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STUDY OF PHYSICO CHEMICAL CHARACTER OF RUBIDIUM SOAPS IN ALCOHOLIC SOLVENTS

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ABSTRACT

The present study is made to investigate the micellar behavior of solutions of rubidium caprylate, caprate and laurate in alcohols (methanol, butanol and pentanol) through the study of density, surface tension and parachore measurements and critical micelle concentration were evaluated from the results. It is revealed that the surface tension of the solution of rubidium soaps increases with the increase in soap concentration. The results of surface tension have been explained on the bases of szyszkowski's empirical equation $\gamma = \gamma_0 (1+ X \ln Y) – X \gamma_0 \ln C$ and the value of X, Y and (-X ln Y) were determined. It is also observed that the parachore of soaps solution increases with the mole fraction of the soap. Critical micelle concentration, CMC. is almost independent of the nature of the solvent and behavior of soaps in alcoholic solution is studied successfully on Hammic and Andrew's mixture equation.

KEYWORDS: surface tension, CMC, inflection, alcohols, parachor, micelle, mole fraction.

1. INTRODUCTION

Metallic soaps are materials of considerable surface activity characterized with both polar and non polar region in molecule, amphiphilic electrolyte becoming indispensable in industry as metal carrier in the form of soluble in organic liquids. The fact has fascinated research workers to determine the physico- chemical properties of metallic soaps to study the critical micelle concentration.[1-7] It is revealed that critical micelle has remarkable character in the vicinity of which dramatic change in the properties such as conductance, surface tension, viscosity and ionic mobility takes place. Thus the nature and structure of metal soaps makes them to play vital role for their important application in various fields such as medicine, catalyst, dryers, fungicide, wettner and polymer stabilizer. Investigation of micelle to find the solubility of mixed sodium soaps in aqueous solution was carried out by measuring surface tension.[8] Number of researchers studied transitional metal soaps.[9],[10],[11],[12],[13] and[14] and reported different finding to reveal the behavioral change in nature of soaps in aqueous and non aqueous solutions. The method and condition of preparation of metallic soaps[15], have been extensively studied to understand the effect on the physico- chemical characteristics and structure of these soaps.

Transition of micelle in aqueous alcoholic solution of alkaline earth metal soaps[16], is reported. Metallic soaps[17], form two types of micelle, hydrophilic oleomicelles and lipophilic hydromicelles under different conditions. The specific and equivalent conductivity of sodium and potassium soaps in alcohol, toluene and pyridine were determined by researchers.[18]

The nature and structure of micelle of metallic soaps in alcohol were investigated.[19] Further studies in the field of material science related to biological studies namely pharmaceutical science yield important results in terms of their physico- chemical properties in various media akin to biological environment[20] and[21]. In this paper, the density, surface tension and parachor of rubidium soaps in alcoholic solvents are investigated to determine CMC and other physical characters.

2. MATERIAL AND METHOD

Experiment

2.1 Soaps were prepared[22] and purified by recrystallisation with pure and dried benzene and the purity of soaps was confirmed by elemental analysis and by determining their melting points.

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

2.2 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± 0.05 ^{0} C) in a thermostat. 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.

3. DISCUSSION OF RESULTS

3.1 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 and 0.042) for (caprylate, caprate and laurate), which corresponds to the critical micelle concentration (CMC.), table- 1.concentration at which the soaps anion agglomerate and starts behaving as colloidal solution.

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

Solvents	Name of soaps		
	Caprylate	**Caprate**	**Laurate**
Methanol	0.045	0.043	0.042
Butanol	0.045	0.043	0.042
Pentanol	0.045	0.043	0.042

It is observed that the values of the CMC are independent of the nature of the solvents.

3.2 The surface tension of the solution of rubidium soaps in alcohol (methanol, butanol and pentanol) increases with the increase in soap concentration may be due to difference in the effects of surface energy of the solvents in the interfacial region. The variation 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, Critical micelle concentration, CMC. is almost independent of the nature of the solvent but depends on the chain length of anion in soaps table-2. The multi molecular aggregation formed ie 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.[23]

Table-2.value of CMC (g mole L^{-1}) from the plots of surface tension, γ vs concentration.

Solvents	Name of soaps		
	Caprylate	Caprate	Laurate
Methanol	0.045	0.043	0.042
Butanol	0.040	0.043	0.042
Pentanol	0.040	0.043	0.042

The plots of surface tension, γ, against the soap concentration, C, have been extrapolated to zero soap concentration and are in agreement with the surface tension of pure alcohol table-2a.

Table- 2a. Extrapolated values of the surface tension, γ_0, of rubidium soaps.

Solvents	Name of soaps			
	Surface tension of solvents at 35^0 C	Caprylate	Caprate	Laurate
Methanol	21.29	21.26	21.30	21.20
Butanol	23.31	23.23	23.24	23.20
Pentanol	23.88	24.15	24.09	24.05

3.2 The variation of the surface tension γ, of soaps solutions against log C, Fig. 1, 1a, & 1b are characterized by an intersection of two straight lines at point corresponding to the CMC. of soaps recorded in table-3 and are in agreement with the Szyskowski's empirical equation for solutions of fatty acid as surface tension γ against log C varies lineally at 35^0C.

Table- 3. values of the CMC (g mole L^{-1}) from the plots of γ vs log C.

Solvents	Name of the soap		
	Caprylate	Caprate	Laurate
Methanol	0.045	0.043	0.042
Butanol	0.045	0.043	0.042
Pentanol	0.045	0.043	0.041

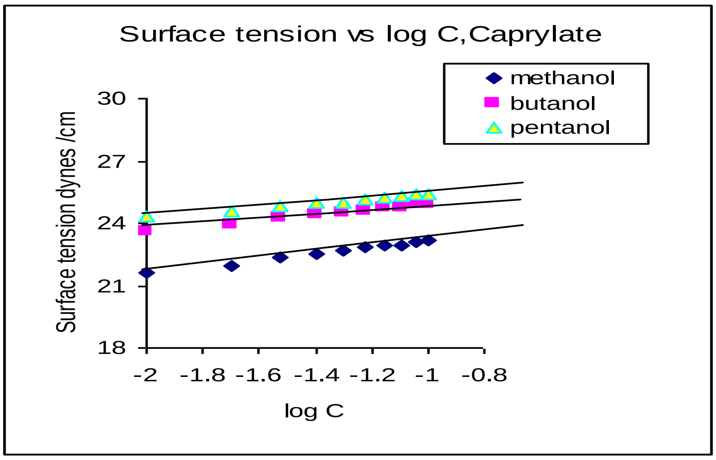


Fig-1 Surface tension vs log C.

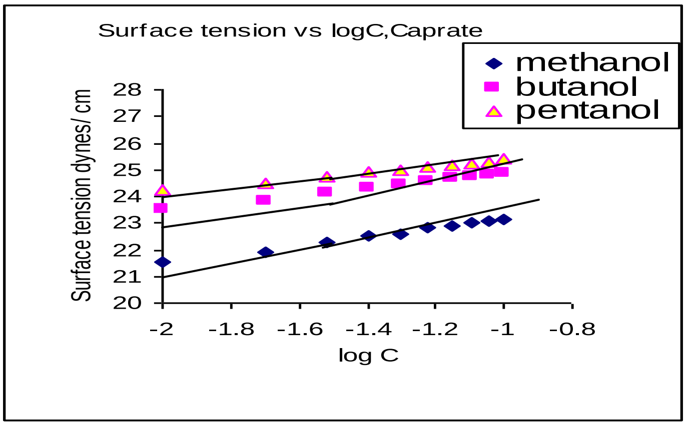


Fig-1a Surface tension vs log C.

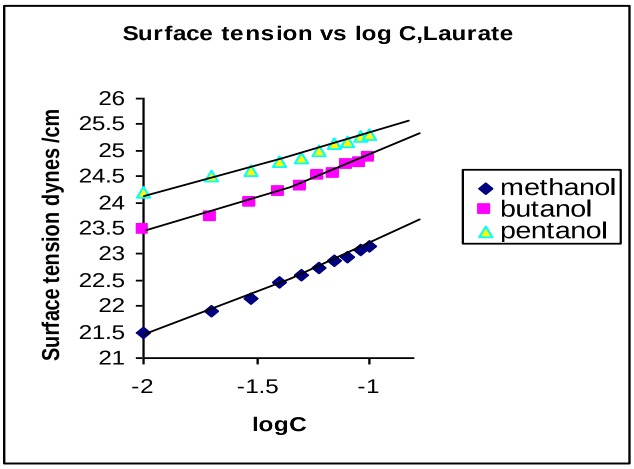


Fig-1b Surface tension vs log C.

3.3. Szyskowski's empirical equation is γ / γ_0 = 1- X 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).

Diferenciate the equation ------------------- (2)

$d\gamma / d\log C = -X \gamma$

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, 4, 5 and 6.

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 methanol to pentanol.

Table-4.value of X from the plots of, γ, vs log C below CMC.

Solvents	Name of soaps		
	Caprylate	Caprate	Laurate
Methanol	0.032	0.031.	0.032
Butanol	0.024	0.024	0.024
Pentanol	0.019	0.019	0.018

Table-5.values of Y and X log Y from the plots of, γ vs log C below CMC.

Solvents	Name of soaps					
	Caprylate		Caprate		Laurate	
	Y	X log Y	Y	X log Y	Y	X log Y
Methanol	267.8	0.1780	233.2	0.1690	124.0	0.1530
Butanol	250.3	0.1350	222.5	0.1300	120.3	0.1140
Pentanol	219.9	0.1020	215.4	0.1010	113.2	0.0840

Table-6, Value of $A10^{-10}$ cm^2 from the plots of γ vs log C below CMC.

Solvents	Name of soaps		
	Caprylate	Caprate	Laurate
Methanol	3.75	3.86	3.75
Butanol	4.46	4.56	4.60
Pentanol	5.62	5.70	5.98

3.4 The parachor, P, of the solution is written as:

$$P = \frac{M\,\gamma^{1/4}}{D} = V\,\gamma^{1/4} \quad \text{———}(3)$$

Where M, D, V and γ are respectively the molecular weight, density, molar volume and surface tension of the solution.

According to Hammic and Andrew's[24] mixture law equation, the parachor of the solution can be written as:

$$P = X.P_{soap} + (1-X)\,P_{solvent} \quad \text{———}(4)$$

Where P, P_{soap} and $P_{solvent}$ refer to the parachors of the solution, soap and solvent respectively and X is mole fraction of the soap in the solution.

The values of the parachor, P, have been plotted against the mole fraction, X, of the soap to test the validity of the equation, intersection of two straight lines occurs at a point corresponding to the CMC. of the soap as shown in fig. 3, 3a & 3 b, 4, 4a, 4b and 5, 5a, 5b. The parachor of the soap solutions increases with the increase of the mole fraction of the soap as evident from tables 7, 8, 9. It may be pointed out that the parachor are independent of the chain length of soap but depends on the nature of solvent.

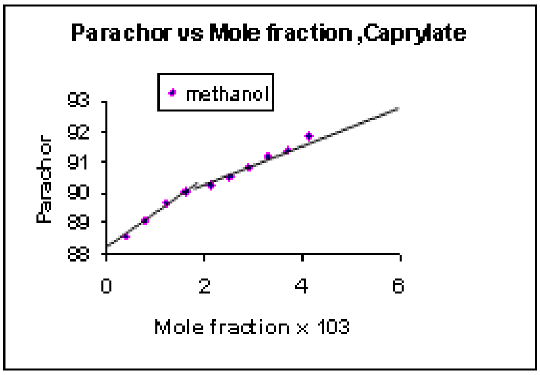


Fig-3 Parachore vs Mole fraction

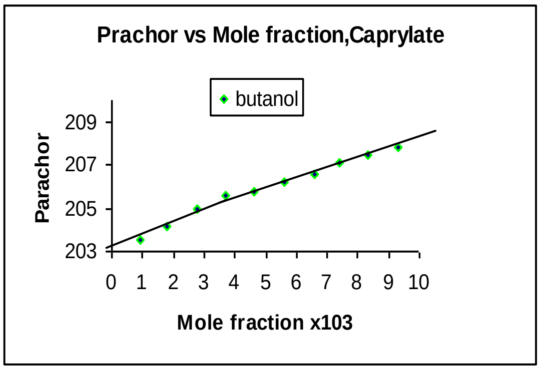


Fig-3a Parachore vs Mole fraction.

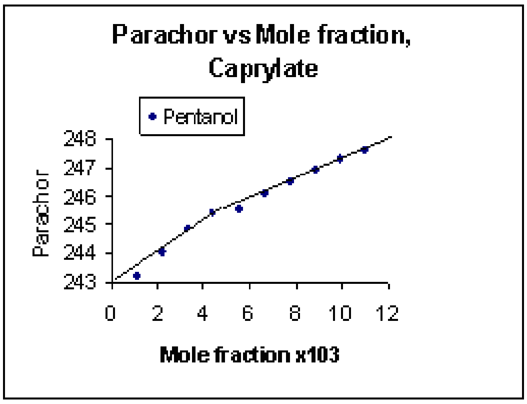


Fig-3b Parachore vs Mole fraction.

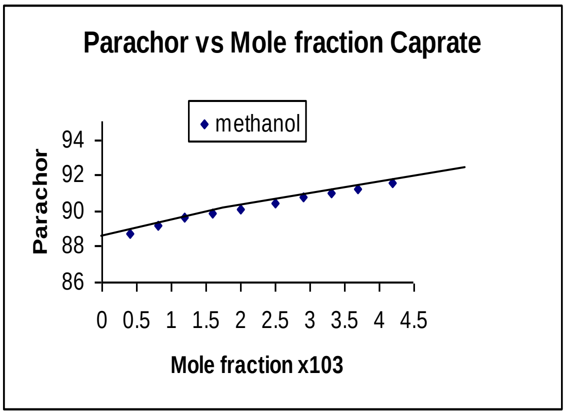


Fig-4 Parachore vs Mole fraction.

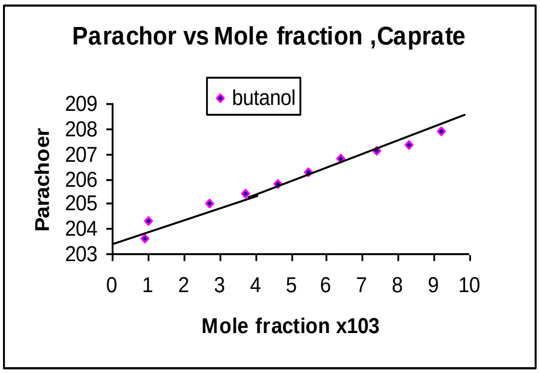


Fig-4 a Parachore vs Mole fraction.

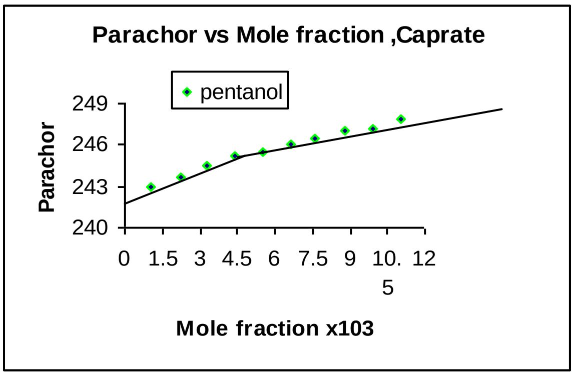
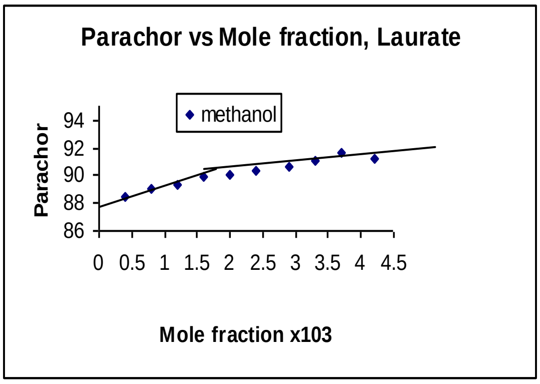


Fig-4 b Parachore vs Mole fraction.



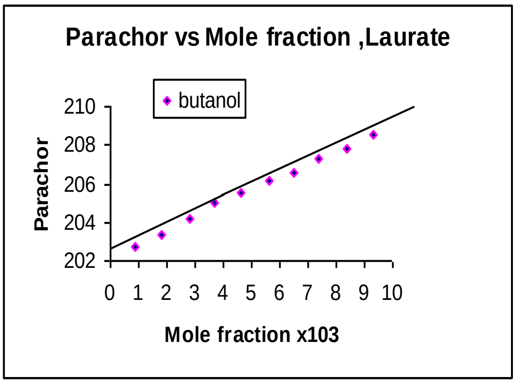


Fig-5 Parachore vs Mole fraction. **Fig-5a Parachore vs Mole fraction.**

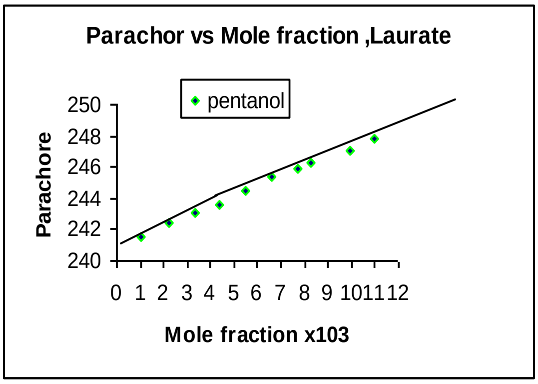


Fig-5b Parachore vs Mole fraction.

Table-7, values of P, Parachore for solution of caprate in solvent.

Concentration of soap in g mole L^{-1}	Methanol		Butanol		Pentanol	
	Mole fraction of soapx10^3	Parachor, P= $V\gamma^{1/4}$	Mole fraction of soapx10^3	Parachor, P= $V\gamma^{1/4}$	Mole fraction of soapx10^3	Parachor, P= $V\gamma^{1/4}$
0.01	0.4	88.55	0.9	203.50	1.1	243.3
0.02	0.8	89.06	1.8	204.20	2.2	244.1
0.03	1.2	89.69	2.8	205.0	3.3	244.9
0.04	1.6	90.07	3.7	205.57	4.4	245.4
0.05	2.1	90.24	4.6	205.80	5.5	245.6
0.06	2.5	90.53	5.6	206.20	6.6	246.1
0.07	2.9	90.80	6.5	206.61	7.7	246.5
0.08	3.3	91.20	7.4	207.10	8.8	246.9
0.09	3.7	91.40	8.3	207.53	9.9	247.3
0.1	4.1	91.85	9.3	207.87	11.0	247.6

Table-8, values of P, Parachor for solutionof caprate in solvent.

Concentration of soap in g $moleL^{-1}$	Methanol		Butanol		Pentanol	
	Mole fraction of soapx10^3	Parachor, P= $V\gamma^{1/4}$	Mole fraction of soapx10^3	Parachor, P= $V\gamma^{1/4}$	Mole fraction of soap x10^3	Parachor, P= $V\gamma^{1/4}$
0.01	0.4	88.7	0.9	203.6	1.0	243.0
0.02	0.8	89.2	1.0	204.3	2.2	243.7
0.03	1.2	89.6	2.7	205.0	3.3	244.5
0.04	1.6	89.9	3.7	205.4	4.4	245.18
0.05	2.0	90.1	4.6	205.80	5.5	245.5
0.06	2.5	90.4	5.5	206.30	6.6	246.0
0.07	2.9	90.8	6.4	206.8	7.7	246.45
0.08	3.3	91.0	7.4	207.10	8.8	247.0
0.09	3.7	91.2	8.3	207.35	9.9	247.20
0.1	4.2	91.6	9.2	207.9	11.0	247.9

Table-9 values of P, Parachor for solution of Laurate in solvent.

Concentration of soap in g $moleL^{-1}$	Methanol		Butanol		Pentanol	
	Mole fraction of soapx10^3	Parachor, P= $V\gamma^{1/4}$	Mole fraction of soapx10^3	Parachor, P= $V\gamma^{1/4}$	Mole fraction of soapx10^3	Parachor, P= $V\gamma^{1/4}$
0.01	0.4	88.5	0.9	202.7	1.0	241.5
0.02	0.8	89.0	1.8	203.40	2.2	242.4
0.03	1.2	89.4	2.8	204.20	3.3	243.1
0.04	1.6	89.85	3.7	205.0	4.4	243.60
0.05	2.0	90.0	4.6	205.50	5.5	244.50
0.06	2.4	90.3	5.6	206.20	6.6	245.40
0.07	2.9	90.7	6.5	206.60	7.7	245.90
0.08	3.3	91.02	7.4	207.30	8.3	246.30
0.09	3.7	91.2	8.4	207.80	9.9	247.09
0.1	4.2	91.7	9.3	208.5	11.0	247.76

4. CONCLUSION

The soaps form micellar aggregates and the CMC determined is found to be independent of the nature of solvent but depends on the chain length of anion. Soap- soap and soap-solvent interaction and the effect of chain length of soap molecule on density and surface tension are observed. The surface energy at interfacial surface due to solute-solvent inter action and ion-ion inter action is changing.

The longer hydrophobic group of soap ion is geometrically favorable for the micelle formation. Szyszkowski's empirical equation $\gamma = \gamma_0 (1+ X \ln Y) - X \gamma_0 \ln C$ is able to explain the behavior of rubidium soaps in alcoholic solution All data are showing that these surfactants definitely play the role of surface activity and are useful colloids which will be of utmost importance in industry and other fields. These parameters show a change at cmc suggesting the micellar behavior of soap.

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