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Micellar Studies of Magnesium Caprylate after Addition of Hydroxy Additives Using Ion-Selective Electrode

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ABSTRACT

Magnesium 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 graphical method. The effect of hydroxy 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: Agglomeration, Ion-Selective Electrode, EMF, Lipophilic hydromicelle, Hydrophilic oleomicelle, Ice-berg, palisade layers

I. INTRODUCTION

By the study of many literatures it reveals that magnesium 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 magnesium 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 magnesium soaps by electrometric method.

II. EXPERIMENTAL

Purification of caprylic acid is done by keeping over anhydrous sodium sulphate for a week and then distilling under reduced pressure. Magnesium soap was prepared by taking calculated amount of magnesium carbonate, suspended in water and the suspension was heated to about 80^{0}C. The method is similar as reported earlier [15-16]. The information about the nature and structure of magnesium 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 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 magnesium 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].

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

$\longleftarrow$ Reference Electode $\longrightarrow$ $\longleftarrow$ ISE $\longrightarrow$

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

III. RESULT AND DISCUSSION

SOLUBILIZATION

The Table 1 presents the solubilities 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 [23]

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

Volume % of methanol in soap solution	Resorcinol	Hydroquinone
10	00.1167	00.0882
20	00.1140	00.0861
30	00.1121	00.0839
40	00.1096	00.0817
50	00.1072	00.0792
60	00.1049	00.0767
70	00.1028	00.0743
80	00.1004	00.0722
90	00.0981	00.0698
Pure Water	00.2281	00.5562

EMF

The EMF values of the cell containing magnesium caprylate 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 [24].

$$E = E_0 \pm \frac{RT}{Z_1 F} \ln \left[a_1 + \sum_{i=2}^{n} K_{1i}^{Pot} (a)_i^{z_i / z_i} \right] \quad \text{--------- (1)}$$

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 ionisation of soap molecules by the addition of these additives.

TABLE – 2 (A) EMF VALUES (in mV) OF THE CELL CONTAINING MAGNESIUM CAPRYLATE SOLUTION IN METHNOL-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	58.23	61.07	57.54	60.11	56.04	59.21	55.01	58.04
0.0015	65.07	67.19	63.11	66.07	61.84	65.01	59.77	63.13
0.0020	71.44	74.07	68.79	72.03	66.49	70.21	64.66	68.31
0.0025	77.57	80.31	74.06	78.14	71.83	75.49	69.21	73.18
0.0030	84.04	87.38	79.64	84.87	76.69	81.19	74.18	78.25
0.0045	90.14	94.08	84.92	90.23	81.26	86.31	77.59	83.08
0.0040	91.43	97.18	85.52	93.49	82.07	89.14	78.15	85.08
0.0045	92.22	97.98	86.62	94.42	83.13	89.92	79.26	86.03
0.0050	93.35	98.49	87.59	94.14	83.46	90.36	79.95	86.83

TABLE – 2 (B) EMF VALUES (in mV) OF THE CELL CONTAINING MAGNESIUM CAPRYLATE SOLUTION IN METHNOL-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	54.26	57.12	53.31	56.03	52.74	55.21	51.05	54.18	50.15	53.48
0.0015	58.22	61.78	57.36	60.49	55.92	59.69	54.66	58.45	53.61	57.62
0.0020	62.75	66.68	60.77	65.14	59.13	64.09	57.24	52.61	56.84	61.73
0.0025	66.29	71.64	64.07	70.08	62.57	68.59	61.47	67.07	60.08	66.01
0.0030	70.23	76.12	68.11	74.07	66.35	72.53	64.16	71.31	62.66	70.04
0.0045	74.43	81.01	71.44	79.09	69.86	77.07	67.54	75.29	66.01	73.82
0.0040	75.08	83.08	72.49	81.12	70.17	79.07	68.34	77.04	65.8	75.49
0.0045	75.96	83.87	72.84	81.93	70.78	79.86	69.21	77.81	66.45	76.18
0.0050	76.28	84.38	73.08	82.29	71.11	80.13	69.8	78.29	67.14	76.61

TABLE – 3 (A) EMF VALUES (in mV) OF THE CELL CONTAINING MAGNESIUM CAPRYLATE SOLUTION IN METHNOL-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	58.23	63.78	57.54	62.51	56.04	61.61	55.01	60.25
0.0015	65.07	70.19	63.11	68.61	61.84	67.07	59.77	65.47
0.0020	71.44	76.61	68.79	74.48	66.49	72.63	64.66	70.42
0.0025	77.57	83.42	74.06	80.22	71.83	77.46	69.21	75.28
0.0030	84.04	89.96	79.64	86.29	76.69	83.33	74.18	80.68
0.0045	90.14	96.07	84.92	92.01	81.26	89.09	77.59	85.41
0.0040	91.43	100.03	85.52	95.38	82.07	92.01	78.15	88.61
0.0045	92.22	100.43	86.62	95.7	83.13	92.51	79.26	89.26
0.0050	93.35	100.68	87.59	96.1	83.46	92.84	79.95	89.78

TABLE – 3 (B) EMF VALUES (in mV) OF THE CELL CONTAINING MAGNESIUM CAPRYLATE SOLUTION IN METHNOL-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	54.26	59.06	53.31	57.88	52.74	56.63	51.05	55.69	50.15	54.66
0.0015	58.22	64.11	57.36	62.63	55.92	61.08	54.66	59.87	53.61	58.44
0.0020	62.75	69.08	60.77	67.17	59.13	65.28	57.24	64.06	56.84	62.49
0.0025	66.29	73.62	64.07	71.7	62.57	70.11	51.47	68.07	60.08	66.59
0.0030	70.23	78.5	68.11	76.05	66.35	74.15	64.16	72.03	62.66	70.18
0.0045	74.43	83.08	71.44	80.56	69.86	78.48	57.54	76.03	66.01	74.04
0.0040	75.08	86.38	72.49	83.43	70.17	81.07	68.34	78.96	65.8	76.48
0.0045	75.96	86.88	72.84	83.9	70.78	81.63	69.21	79.4	66.45	76.98
0.0050	76.28	87.13	73.08	84.28	71.11	82.11	69.8	79.95	67.14	77.28

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 to increase 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 amide compounds. [26-30]

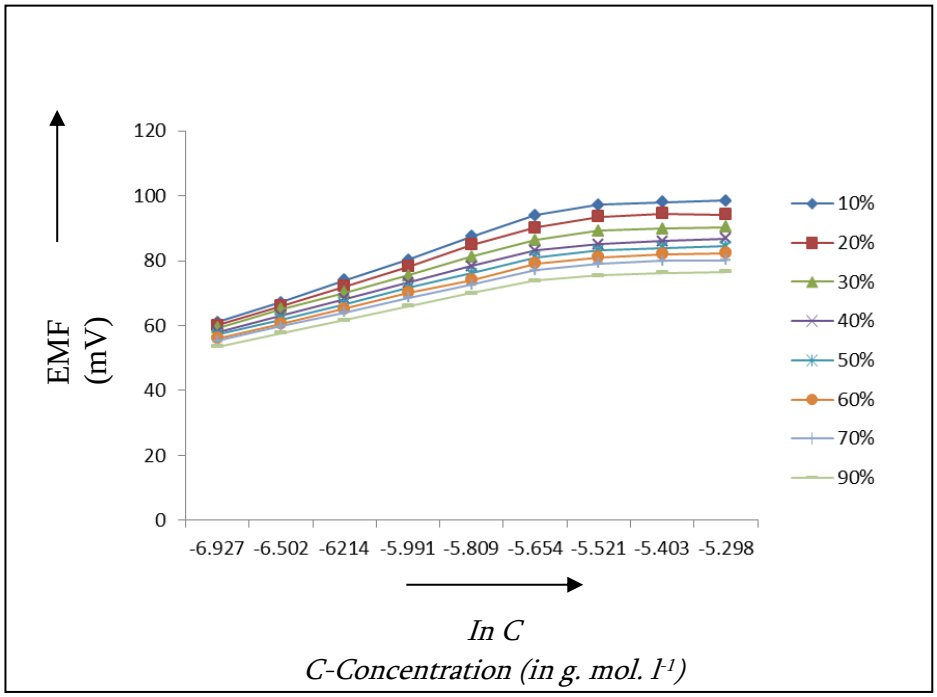

Fig. 1 : Plot of EMF of the cell containing magnesium caprylate solutions against logarithm of soap concentration in methanol-water solvent mixture after the addition of Resorcinol

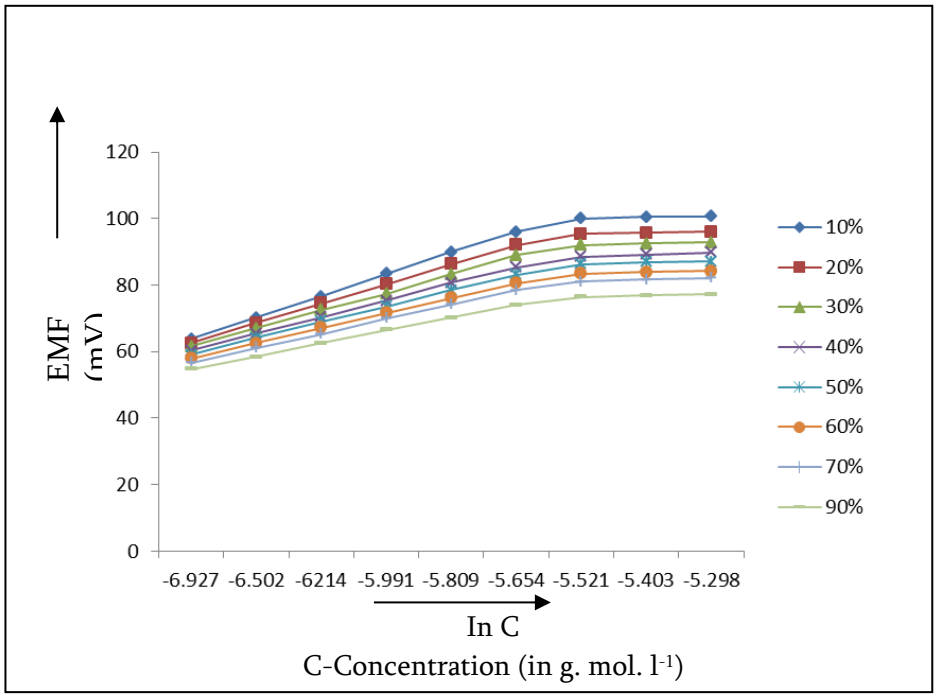

Fig. 2 : Plot of EMF of the cell containing magnesium caprylate solutions against logarithm of soap concentration in methanol-water solvent mixture after the addition of Hydroquinone

The plots (figs. 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 magnesium caprylate, before and after the addition of resorcinol and hydroquinone, are summarized in Table 4.

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

Name of Additives		
Without any Additives	**Hydroquinone**	**Resorcional**
30.00	0.033	0.0037

It is revealed from the table that the CMC of magnesium caprylate has been increased by the addition of these hydroxy compounds. This result is similar to that of amide additives [23] and can be explained on the basis of importance of "ice-berg" water structrue. 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. The plots of volume percent of methanol show a break at about 60% methanol concentration. This indicates that the change in the nature of micelles from hydrophilic oleomicelles to lipophilic hydromicelles takes place at about 60% methanol concentration.

FREE ENERGY CHANGE

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

$$\Delta G = -nEF$$

The calculated values of free energy change for cell reaction in magnesium 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 MAGNESIUM 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	-2819.74	-2775.41	-2733.86	-2679.84	-2637.36	-2587.03	-2549.17	-2501.61	-2469.29
0.0015	-3102.31	-3050.60	-3001.66	-2914.85	-2852.52	-2792.96	-2756.02	-2698.77	-2660.44
0.0020	-3419.98	-3325.79	-3241.75	-3154.03	-3078.77	-3007.66	-2959.18	-2890.84	-2850.21
0.0025	-3708.09	-3607.90	-3485.54	-3378.89	-3307.78	-3235.75	-3166.95	-3096.77	-3047.83
0.0030	-4034.53	-3918.64	-3748.72	-3612.98	-3514.63	-3419.98	-3348.87	-3292.54	-3233.90
0.0045	-4343.89	-4166.12	-3985.13	-3835.99	-3740.41	-3651.76	-3558.50	-3456.31	-3408.44
0.0040	-4487.02	-4316.64	-4115.79	-3928.33	-3835.99	-3745.49	-3650.84	-3557.11	-3485.54
0.0045	-4523.96	-4359.58	-4151.81	-3972.20	-3872.47	-3782.89	-3687.32	-3592.66	-3517.40
0.0050	-4547.50	-4346.66	-4172.12	-4009.14	-3896.01	-3799.51	-3699.78	-3614.83	-3537.26

TABLE – 6 THE CALCULATED VALUES OF ΔG (IN CALORIES)FOR MAGNESIUM 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	-2944.87	-2886.23	-2844.67	-2781.88	-2726.93	-2672.45	-2614.73	-2571.33	-2523.78
0.0015	-3240.83	-3167.88	-3096.77	-3022.90	-2960.10	-2891.77	-2820.20	-2764.33	-2698.31
0.0020	-3537.26	-3438.91	-3353.49	-3251.45	-3189.58	-3101.39	-3014.12	-2957.79	-2885.30
0.0025	-3851.69	-3703.94	-3576.50	-3475.85	-3399.20	-3310.55	-3237.14	-3142.94	-3074.61
0.0030	-4153.66	-3984.20	-3847.53	-3725.18	-3624.52	-3511.40	-3423.67	-3325.79	-3240.37
0.0045	-4435.77	-4248.31	-4113.49	-3943.57	-3835.99	-3719.64	-3623.60	-3510.48	-3418.59
0.0040	-4618.61	-4403.91	-4248.31	-4091.32	-3988.36	-3852.15	-3743.18	-3645.76	-3531.25
0.0045	-4637.08	-4418.68	-4271.39	-4121.33	-4011.44	-3873.85	-3769.04	-3666.08	-3554.34
0.0050	-4648.62	-4437.15	-4286.63	-4145.34	-4022.99	-3891.40	-3791.20	-3691.47	-3568.19

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 amides additives in previous paper[31]

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