Calculation of Free Energy of Micellization of Alkaline Earth Metal Soaps after Addition of Amide Additives Using ISE

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ABSTRACT

Magnesium & 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. By plotting the electromotive force of the cell against soap concentration we calculate slopes of graphical lines before and after the CMC and from these values we calculate degree of ionisation and from these values we calculate free energy of micellization. We observed the effect of amide additives on free energy of micellization.

Keywords: Hydrophilic Oleomicelle, Agglomeration, Palisade Layers, Micellization, 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 and the effect of organic additives on the micellization is reported.

II. PREPARATION AND EXPERIMENTAL

Magnesium & Calcium soaps of caproic and caprylic acids were prepared. The method is similar as reported earlier [15-16].

The information about the nature and structure of magnesium and 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 soap solutions of different soap concentration from 0.005M to 0.050M and 0.001M to 0.005M for magnesium and calcium 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 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$_2$Cl$_2$ | Sat. KCl | Soap solution | Membrane | Sat. Soln. | AgCl | Ag

← Reference Electrode → ← ISE →
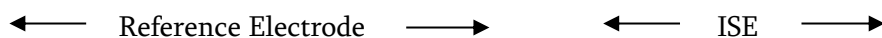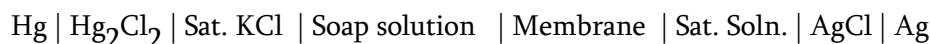
The Electro-Motive Force (EMF) of the cell was measured potentiometrically.

FREE ENERGY OF MICELLIZATION :

The free energy of micellization (ΔG^0_M) at CMC has been calculated by using the following relation[27].

$$\Delta G^0_M = (2 - \alpha) \, RT \ln CMC$$

Where : α - Degree of ionization of an ionic micelle

CMC - Critical Micelle Concentration

The degree of ionization 'α' of an ionic micelle depends on the method of determination [28]. It is computed from the ratio of slopes [29-30] of the plots of EMF against logarithm of soap concentration is:

$$\alpha = b/a$$

Where : a - Slope of linear portion of plot before CMC.

b - Slope of linear portion of plot after CMC.

The values of degree of ionization (α) of ionic micelles of magnesium and calcium soaps were calculated from calculated values of a & b from graphical methods which were given in previous papers of the authors [31-32].

III. RESULT AND DISCUSSION

The results show that the slope of first linear portion (before CMC) is greater than that of second linear portion (after CMC) and these values of slopes are higher for caprylate soaps than that for caproate soaps, so the order of slopes for soaps is :

Caprylate > Caproate

This result is in fair agreement with those reported earlier by Verma et al.[33]. It is also pointed out from the results that the degree of ionization 'α' increases up to 60% methanol concentration but after this concentration there is no significant trend observed because of the change in the nature of the micelles from hydrophilic oleomicelles to lipophilic hydromicelles.

It is also evident from the results that the degree of ionization of ionic micelles of caproate soap is greater than that of caprylate soap, so the activity of cation in caproate soap solution is greater than that of caprylate soap solution resulting in increase in the EMF values of soap solutions. This result is in good agreement with those obtained by EMF measurements in previous papers of authors [7].

It is also observed from the Tables that the order of degree of ionization 'α' of micelles for magnesium and calcium soaps is :

Mg soap > Ca soap

This is probably due to the higher hydration number of magnesium ion than that of calcium ion.

The calculated values of degree of ionization of micelle of magnesium and calcium soap after the addition of urea, acetamide, benzamide, are listed in **Tables – 1 to 4** respectively.

TABLE – 1 CALCULATED VALUES OF DEGREE OF IONISATION (α) OF SOAP BY THE MEASUREMENTS OF SLOPES (a & b) OF PLOTS OF EMF Vs SOAP CONCENTRATION TEMP. - $(40\pm2)^0$C **BEFORE ADDITION**

Name of soaps	Volume percent of methanol in the solvent mixture								
	10%	20%	30%	40%	50%	60%	70%	80%	90%
Magnesium caproate	0.264	0.271	0.287	0.336	0.377	0.395	0.330	0.318	0.336
Magnesium caprylate	0.128	0.142	0.126	0.135	0.125	0.144	0.155	0.139	0.145
Calcium caproate	0.200	0.246	0.264	0.305	0.302	0.326	0.293	0.242	0.263
Calcium caprylate	0.115	0.141	0.137	0.212	0.223	0.217	0.192	0.181	1.680

TABLE – 2 CALCULATED VALUES OF DEGREE OF IONISATION (α) OF SOAP BY THE MEASUREMENTS OF SLOPES (a & b) OF PLOTS OF EMF Vs SOAP CONCENTRATION **AFTER ADDITION (UREA)**

Name of soaps	Volume percent of methanol in the solvent mixture								
	10%	20%	30%	40%	50%	60%	70%	80%	90%
Magnesium caproate	0.094	0.119	0.134	0.199	0.141	0.155	0.170	0.151	0.160
Magnesium caprylate	0.065	0.073	0.081	0.069	0.074	0.076	0.061	0.064	0.064
Calcium caproate	0.098	0.11	0.109	0.122	0.122	0.129	0.199	0.150	0.155
Calcium caprylate	0.042	0.048	0.056	0.050	0.06	0.066	0.071	0.061	0.064

TABLE – 3 CALCULATED VALUES OF DEGREE OF IONISATION (α) OF SOAP BY THE MEASUREMENTS OF SLOPES (a & b) OF PLOTS OF EMF Vs SOAP CONCENTRATION **AFTER ADDITION (ACETAMIDE)**

Name of soaps	Volume percent of methanol in the solvent mixture								
	10%	20%	30%	40%	50%	60%	70%	80%	90%
Magnesium caproate	0.096	0.111	0.95	0.110	0.097	0.106	0.166	0.135	0.160
Magnesium caprylate	0.079	0.085	0.094	0.084	0.093	0.096	0.100	0.145	0.145
Calcium caproate	0.076	0.088	0.097	0.087	0.096	0.100	0.082	0.064	0.043
Calcium caprylate	0.053	0.052	0.058	0.065	0.06	0.066	0.052	0.055	0.037

TABLE – 4 CALCULATED VALUES OF DEGREE OF IONISATION (α) OF SOAP BY THE MEASUREMENTS OF SLOPES (a & b) OF PLOTS OF EMF Vs SOAP CONCENTRATION **AFTER ADDITION (BENZAMIDE)**

Name of soaps	Volume percent of methanol in the solvent mixture								
	10%	20%	30%	40%	50%	60%	70%	80%	90%
Magnesium caproate	0.096	0.111	0.124	0.168	0.1977	0.2156	0.2253	0.105	0.247
Magnesium caprylate	0.026	0.045	0.048	0.052	0.036	0.037	0.0391	0.034	0.042
Calcium caproate	0.061	0.088	0.101	0.1355	0.082	0.088	0.074	0.052	0.090
Calcium caprylate	0.042	0.058	0.065	0.0919	0.1099	0.122	0.135	0.140	0.192

The examination of result shows that the degree of ionization of micelle has decreased by the addition of these additives. The calculated values of free energy of micellization (ΔG^0_M) of magnesium and calcium soaps are shown in **Table – 5 to 8** respectively.

TABLE – 5 CALCULATED VALUES OF FREE ENERGY CHANGE OF MICELLIZATION ((ΔG^0_M IN CAL. MOL.$^{-1}$) FOR MAGNESIUM & CALCIUM SOAPS **BEFORE ADDITIVES**

Name of soaps	Volume percent of methanol in the solvent mixture								
	10%	20%	30%	40%	50%	60%	70%	80%	90%
Magnesium caproate	–3579.12	–3558.43	–3537.75	–3434.30	–3351.55	–3310.17	–3434.30	–3475.68	–3434.30
Magnesium caprylate	–6239.14	–6172.41	–6239.14	–6205.77	–6239.14	–6172.41	–6139.04	–6205.03	–6172.41
Calcium caproate	–4460.07	–4336.18	–4286.62	–4187.51	–4187.51	–4137.95	–4212.29	–4336.18	–4286.62
Calcium caprylate	–6793.22	–6783.22	–6819.89	–6526.56	–6489.89	–6526.56	–6599.89	–6636.56	–6709.89

TABLE – 6 CALCULATED VALUES OF FREE ENERGY CHANGE OF MICELLIZATION ((ΔG^0_M IN CAL. MOL.$^{-1}$) FOR MAGNESIUM & CALCIUM SOAPS AFTER THE ADDITION OF **UREA**

Name of soaps	Volume percent of methanol in the solvent mixture								
	10%	20%	30%	40%	50%	60%	70%	80%	90%
Magnesium caproate	–3841.11	–3800.68	–3708.25	–3800.68	–3740.03	–3719.81	–3679.38	–3719.81	–3699.60
Magnesium caprylate	–6370.64	–6327.80	–6294.84	–6360.75	–6327.80	–6327.80	–6370.64	–6370.64	–6370.64
Calcium caproate	–4707.85	–4658.30	–4683.07	–4633.52	–4658.30	–4633.52	–4658.30	–4583.96	–4559.18
Calcium caprylate	–7040.25	–7040.25	–7004.15	–7004.15	–7004.15	–6968.04	–6931.94	–6968.04	–6968.14

TABLE – 7 CALCULATED VALUES OF FREE ENERGY CHANGE OF MICELLIZATION ((ΔG^0_M IN CAL. MOL.$^{-1}$) FOR MAGNESIUM & CALCIUM SOAPS AFTER THE ADDITION OF **ACETAMIDE**

Name of soaps	Volume percent of methanol in the solvent mixture								
	10%	20%	30%	40%	50%	60%	70%	80%	90%
Magnesium caproate	-3823.99	-3783.74	-3823.99	-3803.87	-3823.99	-3803.87	-3783.74	-3743.47	-3683.11
Magnesium caprylate	-6312.80	-6279.92	-6247.04	-6279.92	-6247.04	-6247.04	-6214.16	-6082.65	-6082.65
Calcium caproate	-4649.45	-4625.23	-4601.02	-4625.23	-4601.02	-4576.80	-4625.23	-4673.66	-4722.10
Calcium caprylate	-6953.25	-6953.25	-6953.25	-6917.40	-6953.25	-6917.40	-6953.25	-6953.25	-7024.93

TABLE – 8 CALCULATED VALUES OF FREE ENERGY CHANGE OF MICELLIZATION ((ΔG^0_M IN CAL. MOL.$^{-1}$) FOR MAGNESIUM & CALCIUM SOAPS AFTER THE ADDITION OF **BENZAMIDE**

Name of soaps	Volume percent of methanol in the solvent mixture								
	10%	20%	30%	40%	50%	60%	70%	80%	90%
Magnesium caproate	-3807.14	-3767.06	-3747.03	-3666.88	-3606.76	-3566.69	-3546.65	-3526.61	-3506.58
Magnesium caprylate	-6462.01	-6396.40	-6396.40	-6363.60	-6429.21	-6429.21	-6429.21	-6396.40	-6396.40
Calcium caproate	-4656.54	-4608.29	-4560.04	-4487.65	-4608.29	-4608.29	-4632.42	-4632.42	-4608.29
Calcium caprylate	-6964.36	-6928.63	-6892.93	-6785.79	-6750.07	-6678.64	-6642.93	-6500.07	-6428.64

It is observed that the values of ΔG^0_M are negative, this indicates that the micellization process is thermodynamically spontaneous and this may be due to the attraction between the two components in micelles, most of which may result from a decrease in the electrostatic energy of the micelles.[34] The value of ΔG^0_M increase with increase in methanol concentration in solvent mixture which may be due to decrease in constant but the trend is only up to 60% methanol concentration after this concentration the

trend is not regular. This is probably due to the change in the nature of micelle at 60% methanol concentration.

It is also noticed from the Tables that ΔG^0_M values have lowered with increase in number of carbon atom in the hydrophobic chain of soaps. Thus the ΔG^0_M value for caproate is greater than that for caprylate. The results also show that the ΔG^0_M values for magnesium soaps are higher than that for calcium soaps. It is expected that this energy depends much on the surface charge density of micelles, ionic strength and little on the size and shape of micelles [34-38] since the charge density is higher for magnesium and the size and shape of caproate soap micelle is lower than that of caprylate.

IV. 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.

The results show that the value of ΔG^0_M has decreased by the addition of these additives. It is also observed that the order ΔG^0_M for amide compounds is :

Urea < Acetamide < Benzamide

V. ACKNOWLEDGMENT

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