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Physico-Chemical Studies on Praseodymium Soaps in Solid State

R.K. SHUKLA* and VIKAS MISHRA
Deptartment of Chemistry
R.B.S. College, Agra-282 004, India

The physico-chemical characteristics of praseodymium soaps (butyrate and caprylate) in solid state were investigated by IR, X-ray diffraction and thermal measurements. The IR results reveal that the fatty acids exist in dimeric state through hydrogen bonding and soaps possess partial ionic character. The X-ray diffraction measurements were used to calculate the long spacings and the results confirm the double layer structure of praseodymium soaps. The decomposition reaction was found kinetically of zero order with energy of activation 8.154 and 7.697 kcal mol^{-1} for butyrate and caprylate, respectively.

Key Words: Physico-chemical studies, Praseodymium soaps, Solid state.

INTRODUCTION

The survey of literature[1–14] reveals that the physico-chemical characteristics of inner transition soaps have not yet been studied thoroughly in spite of the wide range of applications of these soaps in various industries. The applications of the soaps depend largely on their physical state, stability and chemical reactivity together with their volalitity and solubility in common solvents. The present work is supplementary to previous communications on studies of lanthanum soaps[15] and deals with the IR, X-ray and thermal studies of praseodymium soaps in solid state and has been initiated with a view to obtain structural information in solid state.

EXPERIMENTAL

All the chemicals used were of BDH grade. Praseodymium soaps (butyrate and caprylate) were prepared by direct metathesis of corresponding potassium soap with slight excess of the solution of praseodymium nitrate at 50–55°C under vigorous stirring. The precipitated soap was filtered and washed with distilled water and acetone and recrystallzed 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^{-1} using potassium bromide disc method.

The X-ray diffraction patterns were obtained with a Richseifert "2002 D" Isodebyeflex Diffractormeter using Cu-K_α radiations filtered by a nickel foil over the range of diffraction angle, $2\theta = 4°$ to $50°$, where θ is Bragg's angle. The readings of the diffraction angle were made up to 0.001° and the wavelength of the radiation was taken as 1.54 Å. The thermogravimetric analyses of praseodymium soaps were carried out by Perkin-Elmer thermogravimetric analyzer TG-S-2 at a constant heating rate of 10°/min in nitrogen atmosphere and maintaining similar conditions throughout the investigations.

RESULTS AND DISCUSSION

Infrared Spectra: The wavenumbers of some important absorption bands in infrared absorption spectra of praseodymium (butyrate and caprylate) were assigned and compared with those of corresponding fatty acids (Table-1). The absorption bands observed at 2660–2580, 1700, 1430–1390, 930–910, 690 and 550 cm^{-1} in the spectra of fatty acids 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^{-1} 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^{-1} in the spectra of 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 symmetic and antisymmetric stretching vibrations of carboxylate ion at 1440–1436 cm^{-1} and 1564–1540 cm^{-1} regions, respectively, in the spectra of praseodymium soaps place of one band of carbonyl frequency near 1700 cm^{-1} confirms the partial ionic nature of these soaps.

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. The assigned frequencies are in agreement with the results of other workers[6, 17].

X-ray Diffraction analysis: Since the metal soaps do not give large crystals for a detailed single crystal examination, so the X-ray powder diffraction patterns of praseodymium soaps have been investigated to characterize the structure of these soaps. The intensities of the diffracted X-rays as a function of the diffraction angle, 2θ for praseodymium soaps were observed and the interplanar spacings, d, have been calculated from the positions of the intense peaks using Bragg's relationship, $n\lambda = 2d \sin \theta$, where λ is the wavelength of the radiation. The calculated spacings together with the relative intensities with respect to the most intense peaks are recorded (Tables 2 and 3). The appearance of the diffractions up to the 5th order in praseodymium butyrate and up to 12th order in praseodymium caprylate confirms good crystallinity for these soaps. The average planar distance, *i.e.*, long spacings of praseodymium caprylate and butyrate are 24.226

and 15.081 Å respectively. The difference in the observed values of long spacings for praseodymium caprylate is 9.145 Å which corresponds to twice the length of the additional methylene (—CH_2—) groups in the fatty acid radical constituent of the soap molecules. The values of the long spacings for these soaps are approximately equal to double the length of the fatty acid radical of the soap molecules. It is therefore, suggested that the zig-zag chains of fatty acid radicals extended straightforward in these soap molecules.

TABLE-1

INFRARED ABSORPTION SPECTRAL FREQUENCIES (cm^{-1})
OF ACIDS AND THEIR SOAPS

Assignments	Butyric acid	Pr. butyrate	Caprylic acid	Pr. caprylate
CH_3, C—H antisym. stretch	2960 w	2960 w	2950 w	2960 vs
CH_2, C—H antisym. stretch	2910 m	2910 vs	2920 s	2940 vs
CH_2, C—H sym. stretch	2855 s	2850 s	2850 s	2860 vs
OH, stretch	2660 s	—	2580 w	—
C═O, stretch	1700 s	—	1700 vs	—
COO^-, C—O antisym-stretch	—	1564 vs	—	1540 ms
COO^-, C—O sym. stretch	—	1436 ms	—	1440 m
C—O stretch + OH in-plane deformation	1390 m	—	1430 m	—
CH_2 (adjacent to COOH group) deformation	1410 s	1410 ms	1370 s	1420 m
CH_2, sym. deformation	1350 w	1340 w	1340 s	1340 m
Progressive bands CH_2 (twist and wagg)	1270– 1220 m	1390– 1200 w	1320– 1140 m	1300– 1210 w
CH_3 rocking	1110 vs	1120 w	1110 vs	1115 m
OH, out-of-plane deformation	930 s	—	910 s	—
CH_2 rocking	720 s	680 ms	720 m	720 w
COOH bending mode	690 m	—	690 m	—
COOH wagging mode	550 m	—	550 m	—
(Pr—O) bond	—	440 m	—	440 ms

The observed values of the long spacing for caprylate (24.226 Å) and butyrate (15.081 Å) of praseodymium are smaller than the calculated dimensions of caprylate (27.0 Å) and butyrate (17.0 Å) ions from Pauling's values of atomic radii and bond angles and this suggests that the molecular axes of these soaps are somewhat inclined to the basal planes. The metal ions fit into spaces between oxygen atoms of the ionized carboxyl group without a large strain of the bonds. A number of diffraction peaks in the intermediate range of the diffraction angles are also observed in the diffraction patterns of praseodymium soaps and these are attributed to the diffraction of X-rays by planes of atoms of much smaller separation than the basal planes. The calculated spacings from these peaks correspond to the shorter side spacings, *i.e.*, the lateral distances between one soap molecule and the next in a layer. It is observed that the long spacing peaks are fairly intense while the short spacing peaks are relatively weak. On the basis of long and short spacings, it is proposed that the metal ions in praseodymium soaps are arranged in a parallel plane, *i.e.*, a basal plane is equally spaced in the soap crystal with fully extended zigzag chains of fatty acid radicals on both side of each basal plane and praseodymium soaps have double layer structure as proposed by Vold and Hattiangdi[18].

TABLE-2
X-RAY DIFFRACTION ANALYSIS OF PRASEODYMIUM BUTYRATE

S. No.	2θ	θ	sin θ	λ/2 sin θ	d	n	I/I_{max}
1.	5.835	2.9175	0.0509	15.1277	15.128	1	1.00
2.	11.766	5.8830	0.1025	7.5122	15.024	2	0.28
3.	17.590	8.7850	0.1529	5.0359	15.108	3	0.22
4.	23.624	11.8120	0.2047	3.7616	15.046	4	0.01
5.	29.547	14.7730	0.2550	3.0196	15.098	5	0.06

Average value of d = 15.081 Å

TABLE-3
X-RAY DIFFRACTION ANALYSIS OF PRASEODYMIUM BUTYRATE

S. No.	2θ	θ	sin θ	$\frac{\lambda}{2 \sin \theta}$	d	n	I/I_{max}
1.	5.96	2.98	0.0520	14.8350	14.835	1	1.0
2.	7.20	3.60	0.0627	12.0960	24.592	2	0.9
3.	11.30	5.65	0.0984	7.8350	23.505	3	1.0
4.	14.80	7.40	0.1287	5.9900	23.960	4	0.3
5.	18.50	9.25	0.1607	4.7970	23.985	5	0.3
6.	22.10	11.05	0.1916	4.0240	24.144	6	0.5
7.	25.80	12.90	0.2232	3.4540	24.178	7	0.2
8.	29.00	14.50	0.2504	3.0790	23.632	8	0.2
9.	33.30	16.65	0.2865	2.6910	24.219	9	0.2
10.	36.60	18.30	0.3139	2.4560	24.563	10	0.2
11.	40.60	20.30	0.3469	2.2220	24.442	11	0.2
12.	44.80	22.40	0.3810	2.0230	24.276	12	0.2

Average value of d = 24.226 Å

Thermogravimetric Analysis: The results of thermogravimetric analysis of praseodymium soaps (caprylate and butryrate) show that the final residue is metal oxide and the weights of the residues are in agreement with the theoretically calculated weight of praseodymium oxide from the molecular formulae of the soaps. A white substance is found deposited at the cold part of the sample tube surrounding the sample and it is identified as caprylone (m.p. 39°C) and butanone (b.p. 79.6°C) in case of caprylate and butyrate, respectively.

The thermal decomposition of praseodymium soaps can be expressed as:

$$\underset{\substack{\text{Praseodymium}\\ \text{soap}}}{2(RCOO)_3Pr} \longrightarrow \underset{\text{Ketone}}{3RCOR} + 3CO_2 + Pr_2O_3$$

The thermogravimetric data have been used to calculate the energy of activation and to find the order of reaction for decomposition of praseodymium soaps using the equation of Freeman-Carroll[19] which may be written as:

$$\frac{\Delta[\log (dw/dt)]}{\Delta(\log W_r)} = \frac{-E}{2.303R} \cdot \frac{\Delta(1/T)}{\Delta(\log W_r)} + n$$

where E = energy of activation, R = gas constant, n = order of decomposition reaction, T = temperature on absolute scale, W_r = difference between the total loss in weight and loss in weight at time, t, *i.e.*, $W_0 - W_t$, and dw/dt = value of rate of weight loss obtained from the loss of weight V_s time curves at appropriate times.

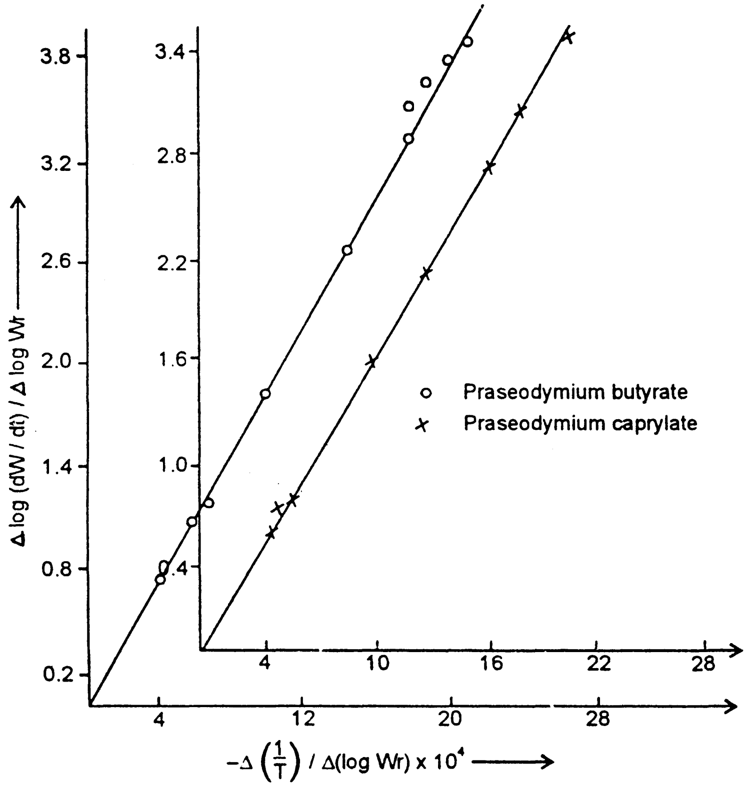

Fig. 1 Freeman-carroll's type plots

The plots of [log (dw/dt)/log W_r] *vs.* [(1/T)/log W_r] have been found to be linear with the intercept equal to zero (Fig. 1). It is, therefore, concluded that the order of reaction for the decomposition of praseodymium soaps is zero and the value of energy of activation from the slope (–E/2.303R) of the plots (Fig. 1) are 8.154 and 7.697 kcal. mol^{-1} for butyrate and caprylate, respectively.

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REFERENCES

1. G. Marwedel, *Farbe U. Lack*, **60**, 530 (1954).
2. L.W. Ryan and W.W. Plechner, *Ind. Eng. Chem.*, **26**, 907 (1934).
3. J.H. Skellon and J.W. Spence, *J. Soc. Chem. (London)*, **67**, 365 (1948).
4. Y. Koga and R. Matuura, *Mem. Fac. Sc. Kyushu Univ. Ser.*, **4**, 1 (1961).
5. J.R. Feraro and M. Beeker, *J. Inorg. Nucl. Chem.*, **32**, 1495 (1970).
6. A.K. Solanki and A.M. Bhandari, *Tenside Detergents*, **18**, 34 (1981).
7. K.N. Mehrotra, A.S. Gahlaut and M. Sharma, *J. Am. Oil Chemist's Soc.*, **63**, 331 (1987).
8. K.N. Mehrotra, M. Chauhan and R.K. Shukla, *J. Appl. Polym. Sci.*, **55**, 431 (1995).
9. ———, *Tenside Surf. Det.*, **33**, 319 (1996).
10. ———, *J. Colloids Surf.*, **A119**, 67 (1996).
11. F. Mains, D. Mills and D.W. White, *Chem. Abstr.*, **3**, 320, 172 (1967).
12. A. Navarro, *Ann. Chim.*, **6**, 349 (1971).
13. S.N. Misra, T.N. Misra and R.C. Mehrotra, *J. Inorg. Nucl. Chem.*, **25**, 195 (1963).
14. R.P. Verma and R. Jindal, *Tenside. Det.*, **20**, 193 (1983).
15. R.K. Shukla and V. Mishra, *Asian J. Chem.*, **15**, 1703 (2003).
16. C. Duval, J. Lecomte and F. Douville, *Ann. Phys.*, **17**, 5 (1942).
17. R.E. Kagarise, *J. Phys. Chem.*, **59**, 271 (1955).
18. R.D. Vold and G.S. Hattiangdi, *Ind. Eng. Chem.*, **41**, 2311 (1949).
19. E.S. Freeman and B. Carroll, *J. Phys. Chem.*, **62**, 399 (1950).

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