Research Paper :

Density, apparent molar volume and expansibility behaviour of alkaline earth metal laurates in non-aqueous medium at different temperatures

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ABSTRACT

The density measurement, ρ (gcm^{-3}) for alkaline earth metal (Mg/Ca/Sr/Ba) laurates in non-aqueous medium (50% methanol +50% chloroform) at different temperatures (30-50^{0}C) has been used to evaluate various significant parameters *viz.* apparent molar volume (Φ_v) and expansibility (E^0_{surf}) to explore their solution behaviour. The critical micelle concentration (c.m.c.) as ascertained from ρ-C plots, is found to decrease with increasing temperature and vary with different metals as Mg>Ca>Sr>Ba. Density for these solutions increases with increasing surfactant concentration and decreasing temperature. Partial molar volume (Φ^0_v) and experimental limiting slope (Sv) as obtained from Masson's equation provide information on solute-solvent and solute-solute interactions, respectively. Apparent molar volume (Φ_v) is found to increase with increasing concentration and increasing temperature.

Key words : Alkaline earth metal laurates, critical micelle concentration (c.m.c), density (ρ), apparent molar volume (Φ_v), partial molar volume (Φ^0_v), expansibility.

Data on molar volume has proved to be a useful tool to study the solute-solvent interactions (Bahadur, 1974). The apparent molar volume of glycine for inorganic salt solution of different concentrations was found to increase linearly with increasing concentration of the ions (Bhargava, 1976). Density data for aqueous solutions of 4-amino butyric acids as 25^{0}C are also found to vary linearly with molarity (Blockhra and Verma, 1977). The apparent molar volume of ammonium acetate solutions was also determined from density data using Young's rule (Blokhra and Thakur, 1981). Dielectric constant of the medium was used to characterize tetraalkylammonium iodides in ethanol-water mixtures (Franks and lves, 1966). Dielectric constant however was found to play a dominating role in controlling the nature of the slope, Sv. Reference (Franks and Quickenden, 1968; Franks *et al.*, 1968; Hepler, 1969; Jalicoeur and Philip, 1975; Kashimoto *et al.*, 2006 and Kay and Evans, 1966) on solute-solvent interactions indicate that density measurements proved useful to detect and explain the process of micellization. The density measurements were employed to study the micellar behaviour of the calcium soaps in water, methanol and water-methanol mixtures (Kim *et al.,* 2006). Density data was also used to determine the c.m.c. of Copper (Lafitte, 2005), iron (Mason, 1947 and Mehrotra *et al.*, 1971) and Cobalt (Millero, 1968) soaps of lower fatty acids in non-aqueous media.

Apparent molar volume and limiting apparent molar volume for electrolytes (Millero, 1970) and non-electrolytes (Millero, 1971) have found application to characterize solute-solute, solute-solvent and solvent-solvent interactions taking place in solutions. Hepler (Ram Gopal and Siddiqi, 1968 and Jolicoeur *et al.* (Ram Gopal *et al.*, 1970) have however studied the effect of temperature on partial molar volume of hydrophobic solutes so as to obtain significant informations on solute-solvent interactions. Recently, however, research workers (Ram Gopal *et al.*, 1973, Ram Gopal and pathak, 1978 and Root, 1933) have shown a keen interest for surface charge density of various amphipathetic substances. Kim *et al.* (Ram Gopal *et al.*, 1973) in the year, 2006 have thus carried out an investigation on polymerized rod like nanoparticles with controlled surface charge density. G. Lafitte and Co-workers (Ram Gopal and Pathak, 1978) have utilized mixtures of mucin and oppositvely charged surfactant aggregates with varying charged density to probe their phase behaviour, association, and dynamics. Kashimoto *et al.* (Root, 1933) have also probed the surface density of surface-active substances through total reflection x-rays absorption fine structure measurement.

Present investigation however incorporates work on partial molar volume and expansibility so as to obtain useful information on micellization and solution behaviour *i.e.* solute-solvent and solute-solute interactions. Increasing surfactant concentration and increasing temperature increases the apparent molar volume which is consistent

with the general expectation. Partial molar expansibility (E^0_{surf}) for these surfactant systems are also found to increase with increasing temperature.

MATERIALS AND METHODS

Anala R-grade chemicals (lauric acid, methanol, chloroform, carbonates of magnesium/calcium/strontium and barium) were obtained from Glaxo Labs Mumbai (India). The conductivity water was prepared by twice redistilling good quality distilled water over alkaline $KMnO_4$

Alkaline earth metal laurates were prepared by direct metathesis. The aqueous solution containing stoichiometric amount of respective metal carbonate and potassium laurate were mixed at nearly 80^0C under constant stirring. As evolution of CO_2 ceased and metathetic displacement reaction completed (phenolphthalein indicator rendered colourless from pink), the desired compound was separated from mother liquor by vacuum filtration. The product was washed several times with benzene and oven dried. All the four compounds so prepared were further purified by recrystallization from methanol-chloroform solvent mixture. The pure and well dried compounds (white amorphous solids) were then stored over calcium chloride. The recrystallized pure compounds are found to decompose between $200-220^0C$. The preparation and quality of these compounds were checked by IR and elemental analyses.

Pyrex glass dilatometers having a 15 ml reservoir were used to determine density (ρ) of these solutions at different temperatures ($\pm 0.05^0C$). The reproductibility of the data is found to be ± 0.002 gcm^{-3}. The accuracy of

the results was also checked by determining the molar volume of sodium chloride at 45^0C. The experimental value (17.57 cm^3 mol^{-1}) has been found consistent with the data (17.59 cm^3 mol^{-1}) as obtained by Millero.

RESULTS AND DISCUSSION

The density, ρ (g.cm^{-3}) for alkaline earth metal (Mg/Ca/Sr/Ba) laurates in non-aqueous medium (50% methanol + 50% chloroform) at (30-50^{0}C) (Table 1 and 2) is found to increase with increasing concentration, C(mol dm^{-3}) as is evident from ρ-C plots (Fig. 1). The critical micelle concentration (c.m.c.) as obtained from ρ-C plots, is found to decrease with increasing metal size and increasing temperature. The graphical values for zero surfactant concentration (ρ-C) plots extrapolated to zero concentration are found to be consistent with experimental ρ_0 (Table 3).

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

The data for apparent molar volume (Φ_v) for these surfactant systems have been evaluated employing the equation (Shukla, 1982)

Table 1 : Density data for Mg laurate and Ca laurate at different temperatures (30-50^{0}C)

| Conc.	Mg laurate					Ca laurate				
	30^{0}C	35^{0}C	40^{0}C	45^{0}C	50^{0}C	30^{0}C	35^{0}C	40^{0}C	45^{0}C	50^{0}C
0.0002	1.093423	1.093274	1.093114	1.092924	1.092719	1.093431	1.093280	1.093119	1.092929	1.092722
0.0004	1.093444	1.093295	1.093132	1.092941	1.092734	1.093460	1.093306	1.093141	1.092950	1.092740
0.0006	1.093465	1.093314	1.093150	1.092958	1.092749	1.093486	1.093331	1.093163	1.092971	1.092757
0.0008	1.093485	1.093334	1.093167	1.092974	1.092762	1.093512	1.093354	1.093184	1.092990	1.092773
0.0010	1.093504	1.093351	1.093183	1.092989	1.092775	1.093536	1.093376	1.093204	1.093009	1.092788
0.0012	1.093522	1.093368	1.093199	1.093005	1.092788	1.093560	1.093396	1.093223	1.093026	1.092801
0.0014	1.093540	1.093385	1.093215	1.093019	1.092801	1.093583	1.093419	1.093243	1.093040	1.092814
0.0016	1.093558	1.093402	1.093230	1.093030	1.092812	1.093605	1.093436	1.093259	1.093050	1.092825
0.0018	1.093576	1.093418	1.093244	1.093042	1.092824	1.093627	1.093454	1.093273	1.093063	1.092834
0.0020	1.093590	1.093432	1.093258	1.093051	1.092833	1.093642	1.093466	1.093287	1.093068	1.092842
0.0022	1.093607	1.093446	1.093272	1.093062	1.092845	1.093659	1.093481	1.093300	1.093078	1.092850
0.0024	1.093621	1.093460	1.093284	1.093072	1.092854	1.093678	1.093494	1.093312	1.093084	1.092857
0.0026	1.093635	1.093473	1.093297	1.093081	1.092864	1.093694	1.093507	1.093323	1.093089	1.092864
0.0028	1.093649	1.093487	1.093309	1.093089	1.092874	1.093708	1.093518	1.093333	1.093094	1.092871
0.0030	1.093662	1.093498	1.093320	1.093095	1.092885	1.093721	1.093528	1.093344	1.093095	1.092874

| Conc.	Sr laurate					Ba laurate				
	30^0C	35^0C	40^0C	45^0C	50^0C	30^0C	35^0C	40^0C	45^0C	50^0C
0.0002	1.093428	1.093278	1.093116	1.092926	1.092718	1.093422	1.093273	1.093114	1.092924	1.092718
0.0004	1.093454	1.093302	1.093137	1.092944	1.092732	1.093442	1.093292	1.093131	1.092940	1.092733
0.0006	1.093479	1.093325	1.093156	1.092962	1.092746	1.093462	1.093311	1.093148	1.092956	1.092747
0.0008	1.093503	1.093346	1.093176	1.092979	1.092759	1.093482	1.093329	1.093165	1.092972	1.092761
0.0010	1.093526	1.093366	1.093194	1.092995	1.092772	1.093500	1.093346	1.093181	1.092987	1.092774
0.0012	1.093548	1.093385	1.093213	1.093011	1.092782	1.093518	1.093364	1.093196	1.093001	1.092787
0.0014	1.093569	1.093405	1.093231	1.093024	1.092793	1.093536	1.093379	1.093211	1.093015	1.092798
0.0016	1.093590	1.093420	1.093242	1.093036	1.092801	1.093552	1.093396	1.093226	1.093029	1.092810
0.0018	1.093609	1.093436	1.093253	1.093046	1.092807	1.093567	1.093412	1.093241	1.093043	1.092822
0.0020	1.093624	1.093450	1.093261	1.093054	1.092813	1.093582	1.093426	1.093253	1.093056	1.092831
0.0022	1.093640	1.093463	1.093271	1.093064	1.092820	1.093596	1.093441	1.093267	1.093069	1.092842
0.0024	1.093654	1.093475	1.093277	1.093072	1.092823	1.093611	1.093457	1.093279	1.093082	1.092852
0.0026	1.093668	1.093486	1.093284	1.093081	1.092828	1.093625	1.093470	1.093292	1.093094	1.092862
0.0028	1.093683	1.093498	1.093288	1.093085	1.092832	1.093638	1.093484	1.093305	1.093105	1.092870
0.0030	1.093694	1.093507	1.093293	1.093089	1.092833	1.093651	1.093498	1.093317	1.093117	1.092880

Table 2 : Density data for Sr laurate and Ba laurate at different temperatures (30-50^{0}C)

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

where, M, ρ, ρ_0 signify for molecular weight, density of solutions, density of solvent the solution concentration, respectively. Table 5 and 6 clearly show that apparent molar volume data increases with increasing surfactant concentration. Φ_v vs $C^{½}$ plots (Fig. 2) are also found to intersect in the vicinity of c.m.c. 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 non-polar portion of amphiphilic molecules all contribute to apparent molar volume and
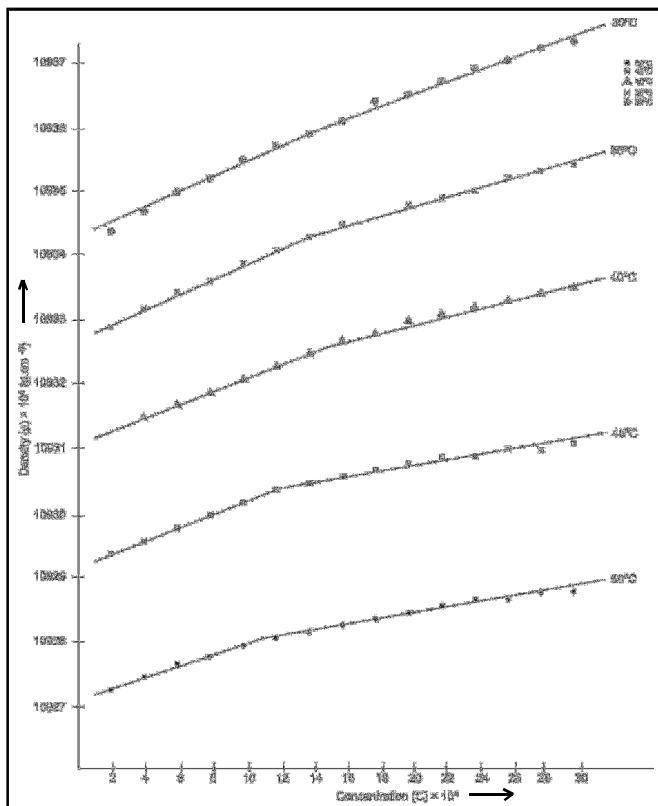
Fig. 1 : The plots of density (ρ) vs. concentration (C) for Ca laurate at different temperature (30-50^{0}C)
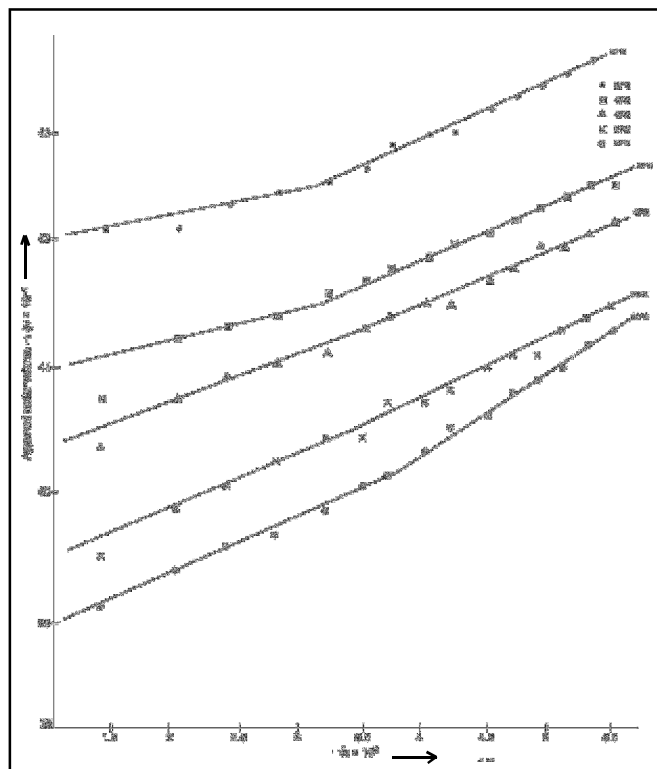
Fig. 2 : The plots of apparent molar volume (ϕv) vs. [concentration (C)]^{½} for Ba laurate at different temperature (30-50^{0}C)

Table 3 : Extrapolated and experimental values of density for alkaline earth metal laurates (for zero concentration) in mixed solvent (50% methanol + 50% chloroform) at different temperatures (30-50⁰C)

Temp. (⁰C)	ρ_o (gcm^{-3}) (obtained from ρ-C plots)				Experimental data for ρ_o
	Mg laurate	Ca laurate	Sr laurate	Ba laurate	
30	1.093400	1.093420	1.093410	1.093400	1.093400
35	1.093255	1.093260	1.093260	1.093250	1.093252
40	1.093100	1.093090	1.093105	1.093100	1.093095
45	1.092900	1.092901	1.092910	1.092905	1.092906
50	1.092700	1.092710	1.092715	1.092705	1.092703

Table 4 : Roots Constants, A and B as obtained from (ρ-ρ_o)/C vs C½ plots

Temp. (⁰C)	Mg laurate				Ca laurate				Sr laurate				Ba laurate			
	A_1	A_2	$-B_1$	$-B_2$	A_1	A_2	$-B_1$	$-B_2$	A_1	A_2	$-B_1$	$-B_2$	A_1	A_2	$-B_1$	$-B_2$
30	0.114	0.121	0.550	0.720	0.159	0.170	1.000	1.200	0.143	0.160	0.800	1.150	0.112	0.118	0.575	0.700
35	0.112	0.115	0.650	0.775	0.143	0.161	0.900	1.350	0.134	0.146	0.900	1.280	0.104	0.106	0.475	0.500
40	0.096	0.102	0.400	0.600	0.121	0.143	0.550	1.150	0.107	0.143	0.400	1.400	0.095	0.097	0.425	0.525
45	0.092	0.101	0.450	0.925	0.118	0.142	0.750	1.850	0.100	0.119	0.500	1.250	0.089	0.091	0.350	0.475
50	0.081	0.082	0.458	0.550	0.099	0.113	0.700	1.250	0.074	0.096	0.250	1.150	0.076	0.082	0.250	0.525

Table 5 : Apparent molar volume (Φv) data for Mg laurate and Ca laurate af different temperatures (30-50⁰C)

Conc.	Mg laurate					Ca laurate				
	30⁰C	35⁰C	40⁰C	45⁰C	50⁰C	30⁰C	35⁰C	40⁰C	45⁰C	50⁰C
0.0002	280.77	285.38	299.15	303.78	312.99	258.76	272.58	290.92	295.55	313.90
0.0004	285.35	287.67	301.44	306.07	315.28	263.39	277.16	295.50	300.12	316.19
0.0006	286.87	291.48	302.20	306.83	316.04	270.49	280.20	297.02	303.17	318.48
0.0008	288.78	292.24	303.73	308.36	318.71	272.54	284.02	298.93	304.70	320.76
0.0010	290.83	295.45	305.56	310.19	320.31	276.20	287.22	300.98	306.53	323.05
0.0012	292.97	297.58	306.78	310.64	321.38	278.64	290.88	303.12	309.27	326.10
0.0014	294.49	299.10	307.65	312.28	322.14	281.03	291.53	303.99	313.20	328.28
0.0016	295.64	300.25	308.87	315.22	323.86	283.40	295.45	306.93	320.71	331.06
0.0018	296.53	301.65	310.33	317.00	324.68	285.24	297.99	310.24	320.96	334.24
0.0020	299.07	303.68	311.50	319.79	326.72	289.92	302.77	312.88	326.66	337.24
0.0022	299.90	305.34	312.46	321.25	327.13	292.91	305.43	315.45	329.24	339.69
0.0024	301.73	306.73	314.02	322.84	328.62	294.64	308.41	317.98	332.91	342.12
0.0026	303.29	308.25	314.99	324.55	329.53	297.16	310.93	320.48	336.37	344.17
0.0028	304.62	309.23	316.14	326.33	330.31	299.98	313.74	322.94	339.34	345.93
0.0030	306.08	311.00	317.45	328.49	330.68	302.72	316.49	324.77	343.13	348.68

may thus affect its value to a different extent. Franks *et al.* (Visser *et al.*, 1977) have however observed a decrease in apparent molar volume of (Φ_v) of NaDS beyond the c.m.c.

Root's equation facilitates plots of (ρ - ρ_o)/c vs C½ (Fig. 3) showing intersection in the vicinity of critical micelle concentration. The data on limiting apparent molar volume (Φ_v) are obtained by extrapolating the linear plots of Φ_v vs. C½ in premicellar region (dilute solutions) in accordance with the equation by Masson,

$$\Phi v = \Phi^0 v + S v^{½}$$

The values for limiting apparent molar volume ($\Phi^0 v$) and experimental limiting slope (S_v), as recorded in Table 7, are a measure of solute-solvent and ion-ion interactions, respectively.

The $\Phi^0 v$ and Sv data for these solutions are found to increase with increasing temperature and vary with the metal. The $\Phi^0 v$ data for these solutions vary as: whereas, Ba >Sr> Mg> Ca whereas the order of S_v values changes as : Ca> Mg> Sr> Ba. The molar expansibility, E^0_{surf} (Table 8) is found to increase with increasing temperature which may be due to the decrease in electrostriction as well as loosening of water structure at

Table 6 : Apparent molar volume (Φv) data for Sr laurate and Ba laurate at different temperatures (30-50^{0}C)

Conc.	Sr laurate					Ba laurate				
	30^{0}C	35^{0}C	40^{0}C	45^{0}C	50^{0}C	30^{0}C	35^{0}C	40^{0}C	45^{0}C	50^{0}C
0.0002	316.10	325.29	348.20	352.84	375.78	389.01	393.64	402.84	407.48	421.28
0.0004	320.67	329.87	348.20	357.42	378.07	393.58	398.21	407.42	412.06	421.28
0.0006	323.72	332.91	351.25	358.94	378.83	395.10	399.74	408.94	413.58	422.81
0.0008	326.39	336.72	351.63	360.85	380.36	395.87	401.64	409.70	414.34	423.57
0.0010	328.90	339.92	353.69	362.91	381.27	398.15	403.70	411.08	415.72	424.94
0.0012	331.34	342.82	354.30	364.28	384.17	399.68	404.31	412.75	417.39	425.86
0.0014	333.74	344.24	355.39	367.22	385.59	400.77	406.70	413.95	418.59	427.82
0.0016	335.53	348.16	360.21	370.00	388.37	402.72	407.36	414.85	419.49	428.72
0.0018	337.95	350.70	363.96	373.17	391.54	404.76	408.37	415.55	420.19	429.42
0.0020	341.71	353.65	368.33	376.63	394.09	406.38	410.10	417.48	421.21	431.05
0.0022	344.37	356.47	371.07	378.63	395.75	408.13	411.10	418.23	422.04	432.10
0.0024	347.35	359.21	374.89	381.05	398.66	409.21	411.55	419.61	422.73	433.10
0.0026	349.87	361.88	377.76	382.75	400.42	410.46	412.99	420.43	423.67	433.95
0.0028	351.70	363.84	381.20	385.85	401.82	411.87	413.89	421.14	424.80	435.34
0.0030	354.51	366.45	383.88	388.53	404.76	413.09	414.68	422.05	425.48	435.93

Table 7: Limiting apparent molar volume ($\Phi^0 V$) and experimental limiting slope (Sv) for alkaline earth metal laurates at different temperatures (30-50^{0}C)

Surfactant	$\Phi^0 V$					S_v				
	30^{0}C	35^{0}C	40^{0}C	45^{0}C	50^{0}C	30^{0}C	350C	40^{0}C	45^{0}C	50^{0}C
Mg Laurate	280.50	283.75	292.50	302.00	312.00	296.61	338.98	381.35	550.85	593.22
Ca Laurate	253.75	267.00	281.00	296.00	311.50	338.98	592.35	635.59	740.20	847.00
Sr Laurate	314.00	322.00	335.75	352.50	375.00	254.00	334.50	447.45	570.57	677.97
Ba Laurate	388.50	394.00	401.00	409.25	420.00	211.86	254.25	381.35	423.73	508.47

Table 8 : Partial molar expansibility ($E^0 surt$) data for alkaline earth metal laurates at different temperatures (30-50^{0}C)

Surfactant	$E^0 surf$			
	35^{0}C	40^{0}C	45^{0}C	50^{0}C
Mg Laurate	0.65	1.75	1.90	2.00
Ca Laurate	2.65	2.80	3.00	3.10
Sr Laurate	1.60	2.75	3.30	4.50
Ba Laurate	1.10	1.40	1.75	2.10

higher temperatures. The plots of molar expansibilities and partial molar volume as a function of temperature confirmed that all these compounds appear to be structure breakers above 35^{0}C 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.

From the above cited results and discussion, it may be conclusively inferred that micelle aggregates are formed in these solutions of alkaline earth metal laurates. Partial molar expansibility data, E^0_{surf} have also been conveniently evaluated for these systems utilizing the temperature dependence of partial molar volume ($\Phi^0 v$).
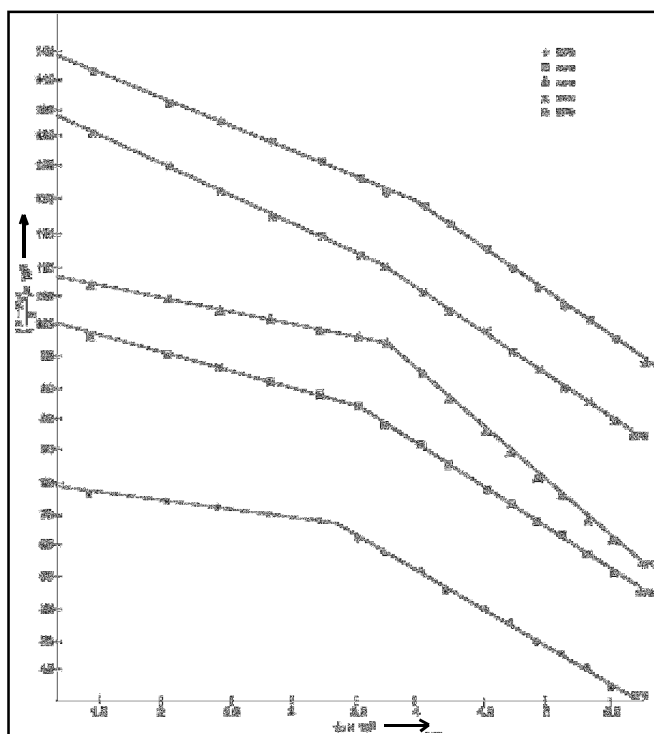
Fig. 3 : The plots of $\rho - \rho_0 /C$ vs. [concentration (c)]$^{1/2}$ of Sr laurate at different temperature (30-50^{0}C)

The fact that E^0_{surf} increase with increasing temperature (Table 8) may by attributed to a decrease in electrostriction as well as loosening of water structure at higher temperatures.

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