

## Spectroscopic & Conductometric Studies of Surfactant (Metal Soaps)

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### Abstract

Infrared spectral studies of praseodymium soaps (hexanoate and decanoate) reveal that fatty acids exist with a dimeric type structure through hydrogen bonding between two molecules of fatty acids, whereas the metal-to-oxygen bonds in these soaps have an ionic character. The pre-micellar association and the formation of micelles in praseodymium soap solutions have been investigated by conductometric measurements in a non-aqueous medium. The molar conductance at infinite dilution, the degree of ionization and the ionization constant have been evaluated. The results show that these soaps behave as weak electrolytes in dilute solutions.

**Keywords:** Praseodymium soaps, IR, conductivity, micellization, and CMC value.

### INTRODUCTION

Salts of higher fatty acids with non-alkaline metals are water insoluble such "Metallic soaps". Surfactants are widespread in nature, industry and everyday life. They play an important role in many technological applications, such as detergents, plasticizers, lubricants, cosmetics, medicines, emulsifiers and water proofing agents. Lanthanide metal soaps have been prepared by Mehrotra et al.; (1995); Upadhyaya et al. (2010); by metathesis and the adding of an organic or inorganic salt of fatty acid and crystallization of the hydrated soaps with a dried organic solvent. Varma and Jindal (1983); C. Singh and S.K. Upadhyaya (2006); Mehrotra et al. (1987); and Shukla et al.

(2004); characterized lanthanide soaps by using the infrared and electronic absorption spectra. Topallar et.al. (1998); investigated the conductance behavior of metal soaps in different solvents. The comparative study on micellization and electrolytic behaviour of dysprosium soaps in methanol were carried out by Shukla et.al, (2009).

The present work was initiated with the view, to study the nature of bonding structure in solid state, and to determine the CMC and nature of electrolytes in benzene and methanol solution of praseodymium soaps (hexanoate and decanoate).

## **EXPERIMENTAL**

Praseodymium soaps (hexanoate and decanoate) were prepared by direct metathesis of corresponding sodium soaps with slight excess of the solution of praseodymium nitrate at 40°C under vigorous stirring the precipitated soap was filtered and washed with distilled water and acetone and recrystallized with a mixture of benzene and methanol and dried under reduced pressure.

The infrared absorption spectra of fatty acids and their corresponding praseodymium soaps were recorded with a Perkin - Elmer "577 model" grating spectrophotometer in the region of 4000-200 cm. using potassium bromide disc method. The conductivity measurements of the solutions of praseodymium soaps in a mixture of benzene - methanol (5:5% v/v) were carried out using a Toshniwal digital conductivity meter (model CL 01.10A) and a dipping type conductivity cell with platinized electrodes.

## **RESULTS AND DISCUSSION**

### **Infrared Spectra:**

The wave number of some important absorption bands in infrared absorption spectra praseodymium (hexanoate and decanoate) were assigned and compared with those of corresponding fatty acid (table-1). The absorption bands observed at 2660-2580, 1700, 1430-1390, 930-910, 690 and 550 cm<sup>-1</sup> in the spectra of fatty acid have indicated the presence of localized (COOH) group in the form of dimeric structure and the existence of intermolecular hydrogen bonding between two molecules of the acid. The evenly spaced progressive bands at 1390-1140 cm<sup>-1</sup>. The wave number of some important absorption bands in infrared absorption spectra of praseodymium (hexanoate and decanoate) also observed which are characteristic of the hydrocarbon chain and remain unchanged during the preparation of the soap. The complete disappearance of the carbonyl frequency at 1700 cm<sup>-1</sup> in the spectra praseodymium soaps indicates that there is a complete resonance between the two C=O bonds of the carboxylic groups of the soap molecule and the two bonds become identical with their force constant assuming an intermediate value between the normal double and single

bonds. The appearance of two absorption bands corresponding to symmetric and antisymmetric stretching vibrations of carboxylate ion at 1440-1436<sup>cm-1</sup> and 1564-1540<sup>cm-1</sup> regions respectively in the spectra of praseodymium soaps place of one band of carbonyl frequency near 1700<sup>cm-1</sup> confirms the partial ionic nature of these soaps.

**Table 1:** Infrared absorption spectra frequencies (cm<sup>-1</sup>) of acids and their soaps.

S.N.	ASSIGNMENTS	HEXANOIC ACID	Pr. HEXANOATE	DECANOIC ACID	Pr. DECANOATE
1.	CH <sub>3</sub> , C-H asymmetrical stretching	2950 W	2960 M	2960 W	2960 M
2.	CH <sub>2</sub> , C-H asymmetrical stretching	2920 M	2930 M	2920 W	2920 M
3.	CH <sub>2</sub> , C-H symmetrical stretching	2860 W	2870 W	2855 S	2855 M
4.	OH, stretching	2580 S	-	2660 S	-
5.	C=O, stretching	1700 S	-	1680 S	-
6.	COO <sup>-</sup> , C-O asymmetrical stretching	-	1540 S	-	1555 S
7.	CH <sub>2</sub> , deformation	1470 M	1460 W	1465 M	1450 VW
8.	COO <sup>-</sup> , C-O symmetrical stretching	-	1550 S	-	1440 M
9.	CH <sub>2</sub> (adjacent to COOH group ) deformation	1370 W	1410 W	1410 S	1420 W
10.	CH <sub>3</sub> , symmetrical deformation	1340 M	1345 W	1350 M	1345 W
11.	Progressive bands (CH <sub>2</sub> twisting and wagging)	1280-1210 M	1310-1340 M	1270-1220 M	1275-1205 W
12.	CH <sub>3</sub> rocking	1100 VS	1110 M	1110 M	1110 M
13.	OH, out-of-plane deformation	930 S	-	930 S	-
14.	CH <sub>2</sub> rocking	720 M	725 M	720 M	720 W
15.	COOH bending mode	690 M	-	690 M	-
16.	COOH wagging mode	560 M	-	550 M	-
17.	Pr-O bond	-	450 M	-	445 MS

Fig. 1.5  
INFRARED ABSORPTION SPECTRUM OF PRASEODYMIUM HEXANOATE

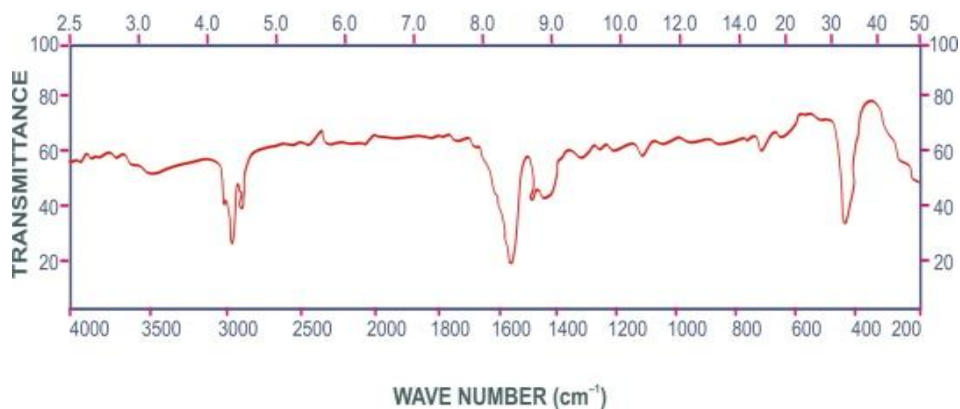
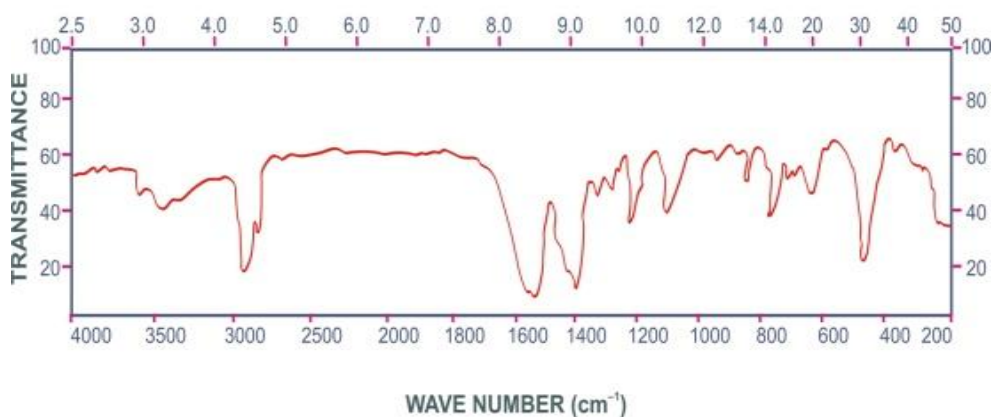


Fig. 1.6  
INFRARED ABSORPTION SPECTRUM OF PRASEODYMIUM DECANOATE



"The results show that the fatty acids in the solid state exist with dimeric structure through hydrogen bonding between carboxyl group of the two acid molecules whereas metal-to-oxygen bonds in praseodymium soaps are not purely ionic, but somewhat covalent in character".

### Specific Conductance:

The specific conductance ( $\kappa$ ) of the solutions of praseodymium soaps (hexanoate and decanoate) in benzene and methanol increase with increasing soap concentration and decreasing chain length of fatty acid constituent of the soap molecule (Table 2). The increase in the specific conductance may be due to the ionisation of praseodymium soaps into simple metal cations,  $\text{Pr}^{3+}$  and fatty acid anions ( $\text{C}_5\text{H}_{11}\text{COO}^-$  &  $\text{C}_9\text{H}_{19}\text{COO}^-$  for hexanoate and decanoate, respectively) in dilute solutions and due to the formation of micelles at higher soap concentrations. The plots of specific conductance vs. soap concentration (Fig.1) are characterized by an intersection of two straight lines at a definite soap concentration which corresponds to the cmc of praseodymium soaps indicating the formation of ionic micelles at this concentration. The results show that the cmc decreases with increasing chain length of fatty acid (Table-3).

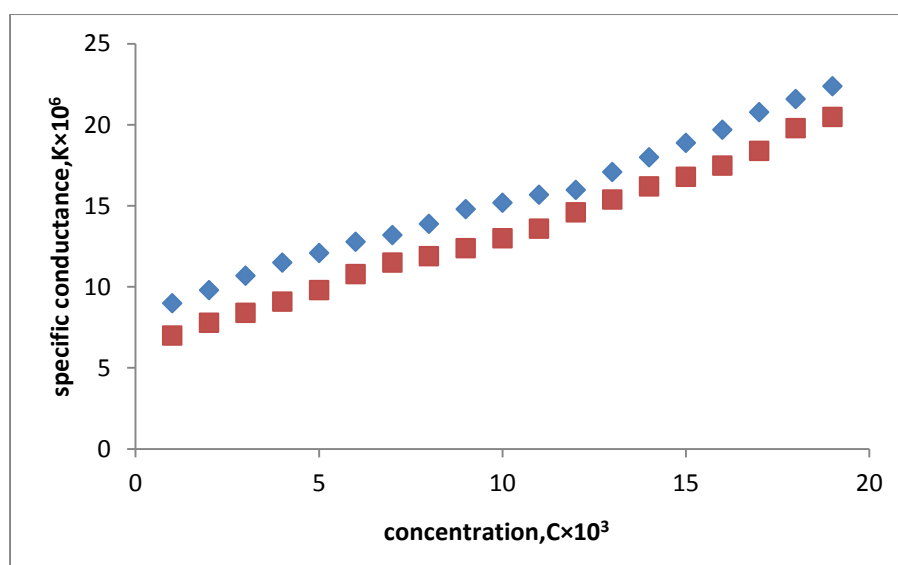
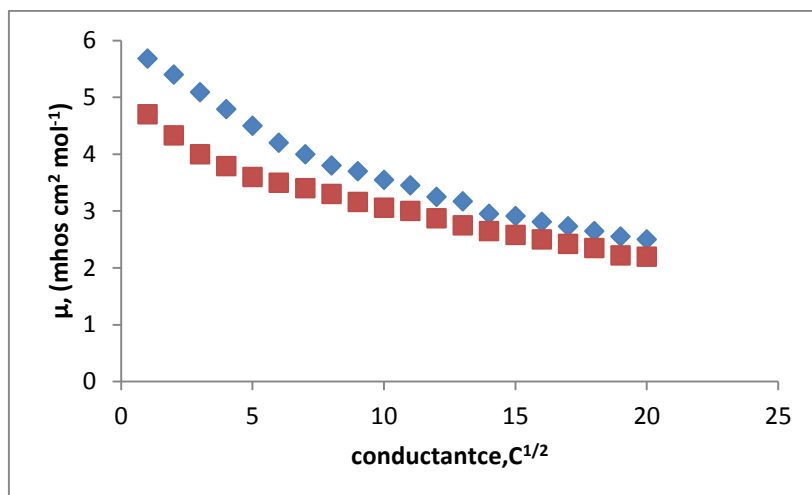


Fig-1: Specific conductance vs concentration, Pr.hexanoate & decanoate

### Molar Conductance ( $\mu$ ) and Dissociation constant (K):

The molar conductance ( $\mu$ ) of the solutions of praseodymium soaps in benzene and methanol decreases with increasing soap concentration (Table-2). The decrease in molar conductance may be due to the combined effects of ionic atmosphere, solvation of ions, and decrease of mobility and ionization with the formation of micelles. The plots of molar conductance ( $\mu$ ) Vs. square root of soap concentration,  $C^{1/2}$  (Fig-2) is not linear which indicates that these soaps behaves as a moderate electrolyte in these solutions. The limiting molar conductance ( $\mu_0$ ), cannot be obtained by usual extrapolation method as the Debye-Huckel Onsager's equation is not applicable to these soap solutions.

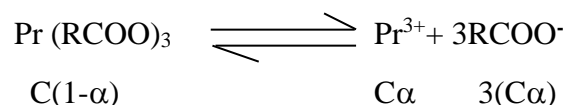


**Fig-2:** Molar conductance vs  $C^{1/2}$  Pr.hexanoate & decanoate

**Table 2:** Conductivity measurements of Praseodymium Soaps in mixture of Benzene and Methanol (5:5 v/v) at  $40 \pm 0.05^\circ C$

$C \times 10^3$ ( $gmol l^{-1}$ )	Pr. Hexanoate			Pr. Decanoate		
	$\kappa \times 10^6$ ( $mhos cm^{-1}$ )	$\mu$	$\alpha$	$\kappa \times 10^6$ ( $mhos cm^{-1}$ )	$\mu$	$\alpha$
10.0	24.0	2.40	0.271	22.0	2.20	0.250
9.2	22.4	2.43	0.273	20.5	2.22	0.253
8.4	21.0	2.50	0.281	19.8	2.35	0.268
7.6	20.8	2.73	0.307	18.4	2.42	0.275
7.0	19.7	2.81	0.316	17.5	2.50	0.283
6.5	18.9	2.91	0.328	16.8	2.58	0.293
6.1	18.0	2.95	0.332	16.2	2.65	0.300
5.4	17.1	3.17	0.357	15.4	2.85	0.323
5.0	16.0	3.20	0.360	14.6	2.92	0.331
4.4	15.7	3.56	0.401	13.6	3.09	0.350
4.1	15.2	3.70	0.417	13.0	3.17	0.359
3.7	14.2	3.83	0.431	12.4	3.35	0.380
3.5	13.9	3.97	0.447	11.9	3.40	0.386
3.3	13.2	4.00	0.450	11.5	3.48	0.395
3.0	12.8	4.27	0.481	10.8	3.60	0.408
2.6	12.1	4.65	0.524	9.8	3.76	0.426
2.4	11.5	4.79	0.540	9.1	3.79	0.430
2.1	10.7	5.09	0.573	8.4	4.00	0.404
1.8	9.8	5.44	0.613	7.8	4.33	0.491
1.6	9.0	5.63	0.635	7.0	4.37	0.496

Assuming that these soaps are completely associated into  $\text{Pr}^{3+}$  and  $\text{RCOO}^-$  ions, and so an expression for the dissociation of praseodymium soaps can be developed on Ostwald's manner. The dissociation of metal soap may be represented as:



Where R is  $\text{C}_5\text{H}_{11}$  and  $\text{C}_9\text{H}_{19}$  for hexanoate and decanoate respectively. The dissociation  $\alpha$  and C are the degree of dissociation and concentration. Dissociation constant (K) can be expressed as :

$$\begin{aligned} K &= \frac{[\text{Pr}^{3+}][\text{RCOO}^-]^3}{[\text{Pr(RCOO)}_3]} \\ K &= \frac{(\text{C}\alpha)(3\text{C}\alpha)^3}{\text{C}(1-\alpha)} \\ K &= \frac{27\text{C}^3\alpha^4}{1-\alpha} \end{aligned} \quad (1)$$

Since the ionic concentrations are low and the interionic effects are almost negligible in these solution. The degree of dissociation ( $\alpha$ ) is equal to the conductance ratio ( $\mu/\mu_0$ ), where  $\mu$  is molar conductance at infinite concentration and  $\mu_0$  is the limiting molar conductance of these ions, after rearranging equation (1) can be written as :

$$\mu^3\text{C}^3 = \frac{K\mu_0^4}{27\mu} - \frac{K\mu_0^3}{27} \quad (2)$$

**Table 3:** CMC and Values of Various Constants for Praseodymium Soaps at  $40+0.05^\circ\text{C}$

Name of Praseodymium soaps	CMC	$\mu_0$	K
Hexanoate	0.0044	8.87	5.40
Decanoate	0.0041	8.81	2.71

The values of K and  $\mu_0$  have been obtained from the slope and intercept of the linear plots of  $\mu^3\text{C}^3$  vs.  $1/\mu$  below the CMC and are recorded in (Table-3).

The results show that the values of limiting molar conductance increases while the

dissociation constant decrease with increasing concentration (Table-3). The values of degree of dissociation ( $\alpha$ ) and dissociation constant (K) have been calculated at different concentrations by using the value of  $\mu_0$  and equation (2). The plots of  $\alpha$  vs.  $c$  show that the praseodymium hexanoate and decanoate behave as a moderate electrolyte in these solutions. The values of dissociation constant remain almost constant in dilute solutions but show drift at higher concentration which may be due to the failure of Debye-Huckel's activity equation at higher soap concentration.

## CONCLUSION

The IR spectra of praseodymium do not show any absorption maxima in the 3500-3300<sup>cm<sup>-1</sup></sup> region which confirms the absence of any co-ordinated water molecule in these soap molecules. The critical micellar concentration of praseodymium soaps (hexanoate and decanoate) in benzene and methanol mixture (5:5 v/v) decrease with increasing chain length of fatty acids constituent of soap molecules.

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