

Electrometric Comparative Studies of Calcium and Magnesium Soaps Using Ion-Selective Electrode

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ABSTRACT

Calcium & Magnesium 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. The effect of various organic additives on CMC values of referred soaps has also been studied by using electrometric method with the aid of ion selective electrode.

Keywords: Agglomeration, Ice-berg, palisade layers, Micellization, Hydrophilic oleomicelle, Lipophilic hydromicelle

I. 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 these 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 these soaps by the electrometric method.

II. PREPARATION AND EXPERIMENTAL

Purification of n-caproic and n-caprylic acids was 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°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 and magnesium

soap was prepared by taking calculated amount of magnesium carbonate, suspended in water and the suspension was heated to about 80°C. The method is similar as reported earlier [15-16].

The information about the nature and structure of calcium and magnesium 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 has been determined by electrometrically method using ISE.

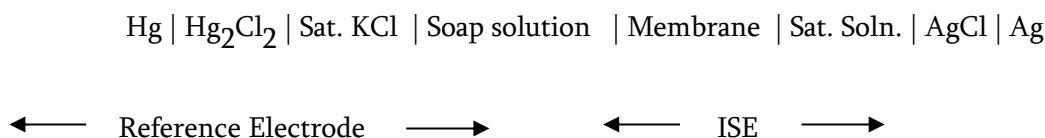
The soap solutions of different soap concentration from 0.005M to 0.050M and 0.001M to 0.005M for

calcium and magnesium caproate and 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 have 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, we can represented cell as the pattern suggested by previous workers [23-26].



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

III. RESULT AND DISCUSSION

SOLUBILITY OF SOAPS

The solubility data of magnesium and calcium soaps in methanol-water solvent mixture of varying compositions are presented in **Table-1**. From a perusal of the data, it is apparent that the solubility of soaps

increases with increase in methanol concentration in solvent mixture. The high solubility in methanol suggests the possibility of some sort of solute-solvent interaction. The factors responsible for higher solubility appears to be the solvation of magnesium and calcium ions and the interaction between the hydrophobic ends of the soap ions and methanol.[23-25]

TABLE – 1 SOLUBILITIES (in g. mol.l⁻¹) OF MAGNESIUM & CALCIUM SOAPS IN METHANOL-WATER SOLVENT MIXTURES

		TEMP. - (40±2)°C							
Name of soaps	Volume percent of methanol in the solvent mixture								
	10%	20%	30%	40%	50%	60%	70%	80%	90%
Magnesium caproate	0.0829	0.0863	0.0894	0.0932	0.0971	0.1013	0.1056	0.1102	0.1151
Magnesium caprylate	0.452	0.0484	0.0516	0.0549	0.0584	0.0622	0.0661	0.0712	0.0766
Calcium caproate	0.0416	0.0441	0.0472	0.0507	0.0546	0.0588	0.0624	0.0661	0.0698
Calcium caprylate	0.0107	0.0118	0.0133	0.0151	0.0173	0.0192	0.0218	0.0244	0.0272

The results show that the solubility of the soaps in methanol-water mixture decreases with increase in the chain length of the acid in the soaps. It has been suggested that mixed films of soap and alcohol are formed and the alcohol take 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[26] so the order of solubility is :

Caproate soap > Caprylate soap

It is also clear from the table that the solubility of magnesium soaps is greater than calcium soaps. This may be due to the fact that the hydration number of Mg⁺² ion (15±2) is greater than that of Ca⁺² ion [27-28] which is only 12. Thus the order of solubility for magnesium and calcium soaps is :

Mg soap > Ca soap

EMF VALUES

The EMF values of the cell for magnesium and calcium soap in methanol-water solvent mixtures of varying compositions are summarized in Table – 2 (A & B) and Table - 3 (A & B) respectively. It is observed from the Tables that the EMF values have decreased with increase in the number of carbon atom in the chain length of the soaps. Thus the values of EMF are greater for caproate than for caprylate. It is also observed that the EMF values of the cell for magnesium soaps solutions are greater than that for calcium soaps solutions. This is probably due to the fact that the charge radius ratio [29] of magnesium ion is also higher than that of calcium ion, results the solubility of magnesium soaps is more than calcium soaps. Thus the activity of magnesium ion in soap solutions is greater than that of calcium ion, and EMF values of the cell for magnesium soap solution is also greater than that for calcium soaps solution and the order for EMF value is :

Mg soap > Ca soap

TABLE – 2 (A) EMF VALUES (in mV) OF THE CELL CONTAINING MAGNESIUM SOAPS SOLUTION IN METHANOL-WATER SOLVENT MIXTURE

CAPROATE

Conc. 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	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 (B) EMF VALUES (in mV) OF THE CELL CONTAINING MAGNESIUM SOAPS SOLUTION IN METHANOL-WATER SOLVENT MIXTURE

CAPRYLATE

Conc. 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	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

TABLE – 3 (A) EMF VALUES (in mV) OF THE CELL CONTAINING CALCIUM SOAPS SOLUTION IN METHANOL-WATER SOLVENT MIXTURE

CAPROATE

Conc. 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	67.14	65.52	67.78	63.91	63.07	62.26	61.31	60.72	59.54
0.006	69.44	67.38	66.05	65.04	64.15	63.34	62.58	61.4	61.02
0.008	74.18	72.39	70.04	68.53	67.29	66.11	64.82	63.75	63.04
0.010	78.93	75.14	73.34	71.65	70.05	68.32	67.14	66.28	65.34
0.012	83.04	79.42	76.54	74.98	73.08	72.49	70.12	68.75	67.54
0.015	90.52	85.04	82.16	79.46	77.62	75.54	73.24	72.59	70.87
0.020	93.07	87.51	84.29	82.77	79.58	77.43	75.56	74.24	72.67
0.025	95.64	90.08	87.33	84.82	81.9	79.04	77.65	75.75	74.08
0.030	98.06	92.74	89.65	87.23	84.15	82.09	79.85	77.44	76.88
0.035	100.12	95.26	92.57	89.24	86.02	83.72	82.16	78.94	77.62

TABLE – 3 (B) EMF VALUES (in mV) OF THE CELL CONTAINING CALCIUM SOAPS SOLUTION IN METHANOL-WATER SOLVENT MIXTURE

CAPRYLATE

Conc. 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	45.07	44.12	43.05	42.55	41.17	40.02	38.87	38.04	37.24
0.0012	49.56	47.32	46.08	44.59	43.11	42.29	40.73	39.51	38.14
0.0015	55.34	52.25	50.14	47.22	45.57	44.63	43.21	41.85	40.12
0.0020	65.46	60.18	56.17	52.62	50.09	47.64	46.08	44.72	43.18
0.0025	67.16	61.55	57.91	54.05	51.73	49.24	47.17	45.5	44.11
0.0030	68.75	62.93	58.08	55.15	52.57	50.08	48.26	46.04	45.01
0.0035	70.02	64.1	60.01	56.24	53.36	51.29	49.19	47.14	45.62
0.0040	72.13	65.84	61.23	57.25	54.78	52.28	50.03	47.97	46.11
0.0045	73.21	67.12	62.51	58.59	55.92	53.14	51.18	48.28	47.35
0.0050	74.58	68.29	63.76	60.04	56.15	54.05	52.14	49.52	47.64

CMC VALUES

The CMC values of referred soaps, before and after the addition of organic additives, are show in Table – 4. The results show that there is a decrease is CMC

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

Calcium caproate > Calcium caprylate		
CMC	0.15M	0.002M
Magnesium caproate > Magnesium caprylate		
CMC	0.030M	0.0035

It is also clear from the table that the CMC values of magnesium and calcium soaps are in the order :

Mg soaps > Ca soaps

This result is due to the higher hydration number of magnesium ion, which having large enveloping of water molecules and will have low probability as to its approach towards micellar aggregates, thus accentuating the process of micelles formation, whereas this tendency is reduced for calcium ions in calcium soaps in view of its low hydration number.

This result is identical to that reported earlier by Mehta et al.

It is also pointed out from the CMC data of soaps in Table – 4 that the CMC has been increased by the addition of amides and hydroxyl compounds.

The order of CMC for amide compounds is :

Benzamide > Acetamide > Urea

and for hydroxyl compounds is :

Hydroquinone > Resorcinol

TABLE – 4 CMC VALUES (in g. mol. l⁻¹ x 10⁻³) OF MAGNESIUM AND CALCIUM SOAPS

Name of Additives	Name of Soaps			
	Magnesium caproate	Magnesium caprylate	Calcium caproate	Calcium caprylate
Nil	30.00	3.50	15.00	2.00
Urea	32.50	3.75	16.00	2.20
Acetamide	33.00	3.80	16.50	2.30
Benzamide	33.50	3.85	16.75	2.35
Hydroquinone	33.00	3.80	16.50	2.30
Resorcinol	32.20	3.70	16.00	2.22

The above result can be analyzed 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 brokek up resulting more increases in CMC.[30-32]

The similar behavior has been observed in hydroxyl compounds, where hydroquinone forms more effective hydrogen bonding with water molecules

than resorcinol results the CMC of hydroquinone is greater than resorcinol.

IV. SOLUBILIZATION

The amides (urea, acetamide and benzamide) and hydroxy compounds (resorcinol and hydroquinone) have much lower solubility in soap solutions in methanol-water solvent mixture than in pure water which we have discussed in previous paper.[33-34]

TABLE – 5 SOLUBILITY OF ORGANIC ADDITIVES (in g. mol. l⁻¹) IN SOAPS SOLUTIONS IN 50% METHANOL-WATER SOLVENT MIXTURE

Name of Additives	Name of Soaps			
	Magnesium caproate	Magnesium caprylate	Calcium caproate	Calcium caprylate
Urea	0.3992	0.3410	0.3447	0.2952
Acetamide	0.0661	0.0562	0.0612	0.0398
Benzamide	0.0511	0.0395	0.0447	0.0296
Resorcinol	0.2015	0.1072	0.1013	0.0927
Hydroquinone	0.0842	0.0792	0.0694	0.0635

It is observed from the solubility data Table – 5 that the solubility of these compounds decreases with increase in the number of carbon atom in the chain length of the soaps therefore, these additives have greater solubility in caproate soap solutions than in caprylate solution. Thus the order of solubility of these compounds in soaps solutions in:

Caproate soap > Caprylate soap

It is also point out from the solubility results that it is greater in magnesium soap solutions than in calcium soaps solutions. Since magnesium has higher hydration number, so these compounds may form more stable adduct with magnesium soap molecule than that with calcium soap molecule.

V. CONCLUSION

The EMF values of the cell for caproate soap solutions are greater than that for caprylate soap solutions. Whereas the values of EMF for magnesium soaps are greater than that for calcium soaps and CMC values is greater for caproate than caprylate. Solubility of additives is greater in caproate soaps than in caprylate soaps and it is also greater for magnesium soaps.

VI. ACKNOWLEDGMENT

I am greatly indebted to Dr. L.C. Heda for valuable suggestions and guidance. I also thank the authorities of NEERI, Nagpur for providing laboratory facilities and the University of Rajasthan, Jaipur for library facilities and UGC for financial assistance.

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Cite this Article

Dushyant Pareek, Chandresh Pareek, Narendra Nirwan, "Electrometric Comparative Studies of Calcium and Magnesium Soaps Using Ion-Selective Electrode", International Journal of Scientific Research in Science and Technology (IJSRST), Online ISSN : 2395-602X, Print ISSN : 2395-6011, Volume 3 Issue 3, pp. 758-765, March-April 2017. Journal URL : <http://ijsrst.com/IJSRST207674>