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Transport Properties of Calcium Soaps in Binary Mixture

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Abstract: The density and viscosity study of calcium soap (Laurate, Myristate and Stearate) in 70% Chloroform and 30% Propylene glycol mixture have been evaluated from Einstein, Vand and JONES-DOLE equation The density (ρ) of the solutions of calcium soaps (laurate, myristate, and stearate) in a mixture of 70% chloroform and 30% propylene glycol (v/v) increases first slowly and then rapidly with increasing soap concentration . The values of CMC and molar volume of calcium soaps calculated from the above equations are in close aggregation. The viscosity, (η) and specific viscosity, η_{sp} of the dilute solutions of calcium soaps (laurate, myristate, and stearate) in a mixture of 70% chloroform and 30% propylene glycol (v/v) increases with increasing soap concentration. The critical micelle concentration (CMC) of Calcium soaps in Binary Mixture show that the CMC is independent of the dielectric constant of the solvent.

Keywords: Calcium (II), density, viscosity, Molar volume Einstein, Vand and JONES-DOLE

I. Introduction

Calcium soaps are generally insoluble in water but pass high solubility in polar and non-polar organic solvents due to this reason calcium carboxylate are materials that serve a wide range of applications in Industries as lubricants, plastics, paints, crayons, Textiles cosmetics, medicines, and paper industries. The thermal spectroscopic studies, nature, and structure of calcium soaps are of great importance for their uses in industries and for explaining their characterization under different stages. Many metallic soaps have been prepared by direct metathesis methods and their physicochemical properties, IR, and X-ray were also studied by different workers (1-15). Ultrasonic study of molecular interaction and compressibility behavior of magnesium soaps has been done by M.K. Rawat (14). Therefore, a detailed study of calcium soaps is required for great importance in industrial and academic fields. I want to report here the density and viscosity of calcium soaps solution in 70%chloroform and 30% propylene glycol mixture to examine their micellar behavior and to check the legality of various equations.

II. Experimental

Preparation of Soaps:

The chemical used for the present research were of AR/GR grade. Calcium soap (Laurate, Myristate, and Stearate) have been prepared by direct metathesis of corresponding potassium soaps with a slight excess of solutions of Calcium nitrate at 50-55oC under vigorous stirring. The precipitated soaps thus obtained were filtered and washed several times with hot distilled water and acetone to remove the excess recrystallization and stored over calcium chloride. The viscosity and density of the solutions of calcium soaps in a mixture of 70% chloroform and 30% propylene glycol were measured by Ostwald, s Viscometer, and Pyknometer at 40 ± 0.05oC.

III. Results and Discussion

Density

The density(ρ) of the solutions of calcium soaps (laurate, myristate, and stearate) in a mixture of 70% chloroform and 30% propylene glycol (v/v) increases first slowly and then rapidly with increasing soap concentration (Tab.-1). The plots of density ρVs soap concentration, C (Fig..) are characterized by an intersection of two straight lines at definite soap concentration which corresponds to the CMC of the soap (Tab.-2) at which there is a sudden change in the aggregation of the soap molecules. The CMC values decrease with an increasing chain length of the soap molecule and the atomic number of the metal ion. The plots of density,ρ Vs soap concentration, C below the CMC are extrapolated to zero soap concentration and the extrapolated values of density, ρ_0 is in harmony with the experimental value of the density of pure solvent mixture The density results have been explained in terms of Root's equation,

$$\rho = \rho_0 + AC - BC^{1/2} \quad (1)$$

Where ρ and $\rho_0$are the densities of the solution and solvent, respectively and C is the soap concentration (mol l-1). The constants A and B represent the solute-solvent and solute-solute interaction, respectively

The plots of $(\rho - \rho_0)$/C Vs $C^{1/2}$ Vs C1/2 (Fig.1) indicate a break at a definite soap concentration, which corresponds to the CMC of the soap. The intercept and slope of $(\rho - \rho_0)$/C Vs $C^{1/2}$ below the CMC represent the values of constants A and B. The values of these constants A and B are recorded in (Tab.-2). The value of constant A is higher than the constant B, which shows that the solute-solvent interaction is larger than the solute-solute interaction in soap solutions. Thus, it is now quite clear that the soap molecules don't show appreciable aggregation below CMC and at the definite soap concentration i.e. at CMC, there occurs a marked increase in the aggregation of the soap molecules.

Viscosity

The viscosity, (η) and specific viscosity, ηsp of the dilute solutions of calcium soaps (laurate, myristate, and stearate) in a mixture of 70% chloroform and 30% propylene glycol (v/v) increases with increasing soap concentration the atomic number of metal ion and chain length of the fatty acid constituent of soap.

The plots of viscosity, η Vs soap concentration, C and specific viscosity, η sp Vs soap concentration, and C are distinguished by an intersection of two straight lines at a concentration, which corresponds to the CMC of the soap. This indicates a marked change in the aggregation of the soap molecules at CMC. The CMC values have close similarity with the values obtained from density and other measurements. The viscosity results have been explained by using the following equations proposed by Einstein (15), Vand(16), and Jones-Dole(17).

Einstein : $$\eta_{sp} = 2.5\ \bar{V} C \quad (2)$$

Vand: $$\frac{1}{C} = \left(\frac{0.921}{\bar{V}}\right)^{-1}\left[\frac{1}{\log \frac{\eta}{\eta_0}}\right] + \varphi\bar{V} \quad (3)$$

Jones-Dole: $$\frac{\eta_{sp}}{\sqrt{C}} = A + B\sqrt{C} \quad (4)$$

Where, ,η , η_{sp}, η_0 ,ϕ, $\bar{V}$ and C are viscosity, specific viscosity, the viscosity of solvent mixture interaction co-efficient, molar volume (l mol-1), and the soap concentration (mol l-1), respectively.

The plots of η_{sp} Vs Care linear below the CMC with intercepts almost equal to zero, which shows that the Einstein's equation applies to these soap solutions.

The values of molar volume ($\bar{V}$) of the calcium soaps obtained from the slops of the plots of Vand equation [1/C Vs 1/log(η / η_0)] are in close agreement with the values obtained from Einstein's equation. The values of the constants A and B of the Jones-Dole equation calculated from the intercept and slope of the linear plots of η_{sp} /$\sqrt{C}$ Vs $\sqrt{C}$below the CMC are recorded in (Tab.-3). The values of B (solute-solvent interaction), are larger than those of A (solute-solute interaction), which confirms that the molecules of calcium soaps in solutions do not show appreciable aggregation below CMC and there is a sudden change in the aggregation above the CMC.

It is, therefore, concluded that the equations of Einstein, Vand, and Jones-Dole are applicable to dilute solutions of calcium soaps in 70% chloroform and 30% propylene glycol (v/v) mixture. The values of CMC and molar volume of calcium soaps calculate from these equations are in close agreement, indicating that these equations satisfy the conditions.

IV. Conclusion

The soap molecules don't show appreciable aggregation below CMC and at the definite soap concentration i.e. at CMC, there occurs a marked increase in the aggregation of the soap molecules. The plots of viscosity, η Vs soap concentration, C and specific viscosity, η sp Vs soap concentration, and C are distinguished by an intersection of two straight lines at a concentration, which corresponds to the CMC of the soap.

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I. Table: Density and viscosity of Calcium Soaps in a mixture of 70% chloroform and 30% Propylene glycol of 40 ± 0.05°C

S. No.	Concentration C x 10^3(mol l^{-1})	Calcium Laurate					Calcium Myristate					Calcium stearate				
		Density ρ (g ml^{-1})	$\rho-\rho_o/C$	Specific viscosity η_{sp}x10^2	$\frac{\eta_{sp}}{\sqrt{C}}$	1/log (η/η_o)	Density ρ (g ml^{-1})	$\rho-\rho_o/C$	Specific viscosity η_{sp}x10^2	$\frac{\eta_{sp}}{\sqrt{C}}$	1/log (η/η_o)	Density ρ (g ml^{-1})	$\rho-\rho_o/C$	Specific viscosity η_{sp}x10^2	$\frac{\eta_{sp}}{\sqrt{C}}$	1/log (η/η_o)
1	4	1.067	0.525	2.940	0.465	47.840	1.068	1.000	4.591	0.726	36.070	1.070	1.125	6.790	1.074	35.040
2	6	1.068	0.633	5.210	0.673	28.990	1.070	1.083	7.733	0.998	30.910	1.072	1.250	10.090	1.303	23.940
3	8	1.070	0.725	7.900	0.883	24.390	1.072	1.125	10.093	1.128	23.950	1.074	1.313	13.370	1.495	18.360
4	10	1.072	0.780	11.210	1.121	18.490	1.074	1.150	13.406	1.341	18.300	1.076	1.350	16.550	1.655	16.210
5	12	1.074	0.817	14.630	1.336	16.420	1.076	1.125	16.772	1.531	14.850	1.078	1.292	19.560	1.786	13.530
6	16	1.075	0.675	17.780	1.406	12.780	1.077	0.875	20.022	1.583	12.610	1.080	1.063	22.810	1.803	11.380
7	20	1.076	0.590	20.980	1.484	11.130	1.078	0.750	23.788	1.682	10.400	1.080	0.850	26.590	1.880	9.770
8	24	1.077	0.533	24.180	1.561	9.900	1.079	0.667	27.003	1.743	9.320	1.081	0.750	30.220	1.951	8.810
9	28	1.077	0.457	27.340	1.634	8.940	1.080	0.607	30.223	1.806	8.480	1.082	0.679	33.690	2.013	7.730
10	32	1.078	0.431	30.530	1.707	8.180	1.080	0.531	33.395	1.867	7.790	1.083	0.625	36.440	2.037	6.920
11	36	1.078	0.383	33.190	1.749	7.830	1.081	0.500	36.626	1.930	7.200	1.084	0.583	40.790	2.150	6.470

II. Table: Values of CMC and constant A and B of density measurements.

S. No.	Name of the metal Soap	CMC	A	B
1.	Calcium Laurate	0.0137	0.82	-8.18
2.	Calcium Myristate	0.0125	1.14	-8.42
3.	Calcium Stearate	0.0123	1.62	-8.57

III. Table: Values of molar volume $\overline{V}$ (1 mol^{-1}) from Einstein's, Vand equation an Jones-Dole constant A & B of Calcium Soaps.

S. No.	Name of the Soap	Einstein's equation	Vands equation	A	B	
					Above CMC	Below CMC
1.	Laurate	5.71	4.60	0.46	14.00	0.26
2.	Myristate	6.00	5.39	0.45	16.00	5.26
3.	Stearate	5.00	6.90	0.75	0.07	5.21

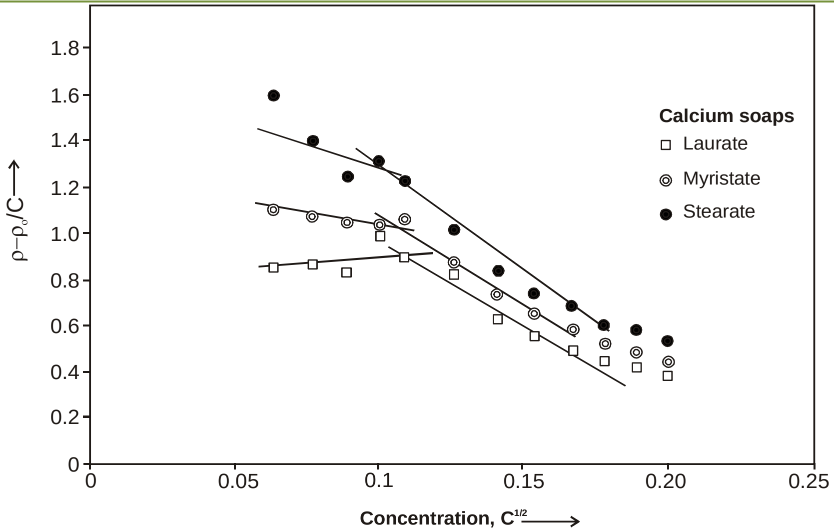

Fig.1: The plots of ρ−ρo/C Vs C1/2

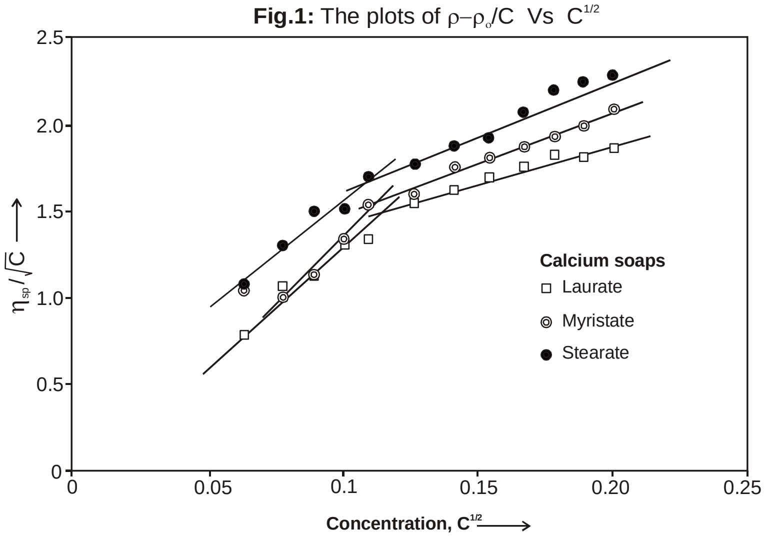

Fig. 2: JONES-DOLE'S TYPE PLOTS

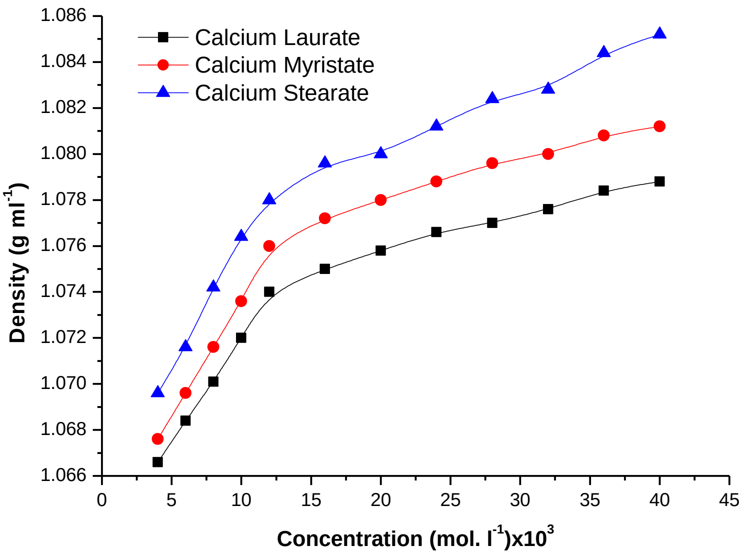

Fig 1.

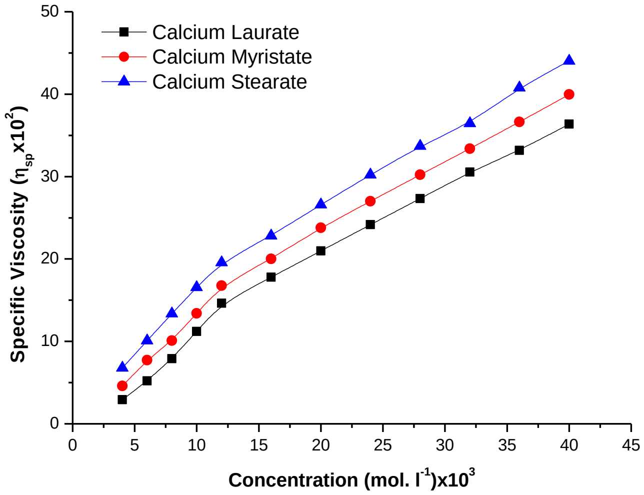

Fig 2.

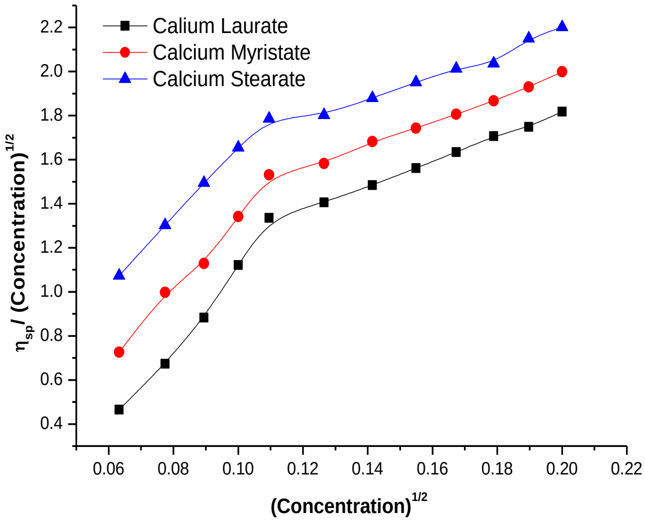

Fig 3.

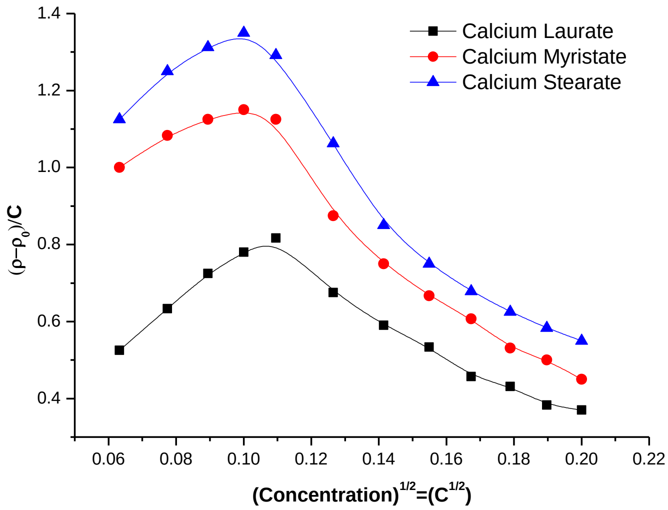

Fig 4.