SOLUTIONS IN METHANOL-WATER MIXTURES

Volume % of Methanol in soap solution	Name of amides compounds		
	Urea	Acetamide	Benzamide
10	00.3587	00.0692	00.0532
20	00.3554	00.0673	00.0514
30	00.3518	00.0654	00.0491
40	00.3482	00.0637	00.0469
50	00.3447	00.0612	00.0447
60	00.3412	00.0584	00.0425
70	00.3380	00.0561	00.0403
80	00.3344	00.0539	00.0382
90	00.3309	00.0512	00.0358
Pure water	19.7614	15.5029	00.1314

EMF

The EMF values of the cell containing calcium caproate soap solutions of varying compositions are plotted with

respect to logarithm of soap concentration (Fig. 1, 2, 3) respectively. It is observed from the Figs. that the EMF value of the cell increases with increase in soap concentration. The result can be explained on the basis of well-known electrode equation [27].

$$E = E_0 \pm \frac{RT}{Z_1 F} \ln \left[a_1 + \sum_{i=2}^{n} K_{li}^{Pot} (a_i)^{z1/zi} \right]$$

The EMF values of the cell containing calcium caproate solutions, after the addition of urea, acetamide and benzamide, are listed in Table – 2 (A & B), 3 (A & B) and 4 (A & B) respectively. It is apparent form the Tables that the EMF values have been increased by the addition of these amide compounds. This may be due to the fact that the degree of dissociation of soap has increased by the addition of these additives. Therefore, the activity of cation has also been increased in soap solutions, resulting in increase in EMF value.

TABLE – 2 (A) EMF VALUES (in mV) OF THE CELL CONTAINING CALCIUM CAPROATE SOLUTIONS IN METHANOL-WATER SOLVENT MIXTURE AFTER THE ADDITION OF UREA

Concentration of Soap (in g.mol. l^{-1})	Volume percent of methanol in the solvent mixture							
	10%		20%		30%		40%	
	Before Addition	After Addition	Before Addition	After Addition	Before Addition	After Addition	Before Addition	After Addition
0.005	67.14	67.28	65.52	66.12	67.78	64.98	63.91	63.59
0.006	69.44	70.05	67.38	68.58	66.05	67.11	65.04	65.73
0.008	74.18	75.33	72.39	73.06	70.04	71.56	68.53	69.78
0.010	78.93	81.22	75.14	78.19	73.34	76.08	71.65	73.66
0.012	83.04	86.75	79.42	82.97	76.54	81.08	74.98	77.25
0.015	90.52	95.09	85.04	90.27	82.16	87.27	79.46	83.55
0.020	93.07	97.17	87.51	93.58	84.29	91.22	82.77	87.44
0.025	95.64	98.67	90.08	95.35	87.33	92.74	84.82	89.02
0.030	98.06	99.88	92.74	97.04	89.65	94.08	87.23	90.77
0.035	100.12	101.26	95.26	98.09	92.57	95.02	89.24	91.82

TABLE – 2 (B) EMF VALUES (in mV) OF THE CELL CONTAINING CALCIUM CAPROATE SOLUTIONS IN METHANOL-WATER SOLVENT MIXTURE AFTER THE ADDITION OF UREA

Concentration of Soap (in g.mol. l^{-1})	Volume percent of methanol in the solvent mixture									
	50%		60%		70%		80%		90%	
	Before Addition	After Addition	Before Addition	After Addition	Before Addition	After Addition	Before Addition	After Addition	Before Addition	After Addition
0.005	63.07	62.75	62.26	62.04	61.31	61.08	60.72	60.26	59.54	79.71
0.006	64.15	64.44	63.34	64.14	62.58	62.66	61.4	61.8	61.02	60.54
0.008	67.29	68.59	66.11	67.01	64.82	65.48	63.75	64.67	63.04	63.29
0.010	70.05	72.32	68.32	70.8	67.14	68.54	66.28	67.74	65.34	66.35
0.012	73.08	76.11	72.49	73.81	70.12	71.65	68.75	70.04	67.54	69.43
0.015	77.62	82.07	75.54	76.77	73.24	76.15	72.59	74.68	70.87	73.18
0.020	79.58	85.01	77.43	81.36	75.56	78.89	74.24	77.16	72.67	75.15
0.025	81.9	86.12	79.04	82.22	77.65	80.1	75.75	77.86	74.08	76.42
0.030	84.15	87.53	82.09	83.14	79.85	81.35	77.44	79.63	76.88	77.49
0.035	86.02	88.06	83.72	84.86	82.16	82.47	78.94	80.56	77.62	78.24

TABLE – 3 (A) EMF VALUES (in mV) OF THE CELL CONTAINING CALCIUM CAPROATE SOLUTIONS IN METHANOL-WATER SOLVENT MIXTURE AFTER THE ADDITION OF ACETAMIDE

Concentration of Soap (in g.mol. l^{-1})	Volume percent of methanol in the solvent mixture							
	10%		20%		30%		40%	
	Before Addition	After Addition	Before Addition	After Addition	Before Addition	After Addition	Before Addition	After Addition
0.005	67.14	68.08	65.52	67.32	64.78	66.17	63.91	65.09
0.006	69.44	71.14	67.38	69.58	66.05	68.02	65.04	67.04
0.008	74.18	76.31	72.39	74.44	70.04	72.18	68.53	71.18
0.010	78.93	82.59	75.14	79.13	73.34	77.36	71.65	75.05
0.012	83.04	87.55	79.42	84.72	76.54	82.12	74.98	79.36
0.015	90.52	96.08	85.04	91.44	82.16	88.20	79.46	85.16
0.020	93.07	98.97	87.51	95.43	84.29	92.18	82.77	88.36
0.025	95.64	100.06	90.08	96.72	87.33	93.14	84.82	90.02
0.030	98.06	100.72	92.74	97.27	89.65	94.29	87.23	91.38
0.035	100.12	101.62	95.26	98.58	92.57	95.36	89.24	92.06

TABLE – 3 (B) EMF VALUES (in mV) OF THE CELL CONTAINING CALCIUM CAPROATE SOLUTIONS IN METHANOL-WATER SOLVENT MIXTURE AFTER THE ADDITION OF ACETAMIDE

Concentration of Soap (in g.mol. l^{-1})	Volume percent of methanol in the solvent mixture									
	50%		60%		70%		80%		90%	
	Before Addition	After Addition	Before Addition	After Addition	Before Addition	After Addition	Before Addition	After Addition	Before Addition	After Addition
0.005	63.07	64.32	62.26	63.18	61.31	62.67	60.72	61.29	59.54	60.43
0.006	64.15	66.21	63.64	64.76	62.58	64.08	61.4	63.35	61.02	61.77
0.008	67.29	69.92	66.11	68.71	64.82	67.47	63.75	66.12	63.04	65.05
0.010	70.05	74.34	68.32	72.16	67.14	70.37	66.28	69.68	65.34	68.22
0.012	73.08	77.63	72.49	75.54	70.12	74.1	68.75	72.25	67.54	71.38
0.015	77.62	82.49	75.54	81.01	72.24	79.23	72.59	77.64	70.57	76.29
0.020	79.58	86.22	77.43	83.64	75.56	81.75	74.24	80.13	72.67	78.42
0.025	81.9	87.24	79.04	84.56	77.65	82.43	75.75	80.39	74.08	78.84
0.030	84.15	87.73	82.09	85.06	79.85	82.92	77.44	80.98	76.88	79.26
0.035	86.02	88.59	83.72	86.13	82.16	83.28	78.94	81.42	77.62	79.94

TABLE – 4 (A) EMF VALUES (in mV) OF THE CELL CONTAINING CALCIUM CAPROATE SOLUTIONS IN METHANOL-WATER SOLVENT MIXTURE AFTER THE ADDITION OF BENZAMIDE

Concentration of Soap (in g.mol. l^{-1})	Volume percent of methanol in the solvent mixture							
	10%		20%		30%		40%	
	Before Addition	After Addition	Before Addition	After Addition	Before Addition	After Addition	Before Addition	After Addition
0.005	67.14	69.23	65.52	68.06	64.78	67.51	63.91	66.31
0.006	69.44	71.38	67.38	70.14	66.05	69.26	65.04	67.58
0.008	74.18	77.62	72.39	75.27	70.04	73.48	68.53	71.78
0.010	78.93	83.07	75.14	80.13	73.34	77.42	71.65	75.12
0.012	83.04	89.11	79.42	85.26	76.54	82.39	74.98	79.08
0.015	90.52	97.46	85.04	92.61	82.16	88.09	79.46	85.06
0.020	93.07	102.36	87.51	97.54	84.29	93.12	82.77	88.73
0.025	95.64	103.49	90.08	98.63	87.33	94.29	84.82	90.07
0.030	98.06	104.51	92.74	99.57	89.65	95.36	87.23	91.05
0.035	100.12	105.06	95.26	100.08	92.57	96.23	89.24	91.14

TABLE – 4 (B) EMF VALUES (in mV) OF THE CELL CONTAINING CALCIUM CAPROATE SOLUTIONS IN METHANOL-WATER SOLVENT MIXTURE AFTER THE ADDITION OF BENZAMIDE

Concentration of Soap (in g.mol. l^{-1})	Volume percent of methanol in the solvent mixture									
	50%		60%		70%		80%		90%	
	Before Addition	After Addition	Before Addition	After Addition	Before Addition	After Addition	Before Addition	After Addition	Before Addition	After Addition
0.005	63.07	65.19	62.26	64.28	61.31	63.67	60.72	62.48	59.54	61.59
0.006	64.15	66.29	63.34	65.38	62.58	64.87	61.4	63.51	61.02	62.47
0.008	67.29	70.16	66.11	69.15	64.82	67.47	63.75	66.64	63.04	65.07
0.010	70.05	74.12	68.32	72.07	67.14	70.67	66.28	69.05	65.34	67.52
0.012	73.08	77.42	72.49	75.21	70.12	73.65	68.75	71.73	67.54	70.05
0.015	77.62	82.71	75.54	80.43	73.24	77.92	72.59	75.63	70.87	73.29
0.020	79.58	85.79	77.43	83.16	75.56	81.06	74.24	76.17	72.67	76.11
0.025	81.9	86.14	79.04	83.63	77.65	81.74	75.75	79.82	74.08	77.08
0.030	84.15	87.53	82.09	84.88	79.85	82.63	77.44	80.14	76.88	77.68
0.035	86.02	88.06	83.72	85.26	82.16	83.57	78.94	81.08	77.62	79.07

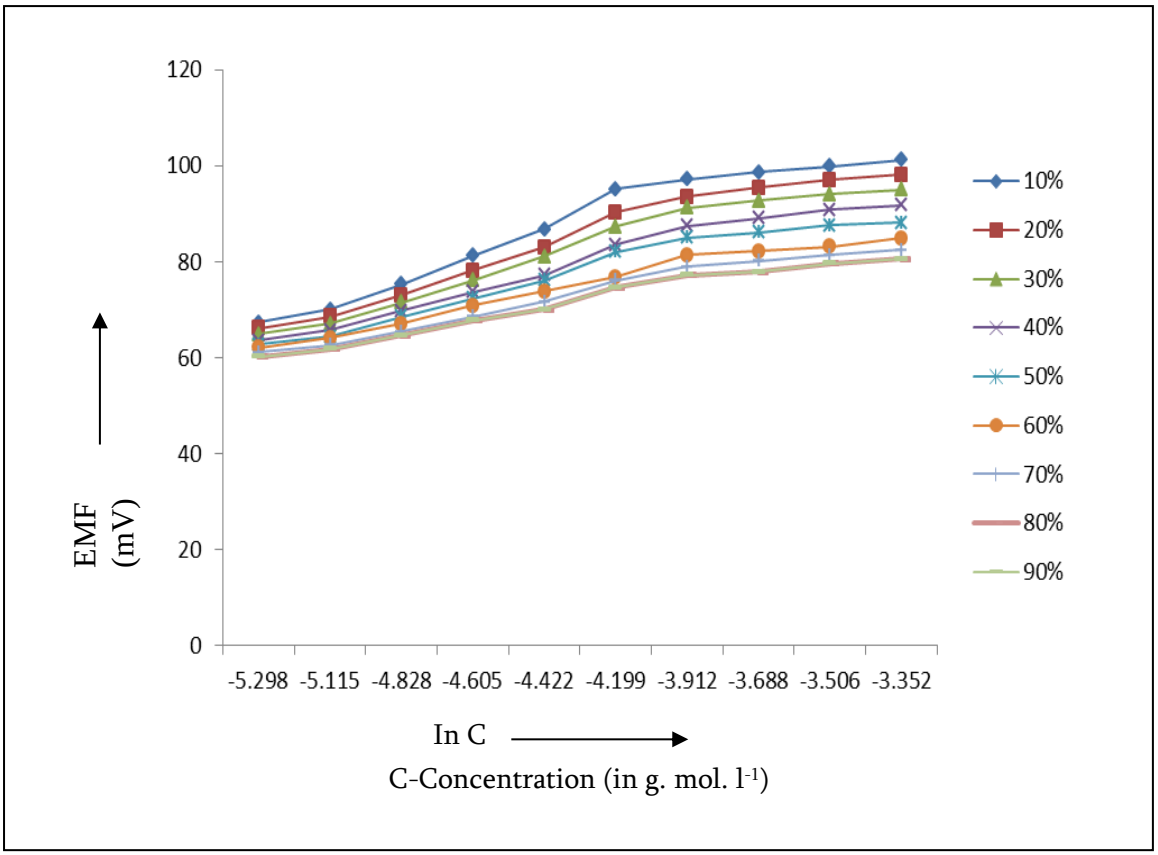

Fig. 1 : Plot of EMF of the cell containing calcium caproate solutions against logarithm of soap concentration in methanol-water solvent mixture after the addition of urea

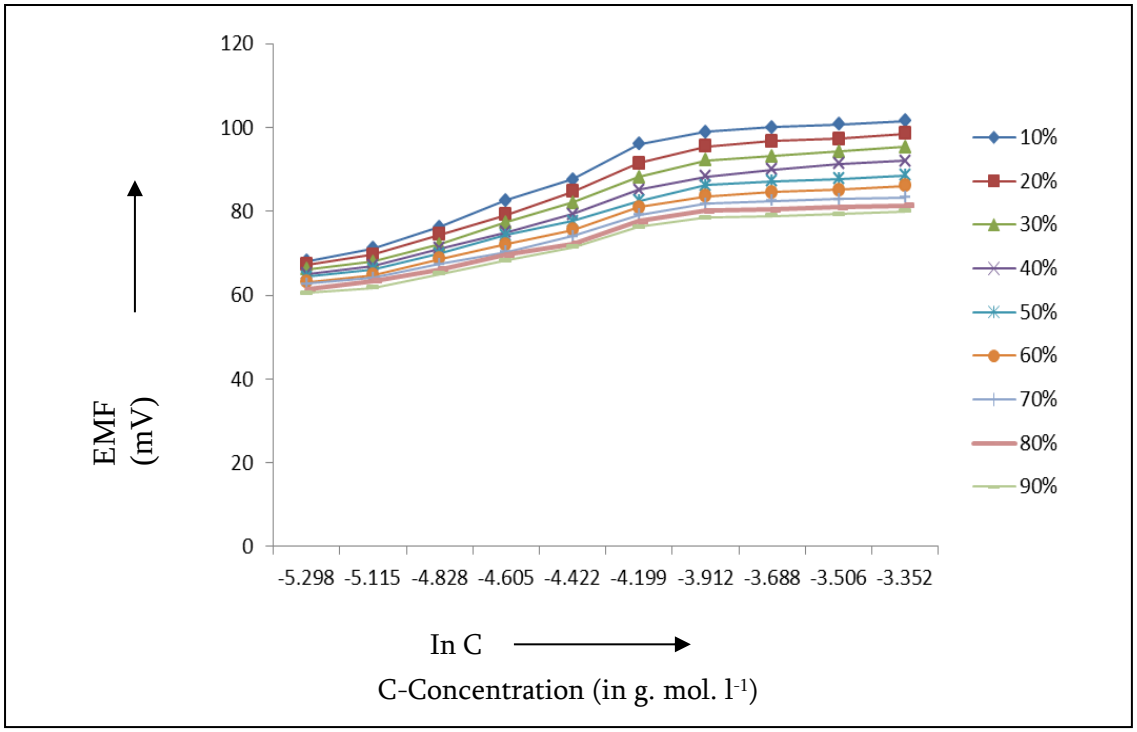

Fig. 2 : Plot of EMF of the cell containing calcium caproate solutions against logarithm of soap concentration in methanol-water solvent mixture after the addition of Acetamide

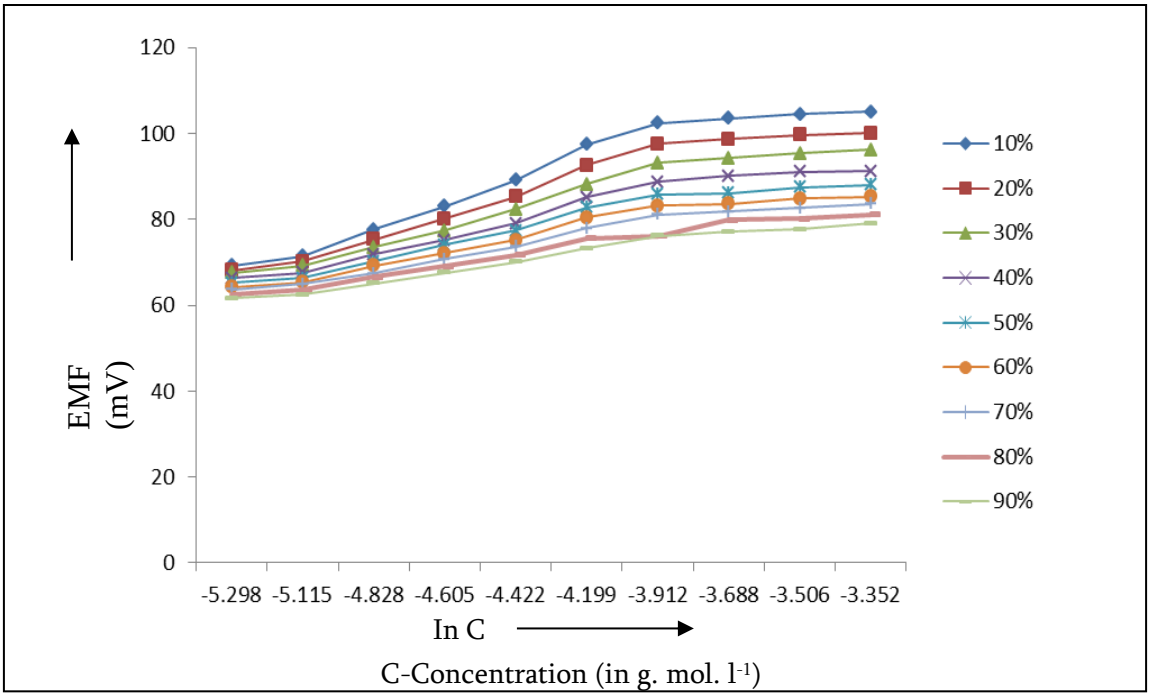

Fig. 3 : Plot of EMF of the cell containing calcium caproate solutions against logarithm of soap concentration in methanol-water solvent mixture after the addition of Benzamide

It has also been observed that the EMF of the cell, in presence of these amides, decreases with increase in methanol concentration in solvent mixtures. This is due to the decreasing of dielectric constant with increasing methanol concentration. The plots of EMF against logarithm of soap concentration (Figs 1,2,3) are characterised by in intersection of two straight lines at a definite soap concentration which corresponds. The

CMC values of calcium caproate, before and after the addition of urea, acetamide and benzamide, are as following:

TABLE – 5 CMC VALUES (in g. dm^{-3}) OF CALCIUM CAPROATE

Name of Additives			
Without any Additives	**Urea**	**Acetamide**	**Benzamide**
15.00	16.00	16.50	16.75

It is the clear that the value of CMC has increased after the addition of amides. This can be explained on the basis of the importance of the water structure on micelle formation. The hypothesis for micelle formation is based on the 'ice-berg' structure of water. According to Frank and Evans [28] the water molecules become more ordered around the non-polar solute, with an increasing extent of hydrogen bonding in this region. Thus in the case of soap solution, the hydrocarbon chain of the soap anions are surrounded by a water structure, i.e. ice berg structure, and represent a comparatively low energy state. [29] The non-polar soap anions surrounded by "ice-berg" water structure are curled up tightly and internal movements are consequently restricted.[30] This concomitant restriction of motion provides a driving force for aggregation which is an entropy effect at lower temperature. Therefore, the more ordered the "ice-berg" structure around the anions greater will be the driving force for the aggregation. It is anticipated, therefore, that structure promoting substances should enhance the tendency of micellization and consequently decrease the CMC of the soap, where as substances that breakup the "ice-berg" water structure around soap anions should retard the tendency of micellization and consequently increase the CMC. Therefore, the effect of amide compounds on CMC can be explained in the light of the "ice-berg" picture of water structure around the non-polar soap anions.

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 to 3) shows that the EMF value increases with 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 decrease in 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. Where as the second factor has a decreasing effect on EMF, since with the increase in methanol concentration in solvent composition the dielectric constant of solution decreases. It is therefore, logical to expect that the difference of these two effects and predominance of dielectric constant, the EMF of the cell decreases with increase in methanol concentration in the system.

The plots of EMF against logarithm of soap concentration (log C) of 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 to 3). It is clear from the plots that the EMF value at first increases rapidly and then gradually which is due to 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 moderately strong electrolyte and with 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 it is similar reported for magnesium caproate.

However, at concentration ranges above the CMC, the behavior of soap is non-ideal due to micellization and 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 appears at the same concentration (i.e. CMC) is same for all methanol-water solvent mixtures of varying compositions. This indicates that the CMC of soap does not depend on methanol concentration in solution. The above result is in good agreement with that obtained by conductivity measurement [29-33].

FREE ENERGY CHANGE

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

$$\Delta G = -nEF$$

The calculated values of free energy change for cell reaction in calcium caproate soap solutions, after the addition of urea, acetamide and benzamide are in Table 6, 7 & 8.

TABLE – 6 THE CALCULATED VALUES OF ΔG (IN CALORIES) FOR CALCIUM CAPROATE SOLUTIONS IN METHANOL-WATER SOLVENT MIXTURE AFTER THE ADDITION OF UREA

Concentration of Soap (in g. mol. l^{-1})	Volume percent of methanol in the solvent mixture								
	10%	20%	30%	40%	50%	60%	70%	80%	90%
0.005	-3106.47	-3052.91	-3000.27	-2936.09	-2897.31	-2864.53	-2820.20	-2782.34	-2756.94
0.006	-3234.37	-3166.49	-3098.62	-3034.90	-2975.34	-2961.49	-2893.15	-2853.44	-2795.27
0.008	-3478.16	-3373.34	-3304.09	-3221.90	-3166.95	-3094.00	-3023.36	-2985.96	-2922.24
0.010	-3750.11	-3610.21	-3512.78	-3401.05	-3339.18	-3269.00	-3164.65	-3127.71	-3063.53
0.012	-4005.44	-3830.91	-3743.65	-3566.81	-3514.17	-3407.97	-3308.24	-3233.90	-3205.74
0.015	-4390.52	-4167.97	-4029.45	-3857.69	-3789.36	-3544.64	-3516.02	-3448.14	-3378.89
0.020	-4486.56	-4320.80	-4211.83	-4037.30	-3925.10	-3756.57	-3642.53	-3562.65	-3469.84
0.025	-4555.82	-4402.52	-4282.01	-4110.25	-3976.35	-3796.28	-3698.40	-3594.97	-3528.48
0.030	-4611.68	-4480.56	-4343.89	-4191.06	-4041.46	-3838.76	-3756.11	-3676.70	-3577.89
0.035	-4675.40	-4529.04	-4384.29	-4239.54	-4065.93	-3918.18	-3807.83	-3719.64	-3612.52

TABLE – 7 THE CALCULATED VALUES OF ΔG (IN CALORIES) FOR CALCIUM CAPROATE SOLUTIONS IN METHANOL-WATER SOLVENT MIXTURE AFTER THE ADDITION OF ACETAMIDE

Concentration of Soap (in g. mol. l^{-1})	Volume percent of methanol in the solvent mixture								
	10%	20%	30%	40%	50%	60%	70%	80%	90%
0.005	-3143.41	-3108.32	-3055.22	-3005.35	-2969.80	-2917.16	-2893.61	-2829.90	-2790.19
0.006	-3284.69	-3212.67	-3140.64	-3095.39	-3057.06	-2990.11	-2958.72	-2925.01	-2852.06
0.008	-3523.40	-3437.06	-3332.71	-3286.54	-3228.36	-3172.50	-3115.24	-3052.91	-3003.50
0.010	-3813.37	-3653.61	-3571.89	-3465.23	-3432.44	-3331.79	-3249.14	-3217.28	-3149.87
0.012	-4042.38	-3911.74	-3791.67	-3664.23	-3584.35	-3487.85	-3421.36	-3335.94	-3295.78
0.015	-4436.23	-4221.99	-4072.39	-3932.03	-3808.75	-3740.41	-3658.23	-3584.81	-3522.48
0.020	-4569.67	-4406.22	-4256.16	-4079.78	-3980.97	-3861.85	-3774.58	-3699.78	-3620.83
0.025	-4620.00	-4465.78	-4300.48	-4156.43	-4028.07	-3904.33	-3805.98	-3711.79	-3640.22
0.030	-4650.47	-4491.17	-4353.58	-4219.22	-4050.69	-3927.41	-3828.60	-3739.03	-3659.61
0.035	-4692.02	-4551.66	-4402.99	-4250.62	-4090.40	-3976.82	-3845.22	-3759.34	-3691.01

TABLE – 8 THE CALCULATED VALUES OF ΔG (IN CALORIES) FOR CALCIUM CAPROATE SOLUTIONS IN METHANOL-WATER SOLVENT MIXTURE AFTER THE ADDITION OF BENZAMIDE

Concentration of Soap (in g. mol. l^{-1})	Volume percent of methanol in the solvent mixture								
	10%	20%	30%	40%	50%	60%	70%	80%	90%
0.005	-3196.50	-3142.48	-3117.09	-3061.68	-3009.97	-2967.95	-2939.79	-2884.84	-2843.75
0.006	-3295.78	-3238.52	-3197.89	-3120.32	-3060.76	-3017.74	-2995.19	-2932.40	-2884.38
0.008	-3583.89	-3475.39	-3392.74	-3314.24	-3239.44	-3192.81	-3115.24	-3076.92	-3004.43
0.010	-3835.53	-3699.78	-3574.66	-3468.46	-3422.29	-3327.63	-3262.99	-3188.19	-3117.55
0.012	-4114.41	-3936.65	-3804.13	-3651.30	-3574.66	-3472.61	-3400.59	-3311.94	-3234.37

0.015	-4499.95	-4276.01	-4067.31	-3927.41	-3818.91	-3713.63	-3597.74	-3492.01	-3383.96
0.020	-4726.19	-4503.64	-4299.56	-4096.86	-3961.12	-3839.68	-3742.72	-3516.94	-3514.17
0.025	-4778.37	-4553.97	-4353.58	-4158.73	-3977.28	-3861.39	-3774.12	-3685.47	-3558.96
0.030	-4825.46	-4597.37	-4402.99	-4203.98	-4041.46	-3919.10	-3815.21	-3700.24	-3586.66
0.035	-4850.86	-4620.92	-4443.16	-4254.31	-4065.93	-3936.65	-3858.61	-3743.65	-3650.84

IV. CONCLUSION & REASON

It is pointed out from the CMC data from Table – 5 the CMC has been increased by the addition of amides.

The order of CMC for amide compounds is :

Benzamide > Acetamide > Urea

The above result can be analysed in the light of the "ice-berg" structure of water molecules. It has been postulated that non-polar hydrocarbon chains get clustered by the "ice-berg" water structure through hydrogen bonding. These additives disrupt the water structure by the formation of hydrogen bonding with water molecules. Since urea has three potential centers of H-bonding that facilitate the formation of new cluster of big size around the soap anions. Whereas in the case of acetamide and benzamide, having only two potential centers, the cluster has braked up resulting more increase in CMC. The results are similar as in magnesium caproate.[34]

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