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ACOUSTIC STUDIES AND MICELLAR FEATURES OF LITHIUM SOAPS AT 313 K IN NON-AQUEOUS SOLVENTS

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ABSTRACT

Colloidal chemical behaviour and micellar characteristics of lithium caprate and laurate in benzene-methanole mixtures have been investigated by ultrasonic velocity and density measurements (313 K). The variation of adiabatic compressibility, intermolecular free length, apparent molal compressibility, apparent molal volume, molar sound velocity primary salvation number show that there is sufficient soap solvent interaction due to which micellar alignment is considerably affected. The results indicate that CMC values decrease with the increase in number of carbon atoms in the hydrophobic chain. The study reveals that change in the micellar organization takes place around 40 percent methanol concentration. Ultrasonic investigations provide revealing interpretations of soap-solvent interaction and structural insight of micelles.

Key words: Acoustic studies, Micelle, Lithium soap, Non- aqueous solvent.

INTRODUCTION

In the recent years there has been considerable progress in the determination of thermodynamic, rheological and acoustical properties of metallic soaps from speed, density and viscosity measurements. The physico-chemical characteristics of metal soaps can be controlled upto an extent by the method and conditions of their preparation and so the studies of metal soap is of great significance as these soaps are used in various industries. The ultrasonic velocity technique has been used for studying solute-solvent interaction in a number of systems including organic liquid and dilute solutions in organic acids[1].

The ultrasonic velocity of the solution of manganese cobalt and copper soaps (caprate, laurate and myristate) were carried out in a mixture of benzene and methanol (50% v/v.) at a constant temperature. The data have been used to evaluate the critical micelle

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concentration (CMC) and to study the soap-soap and soap-solvent interactions. The results confirm that there is a significant interaction between the soap and solvent molecules[2].

Features of micellization and aggregations of lithium soaps were studied in benzene plus methanol mixtures of varying compositions. The various physical properties (viz.: density, molar volume, viscosity, ultrasonic velocity, conductance, surface tension) of the system lithium soap-benzene and methanol, have been investigated in order to find out the critical micelle concentration, nature and size of the micelles formed and to test the validity of various equations under different conditions. The parameters pertaining to ultrasonic investigations provide revealing interpretations of soap-solvent interaction and structural insight of miscelles.

Anionic surfactants bearing lithium ion are ideal for investigation because of their valuable characteristics foaming, wetting, detergency etc. Ultrasonic investigations have established its versatility to furnish information as to the understanding of ion-solvent interaction. A number of workers have discussed the physico-chemical aspects of binary liquid mixtures in terms of ultrasonic velocity and related parameters.[3-9] Ultrasonic measurements have also been used to determine the solvation number in aquous media.[10-14] Recently apparent molal volume, adiabatic compressibility, intermolecular free length, specific acoustic impedence and relative association of substituted azoles in N, N-dimethyl formamide in different concentrations at different temperatures have been investigated.[15]

EXPERIMENTAL

All reagents used were of BDH grade and soaps were prepared by the method described earlier[16].

Ultrasonic velocity in sample was measured with the help of a single crystal ultrasonic, interferometer (Mittal Enterprises, New Delhi) working at a fixed frequency 2 MHz. Water maintained at $40 \pm 0.1^{o}C$ temperature in a thermostat was passed through the jacket of the cell before the measurement was actually made. The measured velocities have been uncertainty of ± 0.5 ms^{-1}.

The operative part of the measurement involves the slow movement of micrometer till the anode current meter shows a maximum. A number of maxima readings of anode current are passed on and their number "n" is counted. The total distance (d) thus moved by the micrometer gives the values of wave length (λ) with the help of the following relation :

$$d = n \text{ x } \lambda/2$$

Once the wavelength (λ) is known the velocity (u) in the liquid can be calculated with the help of following relation :

$$u = \lambda \times L_f$$

RESULTS AND DISCUSSION

The values of ultrasonic velocity have been utilized to evaluate acoustical parameters such as specific acoustic impedance (Z)[17], adiabatic compressibility β, intermolecular free length L_f[18], apparent molal compressibility $Ø_k$ for each system at different concentrations using following equations :

$$Z = \rho u \quad \ldots(1)$$

$$B = \frac{1}{u_2 \rho} \quad \ldots(2)$$

$$L_f = K\sqrt{\beta} \quad \ldots(3)$$

$$Ø_k = \frac{1000}{C\rho_o}[\rho_o\beta - \beta_o\rho] + \beta_o M\rho_o^{-1} \quad \ldots(4)$$

Where ρ_o, ρ, β_o, β are the density, adiabatic compressibility of the solvent and soap solutions respectively. K, C, M and u are the temperature dependent Jacobsons constant[18], concentration molecular weight and ultrasonic velocity, respectively.

The values of u and allied parameters for the system

Lithium (Li^+) soap – benzene plus methanol mixtures are recorded in (Table 1) and (Table 2) for caprate and laurate, respectively. It is observed from the data that the numerical values of u and z increases whereas β and L_f decreases consistently with the increase in the soap concentration in all the composition of benzene and methanol measures. The results are consistent to our similar investigation for magnesium and copper soaps reported earlier[19-20]. The values of du/dc for lithium caprate and laurate are positive showing resemblance with the results of other workers[21-26].

The acoustic parameters viz. β, L_f and z are plotted against soap concentration c (Fig. 1). These plots yield two straight lines showing a break corresponding to CMC of lithium laurate (Table 3). It is apparent from Table III that the CMC is dependent on the composition of the solvent mixtures. With regards to chain length of the soap, the CMC values follow the order:

Caprate > Laurate

Table 1: Ultrasonic velocity and acoustic parameters of Lithium caprate at 40 ± 0.1°C

$C \times 10^2$ M	P ($g.cm^{-3}$)	$u \times 10^{-5}$ (cms^{-1})	$z \times 10^{-5}$ ($g/cm^2.sec$)	$B_{ad} \times 10^{11}$ ($cm^2\ dyn^{-1}$)	$L_f \times A^0$	$Ø_k \times 10^{10}$
Benzene – Methanol (9V : IV) [β_o = 2.2699]						
.010	0.8080	2.4615	1.9818	2.0420	.29850	- 7.227
.015	0.8083	2.5000	2.0201	1.9790	.29380	- 8.887
.020	0.8085	2.5396	2.0520	1.9170	.28930	-9.650
.025	0.8088	2.5806	2.0891	1.8540	.28440	-10.311
.030	0.8091	2.6220	2.1211	1.7960	.28000	-10.377
.040	0.8093	2.6660	2.1570	1.7371	.27530	- 9.159
.050	0.8095	2.7110	2.1940	1.6790	.27071	-8.397
.060	0.8098	2.7580	2.2330	1.6220	.26610	-7.892
Benzene – Methanol (8V : 2V) [β_o = 2.1232]						
.010	0.8096	2.5000	2.0240	1.9761	.29370	-0.124
.015	0.8098	2.5396	2.0566	1.9144	.28908	-0.123
.020	0.8100	2.5806	2.0905	1.8535	.28445	-0.121
.025	0.8103	2.6229	2.1255	1.7936	.27981	-0.120
.030	0.8105	2.6666	2.1612	1.7350	.27520	-0.119
.040	0.8107	2.7118	2.1987	1.6770	.27057	-0.103
.050	0.8110	2.7586	2.2373	1.6202	.26594	-0.093
.060	0.8113	2.8070	2.2773	1.5643	2.6131	-0.090
Benzene – Methanol (7V : 3V) [β_o = 2.1231]						
.010	0.8183	2.4615	2.0144	2.0166	.29670	-5.9770
.015	0.8186	2.5000	2.0466	1.9544	.29308	-8.0316
.020	0.8188	2.5396	2.0796	1.8933	.28748	-8.9844
.025	0.8192	2.5806	2.1140	1.8329	.28286	-9.5470
.030	0.8194	2.6229	2.1492	1.7738	.27826	-9.8690
.040	0.8196	2.6666	2.1857	1.7155	.27365	-9.2168
.050	0.8199	2.7118	2.2235	1.6583	.26905	-8.0799
.060	0.8200	2.7586	2.2620	1.6025	.26448	-7.5887

Cont…

C x 10^2 M	**P (g.cm^{-3})**	**u x 10^{-5} (cms^{-1})**	**z x 10^{-5} (g/cm^2.sec)**	**B_{ad} x 10^{11} (cm^2 dyn^{-1})**	**L_f x A^0**	**$Ø_k$ x 10^{10}**
Benzene – Methanol (6V : 4V) [β_o = 2.0894]						
.010	0.8292	2.4242	2.0101	2.0520	.29929	-6.000
.015	0.8294	2.4615	2.0416	1.9897	.29421	-8.039
.020	0.8297	2.5000	2.0744	1.9282	.29011	-9.035
.025	0.8301	2.5396	2.1082	1.8676	.28552	-9.598
.030	0.8305	2.5806	2.1432	1.8079	.28092	-9.945
.040	0.8309	2.6229	2.1796	1.7492	.27632	-8.842
.050	0.8313	2.6666	2.2169	1.6914	.27171	-8.157
.060	0.8316	2.7118	2.2551	1.6350	.26715	-7.673
Benzene – Methanol (5V : 5V) [β_o = 2.1195]						
.010	0.8309	2.4615	2.0454	1.9861	.29445	-6.344
.015	0.8312	2.5000	2.0782	1.9247	.28985	-8.371
.020	0.8316	2.5396	2.1121	1.8642	.28527	-8.915
.025	0.8320	2.5806	2.1472	1.8046	.28067	-9.462
.030	0.8325	2.6229	2.1836	1.7456	.27607	-9.810
.040	0.8330	2.6666	2.2213	1.6881	.27146	-8.7222
.050	0.8333	2.7118	2.2599	1.7317	.26688	-8.036
.060	0.8337	2.7586	2.3000	1.5760	.26229	-7.567
Benzene – Methanol (4V : 6V) [β_o = 2.0381]						
.010	0.8342	2.4242	2.0223	2.0397	.29839	-5.966
.015	0.8345	2.4615	2.0543	1.9775	.29350	-8.025
.020	0.8348	2.5000	2.0872	1.9164	.28923	-9.000
.025	0.8352	2.5396	2.1210	1.8564	.28467	-9.543
.030	0.8354	2.5806	2.1559	1.7974	.28010	-9.864
.040	0.8358	2.6229	2.1924	1.7389	.27551	-8.776
.050	0.8361	2.6666	2.2297	1,6818	.27095	-8.089
.060	0.8365	3.7118	2.2685	1.6255	.26638	-7.619

Cont…

C x 10^2 M	P (g.cm^{-3})	u x 10^{-5} (cms^{-1})	z x 10^{-5} (g/cm^2.sec)	B_{ad} x 10^{11} (cm^2 dyn^{-1})	L_f x A^0	$Ø_k$ x 10^{10}
Benzene – Methanol (3V : 7V) [β_o = 2.0636]						
.010	0.8356	2.4615	2.0569	1.9749	.29361	-5.8380
.015	0.8359	2.5000	2.0899	1.9139	.28904	-7.8581
.020	0.8363	2.5390	2.1234	1.8538	.28446	-8.8376
.025	0.8366	2.5806	2.1590	1.7947	.27989	-9.3773
.030	0.8369	2.6220	2.1945	1.7366	.27533	-9.7012
.040	0.8374	2.6666	2.2330	1.6792	.27074	-8.6340
.050	0.8378	2.7118	2.2720	1.6229	.26616	-7.9670
.060	0.8382	2.7586	2.3124	1.5676	.26159	-7.5046

Table 2: Ultrasonic velocity and acoustic parameters of Lithium laurate at 40 ± 0.1°C.

C x 10^2 M	P (g.cm^{-3})	u x 10^{-5} (cms^{-1})	z x 10^{-5} (g/cm^2.sec)	B_{ad} x 10^{11} (cm^2 dyn^{-1})	L_f x A^0	$Ø_k$ x 10^{10}
Benzene – Methanol (9V : 1V) [β_o = 2.2699]						
.010	0.7897	2.388	1.8850	2.2205	.31133	-2.642
.015	0.7901	2.4242	1.9153	2.1536	.30660	-6.114
.020	0.7904	2.4615	1.9457	2.0879	.30189	-7.756
.025	0.7908	2.500	1.9771	2.0231	.29716	-8.721
.030	0.7911	2.5396	2.0092	1.9597	.29247	-9.315
.040	0.7914	2.5800	2.0425	1.8972	.28773	-8.424
.050	0.7917	2.6660	2.1107	1.7770	.27851	-9.044
.060	0.7920	2.7580	2.1845	1.6597	.26967	-9.407
Benzene – Methanol (8V : 2V) [β_o = 2.1232]						
.010	0.8015	2.4242	1.9431	2.1228	.30441	--
.015	0.8017	2.4615	1.9734	2.0585	.29977	-3.8254
.020	0.8018	2.5000	2.0045	1.9955	.29514	5.8934
.025	0.8019	2.5806	2.0694	1.8724	.28589	-9.5457

Cont…

$C \times 10^2$ M	P ($g.cm^{-3}$)	$u \times 10^{-5}$ (cms^{-1})	$z \times 10^{-5}$ ($g/cm^2.sec$)	$B_{ad} \times 10^{11}$ ($cm^2\ dyn^{-1}$)	$L_f \times A^0$	$Ø_k \times 10^{10}$
.030	0.8020	2.6229	2.1036	1.8122	.28126	-9.8822
.040	0.8022	2.6666	2.1391	1.7529	.27662	-3.7663
.050	0.8024	2.7586	2.2135	1.6376	.26737	-9.2209
.060	0.8026	2.8571	2.2931	1.5262	.25811	-9.4587
Benzene – Methanol (7V : 3V) [β_o = 2.1231]						
.010	0.8015	2.4615	1.9728	2.0591	.29980	-5.8681
.015	0.8017	2.5000	2.0040	1.9957	.29515	-7.9977
.020	0.8018	2.5396	2.0363	1.9335	.29052	-8.9876
.025	0.8020	2.5806	2.0696	1.8722	.28587	-9.5516
.030	0.8021	2.6666	2.1390	1.7530	.27663	-11.8570
.040	0.8024	2.7111	2.1754	1.6946	.27198	-10.2310
.050	0.8025	2.7586	2.2139	1.6373	.26734	-9.2317
.060	0.8027	2.8070	2.2534	1.5809	.26270	8.5505
Benzene – Methanol (6V : 4V) [β_o = 2.0894]						
.010	0.8114	2.4242	1.9668	2.0970	.30255	--
.015	0.8118	2.4615	1.9982	2.0330	.29789	-2.7872
.020	0.8121	2.4615	1.9991	2.0320	.29782	-2.0626
.025	0.8125	2.5000	2.0312	1.9692	.29319	-4.0887
.030	0.8129	2.5396	2.0644	1.9078	.28853	-5.4066
.040	0.8132	2.5806	2.0998	1.8464	.28390	-5.9863
.050	0.8137	2.6229	2.1342	1.7863	.27924	-5.4885
.060	0.8141	2.6666	2.1711	1.7271	.27457	-5.4883
Benzene – Methanol (5V : 5V) [β_o = 2.1195]						
.010	0.8274	2.388	1.9760	2.1191	.30414	--
.015	0.8280	2.461	2.0381	1.9931	.29496	-8.0306
.020	0.8283	2.500	2.0708	1.9316	.29037	-8.9972

Cont…

C x 10^2 M	**P ($g.cm^{-3}$)**	**u x 10^{-5} (cms^{-1})**	**z x 10^{-5} ($g/cm^2.sec$)**	**B_{ad} x 10^{11} (cm^2 dyn^{-1})**	**L_f x A^0**	**$Ø_k$ x 10^{10}**
.025	0.8270	2.539	2.1045	1.8708	.28577	-9.5632
.030	0.8291	2.580	2.1397	1.8109	.28116	-9.9238
.040	0.8295	2.622	2.1757	1.7522	.27656	-8.7976
.050	0.8297	2.666	2.2124	1.6948	.27200	-8.0883
.060	0.8301	2.666	2.2137	1.6939	.27192	-7.9391
Benzene – Methanol (4V : 6V) [β_o = 2.0381]						
.010	0.8350	2.4242	2.0242	2.0377	.29825	--
.015	0.8353	2.5000	2.0884	1.9153	.28915	-7.7626
.020	0.8360	2.5396	2.1231	1.8545	.28452	-8.8161
.025	0.8363	2.5806	2.1583	1.7953	.27994	-9.3529
.030	0.8367	2.6229	2.1946	1.7371	.27537	-9.6788
.040	0.8370	2.6666	2.2319	1.6801	.27081	-8.5765
.050	0.8373	2.6666	2.2329	1.6793	.27015	-6.7966
.060	0.8377	2.7586	2.3110	1.5685	.26167	-7.4425
Benzene – Methanol (3V : 7V) [β_o = 2.636]						
.010	0.8502	2.3880	2.030	2.0623	.30004	--
.015	0.8504	2.4242	2.0616	2.0008	.29553	-3.8074
.020	0.8506	2.4615	2.0938	1.9403	.29103	-5.7785
.025	0.8508	2.5000	2.1272	1.8803	.28649	-6.9425
.030	0.8511	2.5396	2.1616	1.8216	.28198	-7.6830
.040	0.8515	2.5806	2.1974	1.7634	.27744	-7.1142
.050	0.8518	2.6229	2.2343	1.7063	.22291	-6.7516
.060	0.8520	2.6660	2.2721	1.6505	.26841	-6.4804

The results are in agreement with the fact that there is decrease in the CMC with increase in number of carbon atoms in the hydrophobic chain[27].

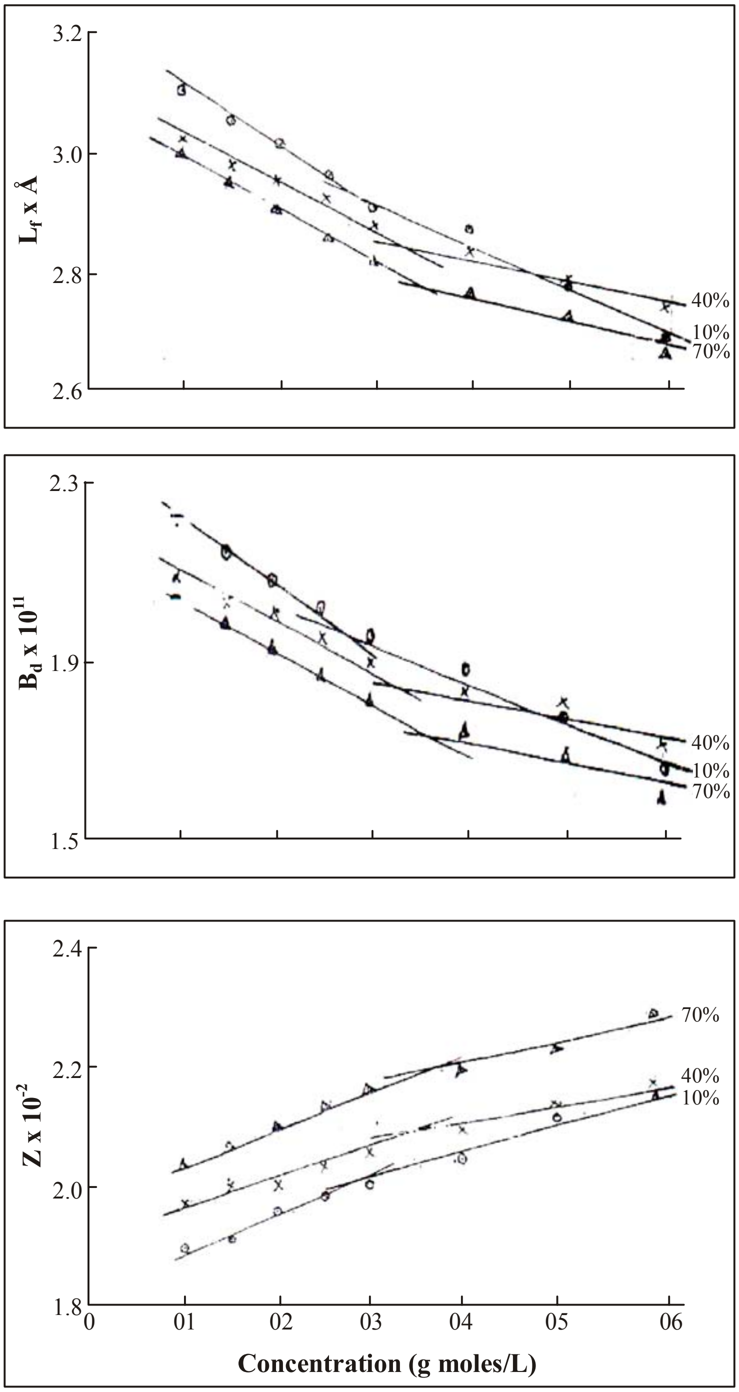

Fig. 1: Plots of Acoustic parameters vs Soap concentration for Lithium laurate in Benzene methanol mixtures at 40°C

The variation of ultrasonic velocity with soap concentration is expressed by the equation:

$$u = u_o + GC$$

(Subscript zero refers to solvent)

Here G is Garnsey's constant. The values of G were evaluated from the u vs. c. (Fig. 2). It is noticed that the value, of G decreases upto 40% methanol concentration and there after increases unabatedly upto 70% methanol. This reinforces the concept that micellar clustering is dis-similar below and above 40% methanol concentration. It is clear that with respect to chain length of the soap the values of G follow the following order:

Caprate > Laurate

To confirm our findings still further, the values of constant A and B were determined from the $[\beta - \beta_o/c]$ vs. $\sqrt{c}$ plots (Fig. 3). A comparison of the results for Caprate and Laurate makes it amply clear that the values of A and B follow the identical trend and supports the proposition that the change in the nature of micellization takes place at the periphery of this concentration. The values of A and B shows the following order :

Caprate > Laurate.

Colloidal chemical behaviour and micellar characteristics of lithium caprate and laurate in benzene methanol mixtured have been investigated by ultrasonic velocity and density measurement (313 K). The variation of adiabatic compressibility, L_f, apparent molal compressibility (Fig. 4) show that there is sufficient soap-solvent interaction due to which micellar alignment is considerably affected.

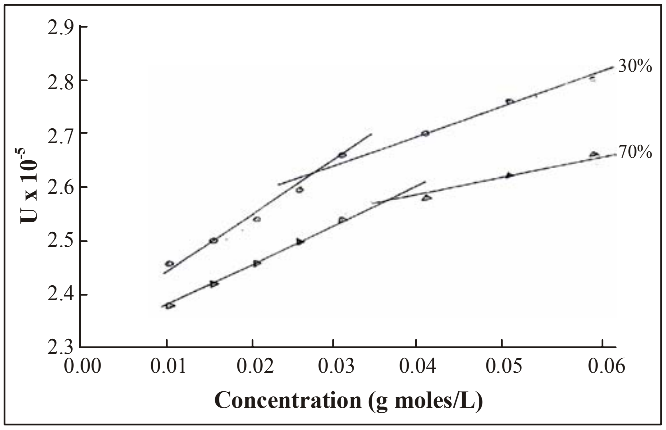

Fig. 2: Plots of Ultrasonic velocity Vs Soap concentration for Lithium laurate in Benzene Methanol mixtures at 40°C

Table 3: Values of the CMC (in M) for Lithium soaps in Benzene-Methanol mixtures

Percent of methanol	Caprate			Laurate		
	Z vs. C	β vs. C.	L_f vs. C	Z vs. C	β vs. C.	L_f vs. C
10	0.0280	0.0280	0.0285	0.0275	0.0275	0.0270
20	0.0285	0.0285	0.0286	0.0280	0.0285	0.0283
30	0.0285	0.0282	0.0285	0.0283	0.0286	0.0283
40	0.0330	0.0325	0.0330	0.0330	0.0335	0.0335
50	0.0333	0.0330	0.0335	0.0335	0.0330	0.0330
60	0.0335	0.0330	0.0335	0.0333	0.0330	0.0330
70	0.0345	0.0340	0.0345	0.0360	0.0365	0.0360

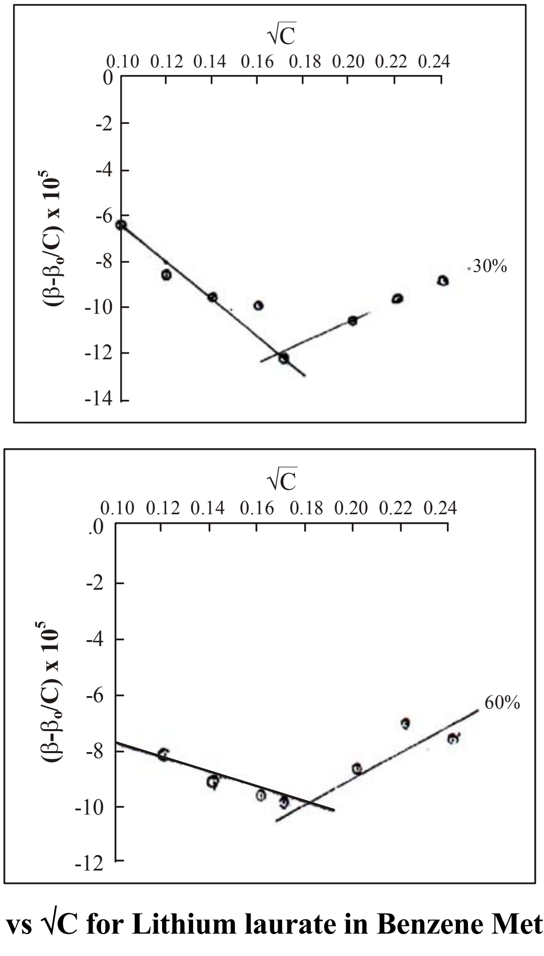

Fig. 3: Plots of β - β_o/ C vs √C for Lithium laurate in Benzene Methanol mixtures at 40°C

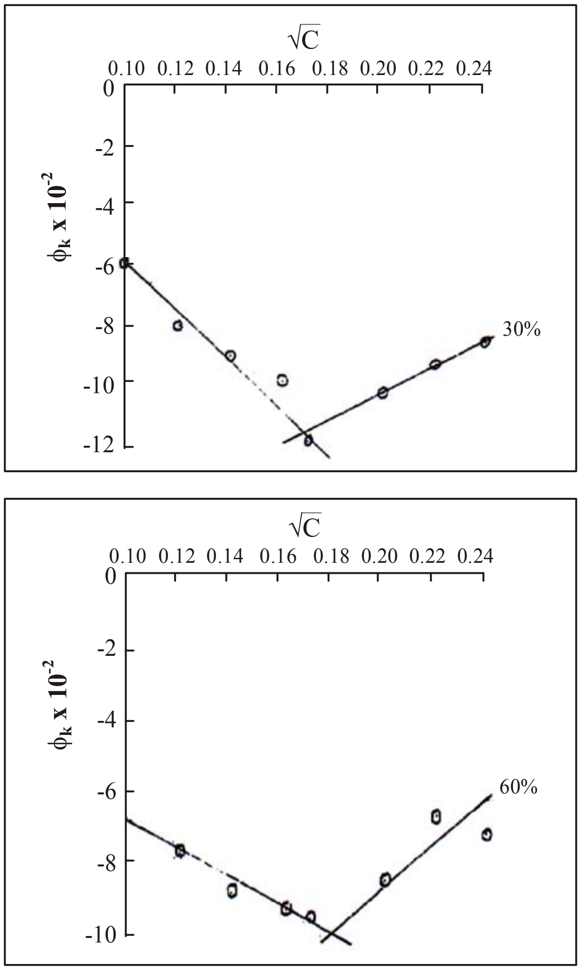

Fig. 4: Plots of ϕ_k x 10^{-2} vs √C for Lithium laurate in Benzene Methanol mixtures at 40°C

The results indicates that CMC values decrease with in increase in number of carbon atoms in the hydrophobic chain. The study reveals that the change in the micellar organization takes place around 40% methanol concentration. It has been also concluded that polarity of the solvent affects the micellar feature of the solute in ternary system.

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