Apparent Molar Volume and Expansibility Behaviour of Magnesium, Calcium and Strontium caprate in Non-aqueous Medium

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ABSTRACT: The density measurements, ρ of magnesium, calcium and strontium caprate in non - aqueous medium at different temperatures (25-40º C) has been used to evaluate various significant parameters viz. apparent molar volume (ϕv),and expansibility (E^0_{soap}) to study their solution behaviour. The critical miceller concentration (CMC), is found to decrease with increasing temperature and vary with different metals as Mg>Ca>Sr. The density of these soap solutions increases with increasing concentration and decreasing temperature. Partial molar volume ($\phi^0 v$) and experimental limiting slope (Sv) as derived from Masson's equation provide useful informations on soap-solvent and soap-soap interactions. The values of apparent molar volume 98 (ϕv) was found to increase with increasing concentration as well as temperature.

Keywords: Critical miceller concentration (CMC); density ρ; apparent molar volume (ϕv); partial moral volume ($\phi^0 v$) and expansibility.

INTRODUCTION: While stupendous developments have taken place in the study of various alkali metal soaps of saturated fatty acids, the studies on alkaline-earth metal soaps have not yet been carried out systematically. The present paper deals with the study of molar volume and the data obtained have been used to study the soap-solvent interactions. Bahadur[1] studied molar volume of barium soap of lower fatty acids. Bhargava[2] studied the apparent molar volume of glycine for inorganic salt solution of different concentrations was found to increase linearly with increasing concentration of the ions, The apparent molar volume of ammonium acetate solutions was also determined from density data using young's rule by Blokhra and Thakur.[3-4] The Dielectric constant of the medium was used to characterize tetralkylammonuimiodides in ethanol - water mixtures by Franks at al.[5-6]

Apparent molar volume and limiting apparent molar volume of electrolytes[7] and non- electrolytes[8] have found applications to characterize solute-solute, solute-solvent and solvent-solvent interactions taking place in solutions. Ram Gopal et al.[9] studied the effect of temperature on partial molar volume of hydrophobic solutes so as to obtain significant information's on solute-solvent interactions. Ram Gopal et al.[10-12] have utilized mixtures of mucin and appositively charged surfactant aggregates with varying changed density in order to study their phase behaviour, association, and dynamics.

The present work deals with the studies of density, partial molar volume and expansibility of magnesium calcium and strontium caprate in methanol-chloroform mixture at different temperatures (25-40ºC).

MATERIALS AND METHODS: Analar-Grade chemicals such as capric acid, methanol, chloroform, and metal acetate salts were used for present study. Metal caprates were prepared by direct metathesis. The aqueous solution containing stoichiometric amount of respective metal acetates and potassium caprate were mixed at nearly 60ºC under constant stirring. The metathesis displacement reaction completed and the pracipited soaps were washed with distilled water followed by acetone to remove the excess of metal and unreacted fatty acid. The pure amorphous soaps were stored over calcium chloride. The recrystallised pure compounds are found to decompose between

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210-240ºC. The purity of these soaps were checked by studying their infrared absorption spectra and elemental analysis.

The density of metal caprates (soap) solutions has been measured in a thermostat having thermal stability of ± 0.05ºC. The 10 ml bicapillary Pyknometer was used for the determination of density.

RESULTS AND DISCUSSION: The density, ρ (gcm^{-3}) of magnesium, calcium and strontium caprate in non-aqueous medium (methanol- chloroform mixture) at (25-40ºC) Table 1& 2 is found to increase with increasing concentration, C. The critical miceller concentration (CMC) as obtained from $\rho - c$ plots is found to decrease with increasing temperature. The graphical values for zero surfactant concentration

($\rho - c$) plots extrapolated to zero concentration are found to be consistent with experimental value of ρ_0 (Table 3).

The equation, $\rho = \rho_0 +AC -BC^{3/2}$ by W.C. Roots[13] and Millers, 1968[14] has been successfully applied to these solutions to evaluate contents, A_1 and B_1 (below the CMC) and A_2, B_2 (above the CMC) as recorded in Table 4. It is observed that $A_1>B_1$ and $A_2>B_2$. The above facts suggest that soap-solvent interactions in pre micellar region are predominant whereas in the post micellar region, soap-soap interactions are predominant. It is therefore concluded that micellization just begin at a particular concentration termed as CMC.

Table 1: Density data for Magnesium caprate and calcium caprate at different temptratures (25-40º C).

Conc.	Magnesium caprate				Calcium caprate			
	25ºC	30ºC	35ºC	40ºC	25ºC	30ºC	35ºC	40ºC
0.0002	1.09342	1.09325	1.09310	1.09290	1.09342	1.093280	1.09310	1.09293
0.0006	1.09345	1.09330	1.09315	1.09295	1.09347	1.093331	1.09315	1.09297
0.0010	1.09350	1.09334	1.09317	1.09297	1.09352	1.093376	1.09320	1.09301
0.0014	1.09353	1.09337	1.09320	1.09301	1.09357	1.093419	1.09325	1.09304
0.0018	1.09356	1.09341	1.09324	1.09303	1.09360	1.093454	1.09327	1.09306
0.0022	1.09359	1.09343	1.09326	1.09305	1.09364	1.093481	1.09330	1.09307
0.0026	1.09363	1.09346	1.09328	1.09307	1.09368	1.093507	1.09333	1.09308
0.0030	1.09365	1.09349	1.09330	1.09309	1.09371	1.93528	1.09335	1.09309

Table 2: Density data for Sr caprate at different temperatures (25-40º C).

Conc.	25ºC	30ºC	35ºC	40ºC
0.0002	1.09333	1.09326	1.09310	1.09290
0.0006	1.09346	1.09332	1.09314	1.09295
0.0010	1.09352	1.09336	1.09319	1.09299
0.0014	1.09355	1.09340	1.09320	1.09303
0.0018	1.09359	1.09342	1.09323	1.09305
0.0022	1.09363	1.09345	1.09326	1.09306
0.0026	1.09365	1.09347	1.09328	1.09307
0.0030	1.09368	1.09350	1.09329	1.09308

Table 3: Extrapolated and experimental values of density for alkaline-earth metal caprate (for zero concentration) in mixed solvent (50% methanol+50% chlorofrom) at different temperatures (25-40˚C).

Temp (ºC)	Mg caprate	Ca caprate	Sr caprate	Experimental data for
25	1.09330	1.09341	1.09340	1.09338
30	1.09320	1.09325	1.09325	1.09324
35	1.09310	1.09308	1.09300	1.09318
40	1.09290	1.09288	1.09293	1.09289

Table 4: Roots constants, A and B obtained from ($\rho - \rho_0$)/C VS C$^{1/2}$ plots.

Temp (ºC)	Mg caprate				Ca caprate				Sr caprate			
	A$_1$	A$_2$	-B$_1$	-B$_2$	A$_1$	A$_2$	-B$_1$	-B$_2$	A$_1$	A$_2$	-B$_1$	-B$_2$
25	0.004	0.120	0.550	0.70	0.158	0.169	1.000	1.200	0.142	0.160	0.800	1.150
30	0.112	0.114	0.650	0.773	0.142	0.160	0.900	1.350	0.133	0.145	0.900	1.280
35	0.095	0.102	0.400	0.600	0.120	0.142	0.550	1.150	0.106	0.142	0.400	1.400
40	0.091	0.101	0.450	0.924	0.116	0.141	0.750	1.850	0.100	0.118	0.500	1.250

Table 5: Apparent molar volume data (ϕv) for magnesium caprate and calcium caprate at different tempratures (25-40ºC).

Conc.	25ºC	30ºC	35ºC	40ºC	25ºC	30ºC	35ºC	40ºC
0.0002	280.75	285.37	299.10	303.69	258.75	272.55	290.90	295.53
0.0006	286.85	291.46	302.12	306.78	270.43	280.17	297.03	303.15
0.0010	290.80	295.43	305.46	310.11	276.20	287.20	300.97	306.52
0.0014	294.48	299.07	307.55	312.20	281.05	291.51	303.98	313.21
0.0018	296.52	301.55	310.30	317.00	285.22	297.96	310.23	320.95
0.0022	299.87	305.30	312.42	321.15	292.92	305.38	315.44	329.25
0.0026	303.27	308.22	314.80	324.45	297.15	310.89	320.47	336.35
0.0030	306.05	311.00	317.42	328.48	302.70	316.50	324.75	343.12

Table 6: Apparent molar volume data (ϕv) for Strontium caprate at different temperatures (25-40ºC).

Conc.	25ºC	30ºC	35ºC	40ºC
0.0002	315.09	324.28	347.21	351.83
0.0006	322.70	331.90	347.25	357.93
0.0010	327.89	338.91	352.68	360.89
0.0012	330.33	342.80	353.28	363.28
0.0014	333.73	343.23	354.38	365.23
0.0018	336.94	359.69	363.94	370.15
0.0022	343.35	355.45	371.06	377.64
0.0026	349.86	360.87	375.75	380.73
0.0030	353.50	365.44	381.87	387.52

$$\emptyset_v = \frac{M}{\rho_0} - \frac{\rho - \rho_0 \times 10^3}{c\rho} \qquad (1)$$

Where, M, ρ, ρ_0 and C signify for molecular weight, density of solutions, density of solvent mixture and soap concentration, respectively. Table 5 and 6 shows that the values of apparent molar volume increase with increasing soap concentration. ϕ_v Vs C$^{1/2}$ plots (Fig. 1) also show a break at the CMC. A number of factors viz. hydration of amphiphilic solutes, electrostriction of solvent molecules of charged moieties, nature of the Ionic head group and the length of nonpolar portion of amphiphilic molecules all contribute to apparent molar volume.

Roots equation facilitates plots of ($\rho - \rho_0$)/C VS C$^{1/2}$ (Fig-2) showing intersection at critical miceller concentration. The values of limiting apparent molar volume ($\phi^0 v$) are obtained by extrapolating the linear plots of $\phi_v V_s C^{1/2}$ in pre micellar region are in accordance with the equation proposed by Masson,[15]

$$\emptyset_v = \emptyset_v^0 + Sv \qquad (2)$$

The values for limiting apparent molar volume (ϕ_v^0) and experimental slope (Sv), as recorded in Table 7, are a measure of soap - solvent and soap-soap interactions, respectively.
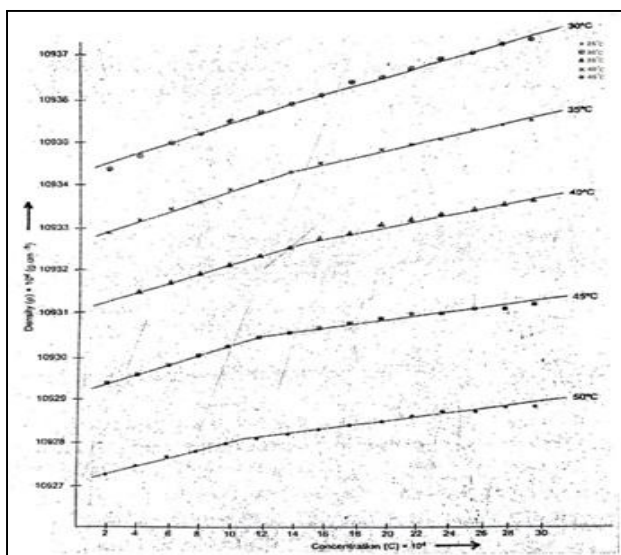
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Figure 1: The plots of density ρ Vs Concentration (C) for Ca caprate at different temperatures (25-40ºC).

The ϕ_v^0 and Sv data for these solutions are found to increase with increasing temperature and vary with the metal. The ϕ_v^0 data for these solutions vary as whereas, Sr>Mg>Ca whereas the order of S_v values changes as Ca>Mg>Sr. The molar expansibility, E_{soap}^0 (Table 8) is found to increase with increasing temperature which may to due to the decrease in electrostriction. The results obtained were found in good agreements[16-21]. The plots of molar expansibilities and partial molar volume as a function of temperature confirmed that all these metal caprates appear to be structure breakers above 30^0C which may be due to the fact that at higher temperatures increased thermal agitation does not allow structure information to an extent detectable by the present technique used.

Table 7: Limiting apparent molar volume and experimental limiting slope for alkaline -earth metal caprate at different temperatures (25-40ºC).

Conc.	25ºC	30ºC	35ºC	40ºC	25ºC	30ºC	35ºC	40ºC
Mg caprate	278.49	282.73	290.55	301.03	295.57	338.98	380.33	551.83
Ca caprate	252.70	267.00	280.09	295.02	338.98	591.34	633.56	738.22
Sr caprate	313.00	321.00	334.76	351.49	254.00	333.49	445.41	569.55

Table 8: Partial molar expansibility (E_{soap}^0) data for alkaline -earth metal caprates at different temperatures (25-40ºC).

Conc.	25ºC	30ºC	35ºC	40ºC
Mg caprate	0.63	1.72	2.99	2.99
Ca caprate	2.63	2.78	4.00	3.89
Sr caprate	1.58	2.72	4.20	4.90

CONCLUSION: From the above cited results and discussion, it may be concluded that the miceller aggregates are formed in these solutions of alkaline - earth metal caprates. Partial molar expansibility data, E_{soap}^0 have also been conveniently evaluated for these systems utilizing the temperature dependence of partial molar volume ($\phi^0 v$). The fact that E_{soap}^0 increases with increasing temperature (Table 8) may be attributed to a decrease in electrostriction.
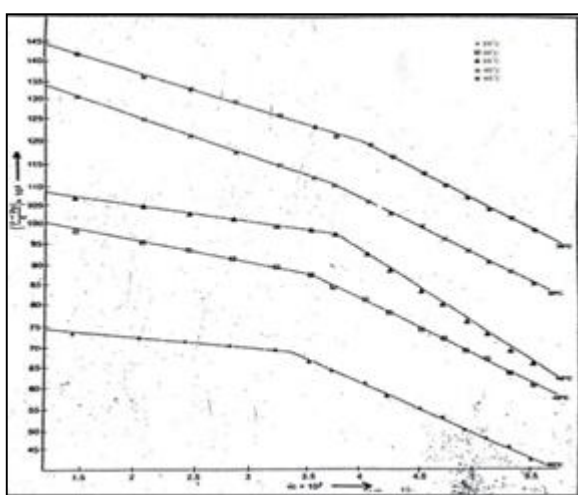
Figure 2: The plots of $\rho - \rho_0/C$ vs concentration $(C)^{1/2}$ of Sr caprate at different temperatures (25-40ºC).

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