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ORIGINAL ARTICLE

Study of Structure of Rubidium Soaps in Solid and Liquid State

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ABSTRACT

The structure of Rubidium soaps (caprate, caprylate and laurate) in solid and liquid state were investigated by X- ray analysis and with the measurement of density and surface tension in alcohols (butanol, octanol) and in aqueous solvents. The calculated values of the inter planar spacing, long spacing are characteristic of each soap and increases as the length of carbon chain in soap increases. The X-ray diffraction results confirm that these soaps have double- layer structure with molecular axes slightly inclined to the basal planes. The data of density and surface tension were to determine critical micelli concentration. The critical micelle concentration have also been determined from inflection of γ vs log C. Szyszkowski's equation is applicable for surface tension of rubidium soaps in alcohols and in aqueous solvent. Hammic and Andrews equation can be applied for soaps solutions .The appearance of the diffraction up to ninth order of spacing is an indicative of a good crystallinity of these soaps.

Key Words: *long spacing, basal plane , surface tension, crystallinity, diffraction, alcohols*

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INTRODUCTION

As a typical amphiphilic electrolyte, alkali and alkaline earth metallic soaps have widely been used in industry as catalyst, dryers, polymer stabilizer due to their interesting behavior in non aqueous environment [1,2]. Further studies in the field of material science related to biological studies namely pharmaceutical science yield important results in terms of their physicochemical properties in various media akin to biological environment [3,4]. The critical micelle concentration (CMC) of copper soaps in non aqueous solvent has been determined by Mehrotra et al [5[. Surface tension of magnesium soaps solutions of higher fatty acids in organic solvents and in multiple component system have been studied at 40^0 C [6,7]. Several researchers have investigated metallic soaps for their behavior in solution [8,9,10].

METHODS AND MATERIAL

Soaps were prepared as K.N.Mehrotra et al [11], purified by recrystallisation with pure and dried methanol and the purity of soaps was confirmed by elemental analysis and by determining their melting points.

Rubidium Caprylate	:	210.0^0C
Rubidium Caprate	:	215.0^0C
Rubidium Laurate	:	210.0^0C

The calibration of stalagomometer and pyknometer was checked with distilled aqueous solution at thermal stability of bath better than ± 0.05 ^{0} C .

The surface tension of soap solution was measured with Traubes stalagomometer and no. of drops were controlled by Harkins method. All measurements were made at constant temperature (35^0 C ± 0.05 ^{0} C) in a thermostat and were repeated many times. The results in tables are in dynes cm^{-1}. Ostwald's modification of the Sprengel pyknometer of capacity 15 ml was used for measuring the density of soaps solutions. The calibration was repeated immediately before and after each measurement of density and surface tension

MEASUREMENT

X-ray

X-ray diffraction patterns for rubidium soaps were determined with a Norelco and a Rigakudenki X-ray spectrophotometer using Cu- Kα radiation filtered by a nickel foil over the range of diffraction angle 2θ = 3^0 -40^0 where θ is the Braggs angle . The voltage applied to the tube was 30 Kv at 20 Ma, time constant 4 , scanning speed , 1^0/min., chart speed , 0.5cm/min. scale factor,16.The readings of the diffraction angle were made up to 0.010 and wave length of Cu –Kα radiation was taken as 1.54 A^0 . The diffraction patterns were determined two times for all the soaps and X-ray diffraction of stearic acid was measured as a check of the apparatus

RESULTS AND DISCUSSION

The density of soap solutions increases with the increase in soap concentration fig.1, 1a and 1b.The plots of density ,d , against the soap concentration, C (g mole L^{-1}) are characterized by an intersection at definite soap concentration (0.045 ,0.043 ,0.042) for (caprylate, caprate and laurate) table. 1 which corresponds to the critical micelle concentration (CMC), independent of the nature of the solvents at which there is a sudden change in the aggregation of solute molecules. This is attributed to balance between the attractive hydrophobic interaction of the long chain hydrocarbon tails and repulsive forces between the ionic head groups. The plots of density, d, against the soap concentration, C, below CMC have been extra polated to zero soap concentration table 2 and are in close agreement with the corresponding experimental values of the density of the solvents. The surface tension of the solution of rubidium soaps in alcohol (butanol and octanol) increases with the increase in soap concentration but decreases in aqueous solution fig.2, 2a, and 2b may be due to difference in the effects of surface energy of the solvents in the interfacial region . The plots of the surface tension ,γ, against the concentration of soaps (g mole L^{-1}) are characterized by an intersection of two straight lines at a definite soaps concentration, a concentration showing sharp change in surface deficiency of the soap table.3 Critical micelle concentration, CMC is almost independent of the nature of the solvent but depends on the chain length of anion in soaps. The multi molecular aggregation formed i-e CMC may be the result of amphiphilic molecules coming together due to ion dipole interaction developing Vander Waals forces. This is in agreement with the fact that there is decrease in CMC with the increase in molecular mass [12,13]

The plots of surface tension, γ, against the soap concentration, C, have been extra polated to zero soap concentration and are summarized in table 4. The extra polated values $\gamma_{0,}$ for soap solution are in agreement with the surface tension of pure alcohol and water.

The plots of γ vs log C are linear at 35^0 C for all the soaps showing that the results are in good agreement with the Szyszkoswki's empirical equation for solutions of fatty acid fig.3,3a and3b.

The variation of the surface tension ,γ , of soaps solutions against log C are characterized by an intersection of two straight lines at point corresponding to the CMC of soaps as in table. 5, (fig.3,3a and3b) and are in agreement with the Szyskowski's empirical equation $\gamma / \gamma_0 = 1- X \text{ Ln } C/Y$ ---(1) where γ and γ_0 are the surface tension of solution and that of solvent , the equation can be written as $\gamma = \gamma_0 (1 + X \ln Y) – X \gamma_0 \ln C$ ---(2)

The values of X, Y and A of Szyskowski's have been calculated from the plots of γ vs log C below and above the CMC and are recorded in table, 6& 7.

The values of X calculated from the slopes, - 2.303 X γ_0 of the lines are independent of the chain length of anion in soap (caprylate , caprate and laurate) but decreases with the increase in the chain length of alcohol.

It may be pointed out that the value of Y and X logY obtained from the intercepts of the lines of the plots of γ vs log C are neither independent of the chain length of soap nor of solvent. The values decrease rapidly from caprylate to laurate and from butanol to octanol with increase in the chain length of the soap and alcohol.

The intensities of the diffracted X-ray as a function of diffraction angle, 2θ , for rubidium soaps are recorded with the help of X-ray spectrophotometer and the curves are shown in fig 4 and 5.The calculated spacings together with the relative intensities with respect to most intense peak in each pattern are tabulated in tables. 10-11

A large number of fairly intense peaks for low angle region up to ninth order of the spacing, arising from the diffraction of X–ray by planes of atoms or metal ions (basal planes) in a large separation , are observed over the range of 3^0 -40^0 of the diffraction angle in the diffraction patterns of these soaps. Bragg's inter planar spacings, d , are calculated from the positions of these peaks using the relation, $n\lambda = 2d \sin \theta$, ---(3) where λ is the wave length of the radiation. The values of these calculated spacings (ie the perpendicular separation of the basal planes known as long spacing) for the soaps approximately correspond to double the length of fatty acid radical constituent of each soap molecule.

The inter planar spacings calculated for 2nd, 3rd,4th, 6th ,7th , 8th and 9th order diffraction for rubidium caprate and that of rubidium laurate for the 2nd, 3rd, 4th, 5th, 6th, 8th, and 9th, order diffraction are recorded in table.8.The average spacing is 40.2 A ^{0}. The value of the inter planar spacings are characteristic of each soap and increases as the length of hydrocarbon chain in the soap increases. The large difference in the values of the inter planar spacings for laurate and caprate indicates that the angle of the inclination of the molecular axes of the soap to the basal plane increases slightly with the decrease in the number of carbon atoms in the anion of the of the soap molecule. The appearance of the diffraction up to the ninth order of the spacings is an indicative of a good crystallinity of these soaps .

It is observed that a strong line exists between two medium lines in the diffraction patterns of these soaps and this behavior is similar to that of the fatty acids. A number of the diffraction peaks in the intermediate range of the diffraction angle 15^{0} -40^{0} are observed and are attributed to the diffraction of X–ray by planes of atoms in much smaller separation than basal planes. The calculated spacings from these peaks correspond to the short or side spacings i-e the lateral distances between one molecule and the next in a layer. It may be pointed out that the long spacing peaks are fairly intense while the side spacing peaks are relatively weak Hattiangdi and Vold proposed a single structure for disoaps and double layer structure for monosoaps whereas the double layer structure for fatty acids through hydrogen bonding is well established [14] . The values of the long spacing for rubidium soaps are in agreement with the structure proposed for the soaps crystals. Kambe suggested that the crystals of fatty acid and their derivatives belong to monoclinic system [15]. The diffraction patterns of rubidium soaps are analysed on the assumption that their crystals belong to monoclinic system and the following results for lattice spacings and constants are obtained and recorded in table 9.

Table -1. value of CMC (g mole L^{-1}) ,the plot of density,d, and concentration

Solvent	Name of soaps		
	Caprylate	Caprate	Laurate
Water	---	0.043	0.042
Butanol	0.045	0.042	0.042
Octanol	0.045	0.043	0.042

Table -2. Extrapolated values of the density ,d , of rubidium soaps

Solvents	Density of solvent at 35^{0} C	Name of soaps		
		Caprylate	Caprate	Laurate
Water	0.9940	-	0.9932	0.9920
Butanol	0.8011	0.7999	0.8004	0.8035
Octanol	0.8045	0.8055	0.8056	0.8102

Table -3. Values of the CMC (g mole L^{-1}), from the plots of γ ,surface tension and concentration of soaps in solvents

Solvents	Name of soaps		
	Caprylate	Caprate	Laurate
Water	-	0.044	0.042
Butanol	0.044	0.042	0.042
Octanol	0.045	0.043	0.041

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Table -4. Extrapolated values of the surface tension , γ, of rubidium soaps

Solvents	Surface tension of solvent at 35^{0}C	Name of soaps		
		Caprylate	Caprate	Laurate
Water	70.37	---	69.70	69.60
Butanol	23.31	23.23	23.24	23.20
Octanol	26.10	26.20	26.20	26.10

Table -5. Values of the CMC (g mole L^{-1}) from the plot of surface tension, γ, vs log C

Solvents	Name of soaps		
	Caprylate	Caprate	Laurate
Water	-	0.043	0.042
Butanol	0.045	0.043	0.04
Octanol	0.045	0.043	0.041

Table -6. The value of χ from the plots of surface tension ,γ , vs log C below CMC

Solvents	Name of soaps		
	Caprylate	Caprate	Laurate
Water	-	0.040	0.039
Butanol	0.024	0.024	0.024
Octanol	0.010	0.010	0.009

Table- 7. Values of Υ and χ log Υ from the plots of surface tension, γ vs log C below CMC

Solvents	Name of soaps					
	Caprylate		Caprate		Laurate	
	Υ	$\chi \log \Upsilon$	Υ	$\chi \log \Upsilon$	Υ	$\chi \log \Upsilon$
Water	-	-	228.6	0.2198	233.9	0.2155
Butanol	250.3	0.1350	222.5	0.1300	120.3	0.1140
Octanol	204.3	0.0550	176.7	0.0530	82.6	0.0420

Table .8.Inter planar spacing for Rubidium soaps

Name of Rb soaps	Inter planar spacing								
	2nd	3rd	4th	5th	6th	7th	8th	9th	Average spacing
Caprate	29.8	29.7	29.2	-	30.0	30.1	30.4	30.6	29.9
laurate	40.2	40.8	40.4	40.5	40.2	-	40.0	39.9	40.2

Table-9. Lattice spacing and Constants

Name of soaps	Lattice spacing		Constant	
	d_{110}	d_{200}	a	b
Caprate	3.48 A^0	3.24 A^0	6.48 A^0	4.12 A^0
Laurate	3.64 A^0	3.37 A^0	6.74 A^0	4.32 A^0

Table-10. X-ray diffraction analysis of Rubidium Caprate, Average value of d, 29.9A^0

Long Spacing				Short Spacing
$\lambda/2\sin\theta$	**d**	**n**	**I/I_0**	3.48
14.9	29.8	2	1.0	3.24
9.9	29.7	3	0.53	3.06
7.3	29.2	4	.0.08	2.90
5.0	30.0	6	0.24	2.27
4.3	30.1	7	0.51	2.27
3.8	30.4	8	0.20	---
3.4	30.6	9	0.20	---

Table-11. X-ray diffraction analysis of Rubidium Laurate, Average value of d, 40.2A^0

Long Spacing				Short Spacing
$\lambda/2\sin\theta$	**d**	**n**	**I/I_0**	3.48
20.1	40.2	2	0.87	3.24
13.6	40.8	3	1.0	3.06
10.1	40.4	4	0.15	2.90
8.1	40.5	5	0.15	2.27
6.7	40.2	6	0.04	2.27
5.0	40.0	8	0.04	--
4.4	39.9	9	0.08	--

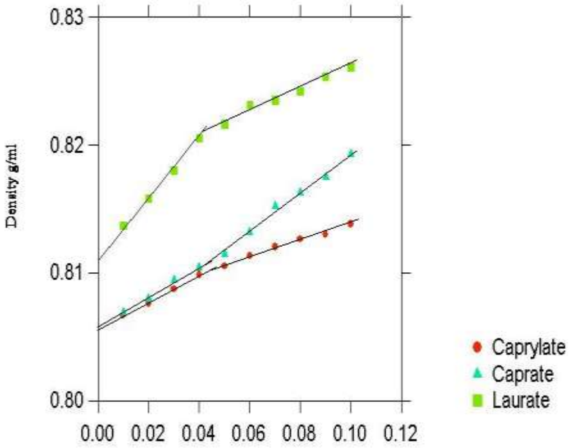

Fig-1. Concentration g mole L^{-1} Density vs Concentration in Octano

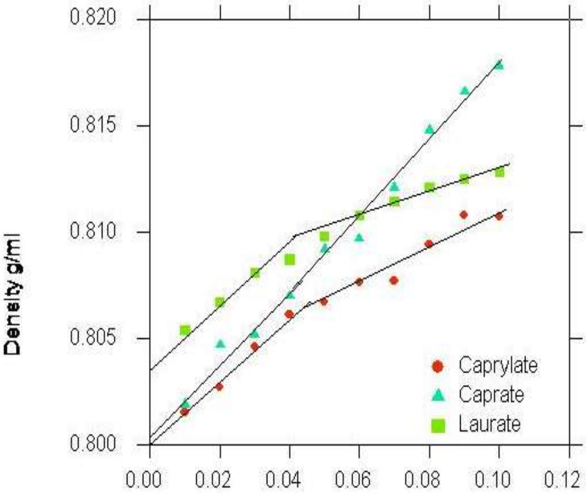

Fig-1a. Concentration g mole L^{-1} Density ^{vs} Concentration in Octanol

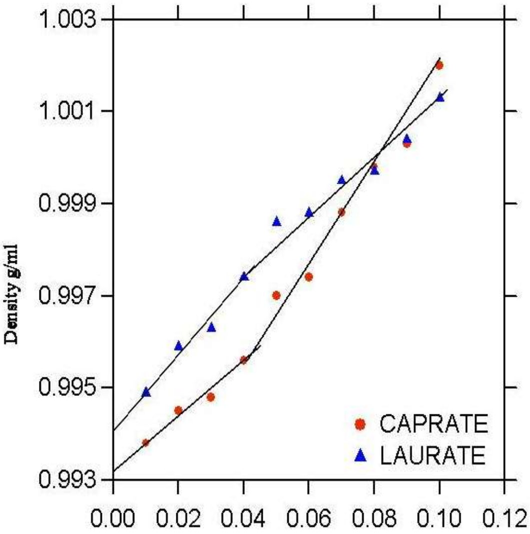

Fig-1b. Concentration g mole L^{-1} Density vs Concentration in Water

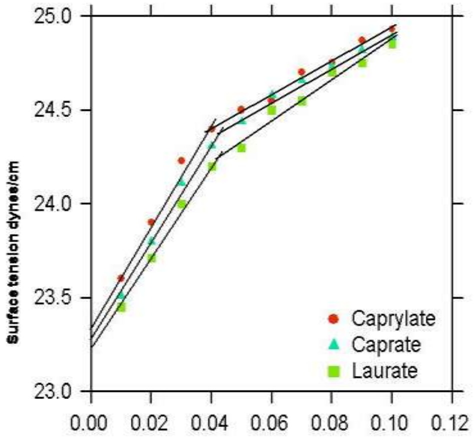

Fig.-2. Concentration g mole L^{-1} Surface tension vs Concentration in Butanol

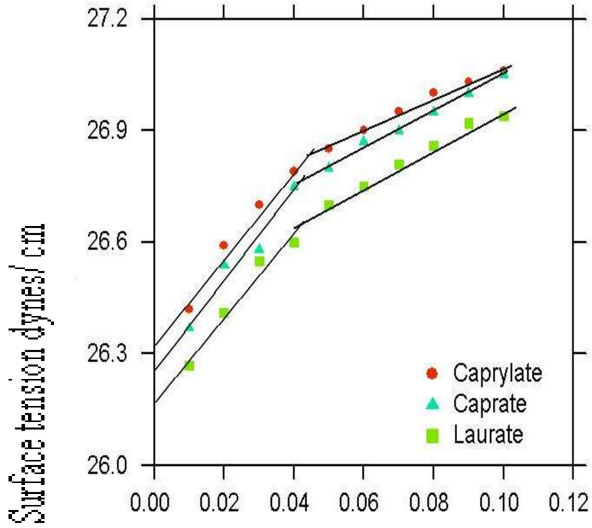

Fig.-2a. Concentration g mole L^{-1}Surface tension vs Concentration in Octanol

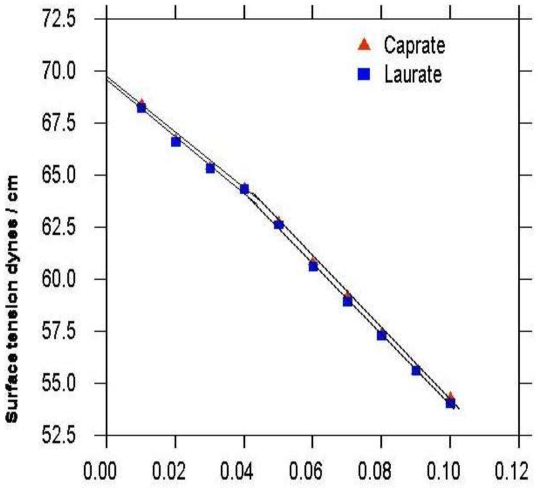

Fig.-2b. Concentration g mole L^{-1} Surface tension vs Concentration in Water

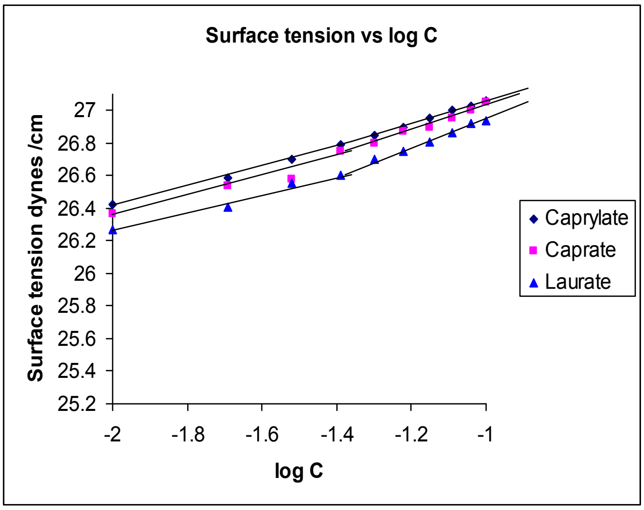

Fig.-3 Surface tension vs log C in Butanol

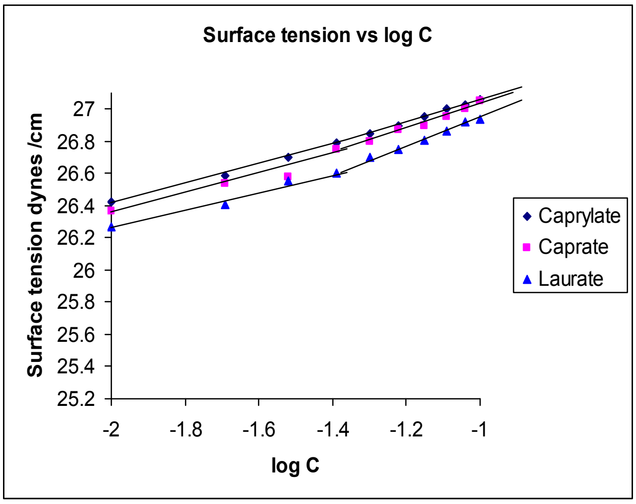

Fig.-3a Surface tension vs log C in Octanol

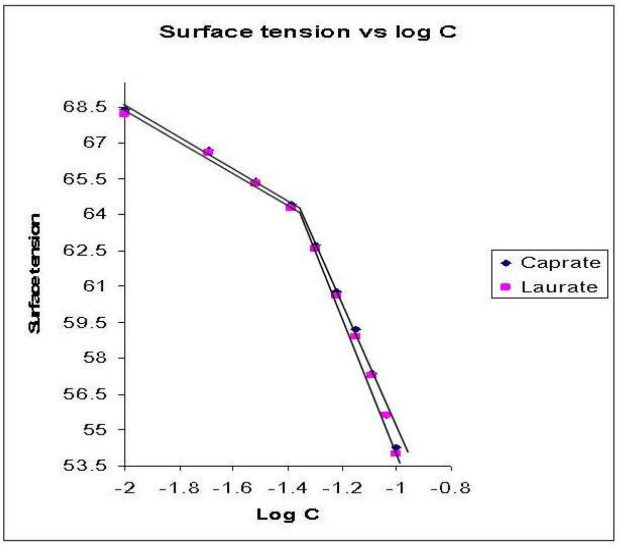

Fig.-3b Surface tension vs log C in Water

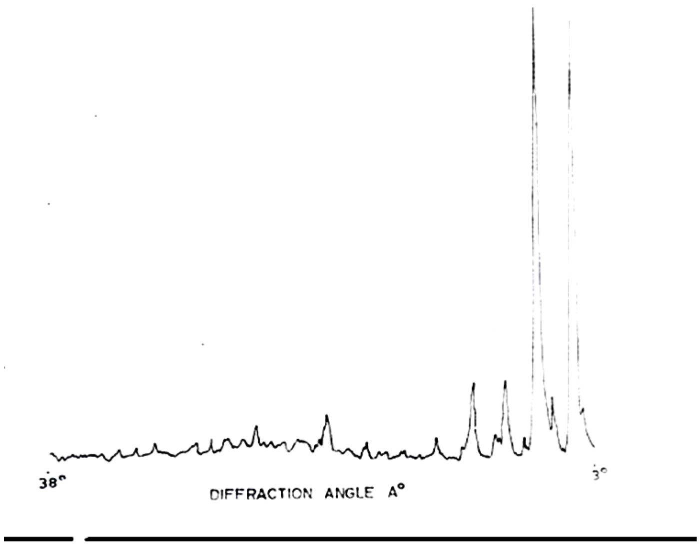

Fig.-4 **X-Ray Diffraction of Rubidium Laurate**

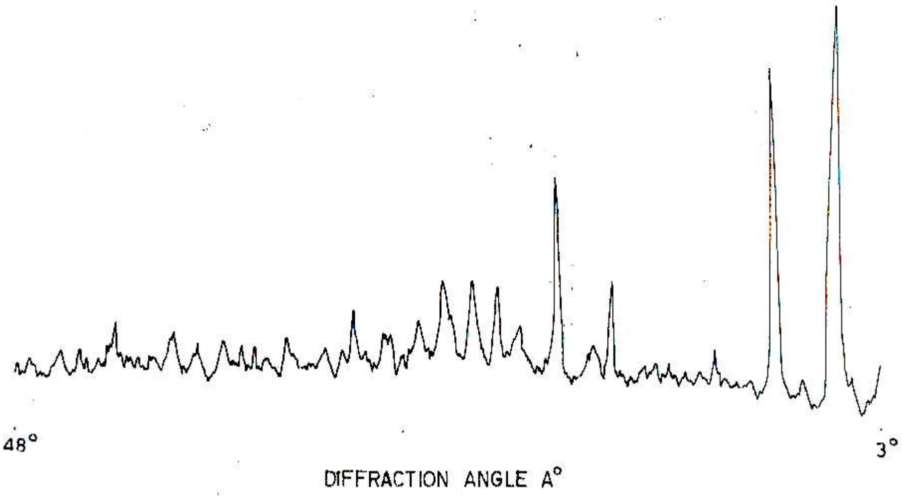

Fig.-5 , X-Ray Diffraction of Rubidium Caprate

CONCLUSION

The value of CMC obtained from density and surface tension are independent to the nature of solvent but depends on the chain length of anion.

The results confirm that there is a significant interaction between soap and solvent molecules in dilute solutions and soap molecules do not aggregate appreciably below the CMC. The longer hydrophobic group of soap ion is geometrically favorable for the micelle formation .Soap- soap and soap-solvent interaction and the effect of chain length of soap molecule on density , surface tension are observed. The surface energy at interfacial surface due to solute-solvent inter action and ion- ion inter action is changing and consequently affecting the density and surface tension All data are showing that these surfactants definitely play the role of surface activity.

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