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Physico-Chemical Studies of Calcium Caprylate after Addition of Hydroxy Additives Using Ion-Selective Electrode

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ABSTRACT

Calcium soap of caprylic acid was prepared and a cell was set up for the measurement of EMF of the cell having 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 effect of hydroxy additives on CMC values of referred soap solution has been studied by graphical method. Free energy change (ΔG) for given cell reaction was determine. 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: EMF, Ion-Selective Electrode, palisade layers, Lipophilic hydromicelle, Hydrophilic oleomicelle, Ice-berg

I. INTRODUCTION

Literature survey 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) has become one of the most useful tools 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

Calcium soap of caprylic acid 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 has been determined electrometrically method using ISE. In the present work the effect of

various organic hydroxy 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 0.001M to 0.005M for calcium caprylate 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].

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

$$\longleftarrow \text{Reference Electode} \longrightarrow \qquad \longleftarrow \text{ISE} \longrightarrow$$

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

III. RESULT AND DISCUSSION

SOLUBILIZATION

The Table 1 presents the solubility of resorcinol and hydroquinone additives in soap solution and in pure water. It is clear that these compounds have much lower solubility in soap solutions than in pure water. This may be due to the fact that these hydroxy compounds are unable to replace the methanol from the palisade layer of the micelles. It is also pointed out from the table that solubility of these compounds decreases with increase in methanol concentration in solvent mixture. This is probably due to the fact that the layers get saturated with small amount of these compounds. The result is similar to that reported in previous paper as for amide.[23]

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

Volume % of methanol in soap solution	Resorcinol	Hydroquinone
10	00.1014	00.0733
20	00.0994	00.0713
30	00.0971	00.0682
40	00.0950	00.0659
50	00.0927	00.0635
60	00.0908	00.0617
70	00.0885	00.0592
80	00.0861	00.0567
90	00.0838	00.0542
Pure Water	00.2281	00.5562

EMF

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

The EMF values of the cell containing Calcium caprylate soap solutions of varying compositions are plotted with respect to logarithm of soap concentration (Fig. 1, 2) 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 [24].

The EMF values of the cell with referred soap solutions, after the addition of resorcinol and hydroquinone are given in Table – 2 (A & B) and 3(A & B) respectively. It is clear from the table that the EMF values have increased by the addition of these hydroxy compounds. This may be due to increase in ionization of soap molecules by the addition of these additives.

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

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
0.0010	45.07	47.38	44.12	46.07	43.05	45.11	42.55	43.78
0.0012	49.56	51.47	47.32	49.41	46.08	47.47	44.59	46.31
0.0015	55.34	57.52	52.25	55.03	50.14	52.83	47.22	50.61
0.0020	65.46	67.61	60.18	64.18	56.17	61.07	52.62	57.49
0.0025	67.16	72.23	61.55	67.49	57.91	64.13	54.05	60.14
0.0030	68.75	72.69	62.93	68.03	58.08	65.07	55.15	61.13
0.0035	70.02	73.12	64.1	68.45	60.01	65.67	56.24	61.64
0.0040	72.13	73.71	65.84	69.13	61.23	66.28	57.25	62.1
0.0045	73.21	74.15	67.12	69.77	62.51	67.03	58.59	63.11
0.0050	74.58	74.52	68.29	70.26	63.76	67.62	60.04	64.13

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

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
0.0010	41.17	42.51	40.02	41.64	38.87	40.25	38.04	39.05	37.24	38.12
0.0012	43.11	45.07	42.29	43.42	40.73	42.11	39.51	42.36	38.14	39.62
0.0015	45.57	48.64	44.63	46.64	43.21	45.13	41.85	43.95	40.12	42.52
0.0020	50.09	54.73	47.64	52.53	46.08	50.36	44.72	48.43	43.18	47.19
0.0025	51.73	57.47	49.24	55.06	47.17	52.55	45.5	50.41	44.11	48.36
0.0030	52.57	57.74	50.08	56.06	48.26	53.62	46.04	52.08	45.01	50.03
0.0035	53.36	59.13	51.29	56.73	49.19	54.08	47.14	52.58	45.62	50.62
0.0040	54.78	59.68	52.28	57.08	50.03	54.87	47.97	53.07	46.11	51.13
0.0045	55.92	60.13	53.14	57.78	51.18	55.24	48.28	53.58	47.35	51.67
0.0050	56.15	60.78	54.05	58.25	52.14	55.92	49.52	54.05	47.64	52.35

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

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
0.0010	45.07	49.13	44.12	48.03	43.05	47.21	42.55	46.09
0.0012	49.56	52.63	47.32	51.18	46.08	50.11	44.59	48.47
0.0015	55.34	59.83	52.25	56.26	50.14	54.77	47.22	52.44
0.0020	65.46	70.13	60.18	65.38	56.17	62.71	52.62	59.15
0.0025	67.16	75.41	61.55	70.02	57.91	66.43	54.05	62.54
0.0030	68.75	76.14	62.93	70.69	58.08	67.08	55.15	63.14
0.0035	70.02	76.77	64.1	71.08	60.01	67.83	56.24	63.68
0.0040	72.13	77.03	65.84	71.48	61.23	68.27	57.25	64.24
0.0045	73.21	77.31	67.12	71.96	62.51	68.84	58.59	64.82
0.0050	74.58	77.68	68.29	72.13	63.76	69.21	60.04	65.29

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

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
0.0010	41.17	45.01	40.02	44.22	38.87	42.61	38.04	42.15	37.24	40.78
0.0012	43.11	47.37	42.29	46.07	40.73	44.73	39.51	43.59	37.14	42.41
0.0015	45.57	50.38	44.63	48.45	43.21	47.39	41.85	46.08	40.12	44.51
0.0020	50.09	56.18	47.64	54.01	46.08	51.81	44.72	50.13	43.18	48.04
0.0025	51.73	59.7	49.24	56.44	47.17	54.63	45.5	52.71	44.11	50.66
0.0030	52.57	60.28	50.08	57.11	48.26	55.42	46.04	53.33	45.01	51.13
0.0035	53.36	60.88	51.29	57.77	49.19	56.08	47.14	53.93	46.62	51.81
0.0040	54.78	61.51	52.28	58.31	50.03	56.62	47.97	54.43	46.11	52.39
0.0045	55.92	62.08	53.14	58.81	51.18	57.18	48.28	54.81	47.35	52.87
0.0050	56.15	62.67	54.05	59.41	52.14	57.67	49.52	55.38	47.64	53.37

It has also been observed from the tables that the EMF value of the cell decreases with increases in methanol concentration in mixture. This may be due the fact that the hydroxy compounds form hydrates with water and these hydrated molecules surround the micelles and results in the increase in the size of the micelles [25]. The increasing size of micelles has decreasing effect on the EMF value but the increase in methanol concentration decreases the hydration and lowers the dielectric constant. The decrease in hydration has an increasing effect on EMF value whereas lowering of dielectric constant does not allow increasing in EMF value. The increase in hydration by the addition of hydroxy compounds and lowering of hydration and of dielectric constant with increase in methanol concentration result the decrease in EMF value, since the dielectric constant effect is predominant. This result is similar to that of hydroxy compounds added in magnesium soap solution. [26-31]

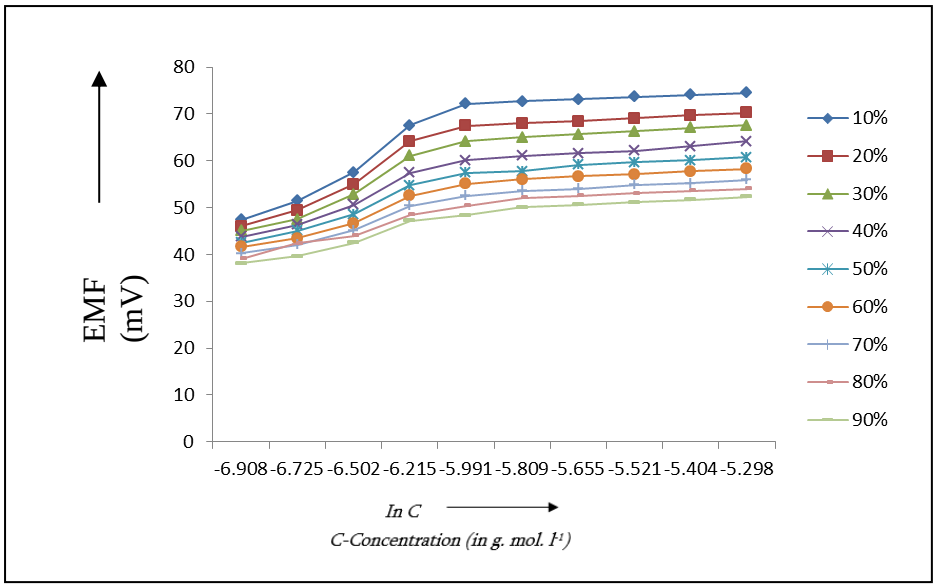

Fig. 1 : Plot of EMF of the cell containing calcium caprylate solutions against logarithm of soap concentration in methanol-water solvent mixture after the addition of Resorcinol

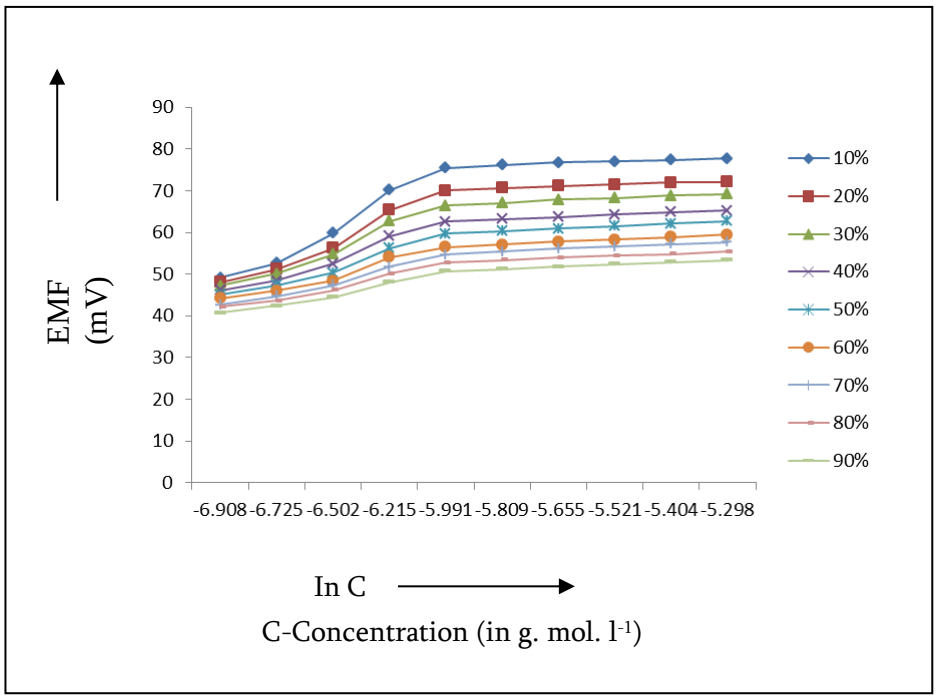

Fig. 2 : Plot of EMF of the cell containing calcium caprylate solutions against logarithm of soap concentration in methanol-water solvent mixture after the addition of Hydroquinone

The plots (fig. 1 and 2) of EMF against logarithm of soap concentration (lnC) are characterised by an intersection of two straight lines at a definite soap concentration, which corresponds to CMC of the refereed soap after the addition of hydroxy compounds. The CMC values of Calcium caprylate, before and after the addition of resorcinol and hydroquinone, are summarized in Table 4.

TABLE – 4 CMC VALUES (in g. d dm^{-3}) OF CALCIUM CAPRYLATE

Name of Additives		
Without any Additives	**Hydroquinone**	**Resorcional**
2.00	2.30	2.22

It is revealed from the table that the CMC of Calcium caprylate has been increased by the addition of these hydroxy compounds. This result is similar to that of hydroxy additives [23] and can be explained on the basis of importance of "ice-berg" water structure. Since the hydroxy compounds may also breakup the "ice-berg" water structure by the formation of H-bonding with water molecules and thus retard the tendency of agglomeration of soap molecules and consequently increase the CMC value. It is also clear by the plots that the difference in successive value of EMF between 10%-20%, 20%-30%, 30%-40% and 40%-50% solvent mixture is greater and for 50%-60%, 60%-70%, 70%-80% & 80%-90% it is not so much. This may be due to change in nature of micelles from hydrophilic oleomicelles to lipophilic hydro micelles.

The plots of volume percent of methanol (fig. 3 & 4) show a break at about 60% methanol concentration. This indicates that the change in the nature of micelles from hydrophilic oleomicelles to lipophilic hydro-micelles takes place at about 60% methanol concentration.

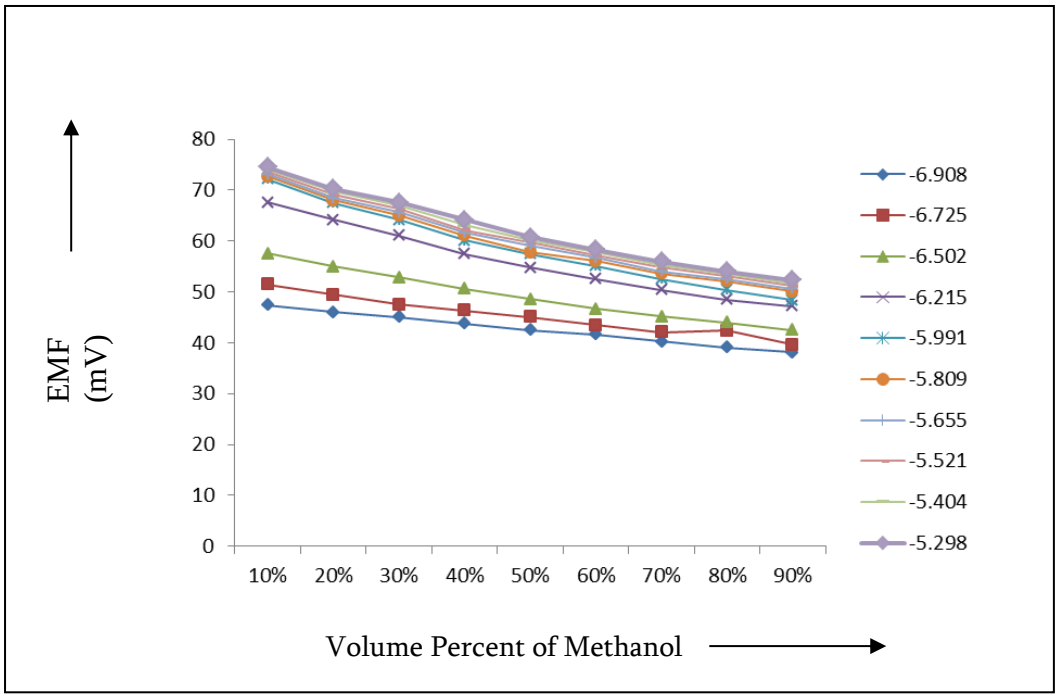

Fig. 3 : Plot of EMF of the cell containing calcium caprylate solutions against volume percent of methanol after the addition of Resorcinol

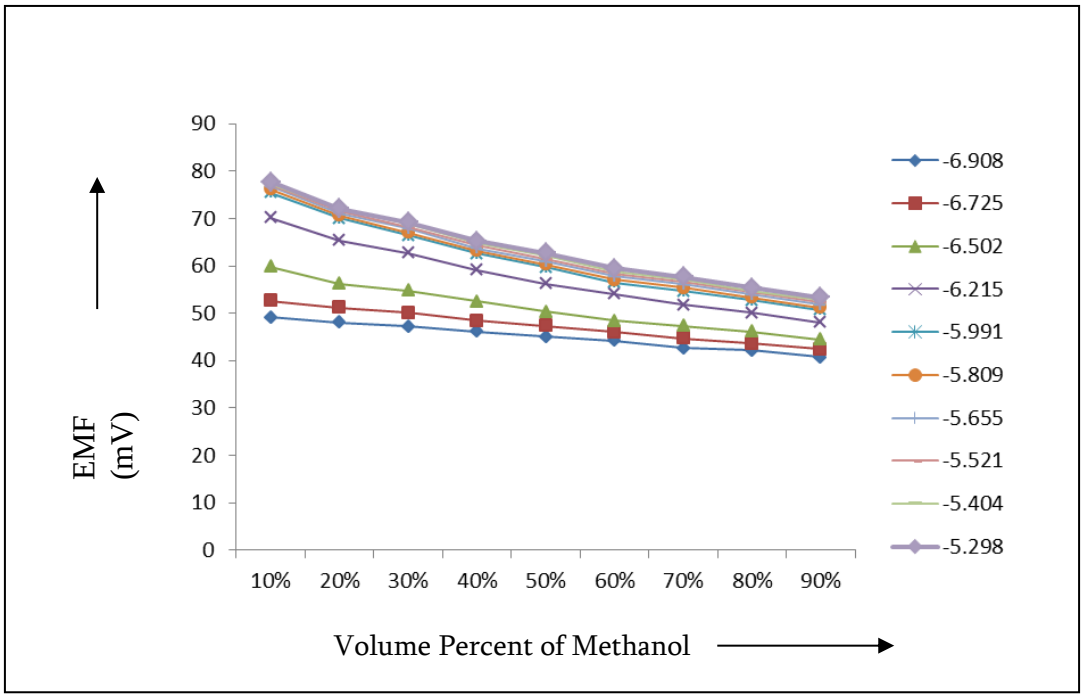

Fig. 4 : Plot of EMF of the cell containing calcium caprylate solutions against volume percent of methanol after the addition of Hydroquinone

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 caprylate soap solutions, after the addition of resorcinol and hydroquinone are in **Table 5 & 6.**

TABLE – 5 THE CALCULATED VALUES OF ΔG (IN CALORIES) FOR CALCIUM CAPRYLATE SOLUTIONS IN METHANOL-WATER SOLVENT MIXTURE AFTER THE ADDITION OF RESORCINOL

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%
0.0010	-2187.64	-2127.16	-2082.83	-2021.42	-1962.78	-1922.61	-1858.43	-1803.03	-1760.09
0.0012	-2376.49	-2281.37	-2191.80	-2138.24	-2080.98	-2004.80	-1944.31	-1955.86	-1829.34
0.0015	-2655.83	-2540.86	-2439.28	-2336.78	-2245.82	-2153.47	-2083.75	-2029.27	-1963.24
0.0020	-3121.71	-2963.33	-2819.74	-2654.44	-2527.01	-2425.43	-2325.23	-2236.12	-2178.87
0.0025	-3335.02	-3116.17	-2961.03	-2776.80	-2653.52	-2542.24	-2426.35	-2327.54	-2232.89
0.0030	-3356.26	-3141.10	-3004.43	-2822.51	-2665.99	-2588.42	-2475.76	-2404.65	-2310.00
0.0035	-3376.11	-3160.49	-3032.13	-2846.06	-2730.17	-2619.35	-2497.00	-2427.74	-2337.24
0.0040	-3403.36	-3191.89	-3060.30	-2867.30	-2755.56	-2635.51	-2533.47	-2450.36	-2360.79
0.0045	-3423.67	-3221.44	-3094.93	-2913.93	-2776.34	-2667.83	-2550.56	-2473.91	-2385.72
0.0050	-3440.76	-3244.06	-3121.17	-2961.03	-280635	-2689.53	-2581.95	-2495.61	-2417.12

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

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%
0.0010	-2268.44	-2217.65	-2179.79	-2128.08	-2078.21	-2041.74	-1967.40	-1946.16	-1882.90
0.0012	-2430.05	-2363.10	-2313.69	-2237.97	-2187.18	-2127.16	-2065.28	-2012.65	-1958.17
0.0015	-2762.49	-2597.65	-2528.85	-2421.27	-2326.16	-2237.05	-2188.10	-2127.62	-2055.13
0.0020	-3238.06	-3018.74	-2895.46	-2731.09	-2593.96	-2493.76	-2392.18	-2314.61	-2218.11
0.0025	-3481.85	-3232.98	-3067.22	-2887.61	-2756.48	-2605.96	-2522.39	-2433.74	-2339.09
0.0030	-3515.56	-3263.92	-3097.23	-2915.32	-2783.26	-2636.90	-2558.87	-2462.37	-2360.79
0.0035	-3544.64	-3281.92	-3131.86	-2940.25	-2810.97	-2667.37	-2589.34	-2490.07	-2392.18
0.0040	-3556.65	-3300.39	-3152.18	-2966.11	-2840.06	-2692.30	-2614.27	-2513.16	-2418.96
0.0045	-3569.58	-3322.56	-3178.50	-2992.89	-2866.37	-2715.39	-2640.13	-2530.70	-2441.13
0.0050	-3586.66	-3330.40	-3195.58	-3014.59	-2893.61	-2743.09	-2662.75	-2557.02	-2464.21

IV. CONCLUSION & REASON

It is pointed out from the CMC data the CMC has been increased by the addition of hydroxy compound. The order of CMC for hydroxy compounds is :

Hydroquinone > Resorcinol

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. The results are similar to hydroxy compound in magnesium caprylate additives in previous paper [31-33].

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