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Physico-Chemical Studies on Samarium Soaps in Solid State

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Summary. The physico-chemical characteristics of samarium soaps (caproate and caprate) in solid state were investigated by IR, X-ray diffraction and TGA measurements. The IR results revealed that the fatty acids exist in dimeric state through hydrogen bonding and samarium soaps possess partial ionic character. The X-ray diffraction measurements were used to calculate the long spacings and the results confirmed the double layer structure of samarium soaps. The decomposition reaction was found kinetically of zero order and the values of energy of activation for the decomposition process for caproate and caprate were found to be 8.0 and 7.8 kcal mol^{-1}, respectively.

Keywords. Soaps; Infrared; X-ray; TGA; Energy of activation.

Physikochemische Untersuchungen an Samariumseifen in festem Zustand

Zusammenfassung. Die physikochemischen Charakteristika von Samariumseifen (Caproat und Caprat) wurden im festen Zustand mittels IR, Röntgendiffraktion und TGA-Messungen untersucht. Die IR-Ergebnisse zeigten, daß die Fettsäuren durch Wasserstoffbrücken dimer vorliegen und daß die Samariumseifen partiell ionischen Charakter besitzen. Die Röntgenuntersuchungen bestätigen die Doppelschichtstruktur der Seifen. Die Zersetzungsreaktion verlief nach nullter Ordnung, und die Aktivierungsenergien für den Zersetzungsprozeß für Caproat und Caprat waren 8.0 und 7.8 kcal mol^{-1}.

Introduction

The alkali, alkaline earth and transition metal soaps have been thoroughly investigated but the studies on lanthanide and actinide soaps have remained almost untouched with the result that only few references [1–14] are available on these soaps. The studies on the nature and structure of these soaps are of great importance for their use in industries and for explaining their characteristics under different conditions. The present work deals with the infrared, X-ray and thermal studies of samarium soaps in solid state and has been initiated with a view to obtain structural informations in solid state.

Experimental

All the chemicals used were of BDH grade. Samarium soaps (caproate and caprate) were prepared by direct methathesis of corresponding potassium soap with required amount of samarium nitrate solution at 50–55°C under vigorous stirring. The precipitated soap was filtered and washed with distilled water and alcohol and recrystallised with a mixture of benzene and methanol and dried under reduced pressure.

The infrared spectra of fatty acids and their corresponding samarium soaps were recorded with a Perkin-Elmer "Model 783" grating spectrophotometer in the region 4000 – 400 cm^{-1} using potassium bromide disc method. The X-ray diffraction patterns were obtained with a Richseifert "2002 D" Isodebyeflex Diffractometer using Cu-K_a radiations filtered by a nickel foil over the range of diffraction angle, $2\theta = 6$–80°, where θ is Bragg's angle. The readings of the diffraction angle were made up to 0.001° and the wavelength of the radiations was taken as 1.54 Å. The thermogravimetric analysis of samarium soaps was carried out by Perkin-Elmer thermogravimetric analyzer 'TG-S-2 at a constant heating rate of 10°/min and maintaining similar conditions throughout the investigations.

Results and Discussion

Infrared Spectra

The wave numbers of some important absorption bands in the infrared absorption spectra of samarium soaps (caproate and caprate) were assigned and compared with those of the corresponding fatty acids (Table 1). The absorption maxima in the spectra of fatty acids near 2 660–2 580, 1 700–1 680, 1 430–1 410, 930, 690 and 560–550 cm^{-1} are associated with the localized carboxyl group of the acid molecule in the dimeric form and confirm the presence of hydrogen bonding between two molecules of fatty acids. The complete disappearance of the carbonyl frequency near 1 700 cm^{-1} in the spectra of samarium 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 constants assuming an intermediate value between those of the normal double and single bonds. The appearance of two absorption bands corresponding to symmetric and antisymmetric stretching vibrations of carboxylate ion near 1 460–1 410 cm^{-1} and 1 560–1 525 cm^{-1}, respectively, in the spectra of samarium soaps instead of one band of carboxyl frequency near 1 700 cm^{-1} confirms the ionic nature of these soaps.

The results show that the fatty acids exist with dimeric structure through hydrogen bonding between carboxyl groups of the two acids molecules whereas samarium soaps are ionic in nature and the metal-to-oxygen bonds in these soaps have ionic character. The assigned frequencies are in agreement with the results of other workers [15–17].

X-Ray Diffraction Analysis

Since the metal soaps do not give large crystals for a detailed single crystal examination, the X-ray diffraction patterns of samarium 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 samarium soaps were observed and the interplanar spacings, d, have been calculated from the positions of the intense peaks using Bragg 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 13th order in samarium caproate and up to 15th order in samarium caprate confirms good crystallinity for these soaps. The average planar distance i.e. long spacing for samarium caproate

Table 1. Infrared absorption spectral frequencies (cm^{-1}) with their assignments (W = weak, B = broad, S = sharp, Str = strong, VW = very weak, M = medium)

S. no.	Assignments	Caproic acid	Sm Caproate	Capric acid	Sm Caprate
1	CH_3, C−H antisym. stretch.	2 950 WB	2 960 M	2 960 WB	2 960 M
2	CH_2, C−H antisym. stretch.	2 920 W	2 920 M	2 920 MS	2 920 MS
3	CH_2, C−H sym. stretch.	2 860 M	2 860 M	2 855 M	2 855 Str
4	OH, stretch.	2 580 Str	–	2 660 Str	–
5	C=O, stretch.	1 700 Str	–	1 680 Str	–
6	COO^-, C−O antisym. stretch.	–	1 555–1 525 Str, B	–	1 560–1 530 Str, B
7	COO^-, C−O sym. stretch.	–	1 460–1 410 Str	–	1 460–1 410 M
8	C−O stretch. + OH inplane deformation	1 410 MB	–	1 430 MS	–
9	CH_2 (adjacent to COOH group) deformation	1 370 W	1 410 VW	1 405 VStr	1 420 VW
10	CH_3, sym. deformation	1 340 M	1 345 M	1 350 W	1 330 W
11	Progressive band CH_2 (twist and wagg)	1 280–1 210 MS	1 310–1 190 MS	1 270–1 220 WS	1 275–1 205 W
12	CH_3, rocking	1 100 MS	1 110 M	1 110 W	1 110 WS
13	OH out of plane deformation	930 MS	–	930 Str	–
14	CH_2, rocking	720 M	730 M	720 Str	720 M
15	COOH, bending mode	690 M	–	690 M	–
16	COOH, wagging	560 M	–	550 M	–
17	Sm-O bond	–	430 M	–	430 M

Table 2. X-ray diffraction analysis of samarium caproate

S. no.	2θ	θ	$\sin\theta$	$D = \lambda/(2\sin\theta)$	n	d(Å)	I/I_0
1	13.44	6.720	0.1170	6.58	3	19.74	0.17
2	17.97	8.985	0.1562	4.93	4	19.72	0.98
3	22.52	11.260	0.1953	3.95	5	19.75	0.23
4	27.08	13.540	0.2341	3.29	6	19.74	0.52
5	31.70	15.850	0.2731	2.82	7	19.74	0.36
6	36.24	18.120	0.3110	2.48	8	19.84	0.10
7	41.59	20.795	0.3550	2.17	9	19.53	0.17
8	46.42	23.210	0.3941	1.95	10	19.50	0.18
9	61.33	30.665	0.5100	1.51	13	19.63	0.08
						19.69 average value	

Table 3. X-ray diffraction analysis of samarium caprate

S. no.	2θ	θ	$\sin\theta$	$D = \lambda/(2\sin\theta)$	n	d(Å)	I/I_0
1	12.00	6.00	0.1045	7.37	4	29.48	0.96
2	15.00	7.50	0.1305	5.90	5	29.50	1.00
3	18.02	9.01	0.1566	4.92	6	29.52	0.24
4	21.02	10.51	0.1824	4.22	7	29.54	0.46
5	24.16	12.08	0.2093	3.68	8	29.44	0.05
6	27.11	13.55	0.2343	3.29	9	29.61	0.20
7	30.18	15.09	0.2602	2.96	10	29.60	0.05
8	33.32	16.66	0.2867	2.69	11	29.59	0.10
9	39.58	19.79	0.3386	2.28	13	29.64	0.06
10	46.32	23.16	0.3933	1.96	15	29.40	0.05
						29.53 average value	

and caprate are 19.69 and 29.53 Å, respectively. The difference in the observed values of long spacings for samarium caprate and caproate is 9.84 Å which corresponds to twice of the length of 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 the double of 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 straight forward in these soap molecules.

The observed values of the long spacings for caprate (29.53 Å) and caproate (19.69 Å) of samarium are smaller than the calculated dimensions of caprate (32.0 Å) anc caproate (22.0 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 the diffraction peaks in the intermediate range of the diffraction angles are also observed in the diffraction patterns of samarium 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 samarium soaps are arranged in a parallel plane, i.e. a basal plane equally spaced in the soap crystal with fully extended zig-zag chains of fatty acid radicals on both sides of each basal plane, and samarium soaps have double layer structure as proposed by Vold and Hattiangdi [18].

Thermogravimetric Analysis

The results of thermogravimetric analysis of samarium soaps (caproate and caprate) show that the final residue is metal oxide and the weights of the residue are in agreement with the theoretically calculated weight of samarium 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 caprone (B.P. 22.8°C) and caprinone (M.P. 58.0°C) in case of caproate and caprate, respectively.

The thermal decomposition of samarium soaps can be expressed as

$$\underset{\text{Samarium soap}}{2\,(R\mathrm{COO})_3\mathrm{Sm}} \rightarrow \underset{\text{Ketone}}{3\,R\mathrm{CO}R} + \underset{\substack{\text{Carbon}\\\text{dioxide}}}{3\,\mathrm{CO_2}} + \underset{\substack{\text{Samarium}\\\text{oxide}}}{\mathrm{Sm_2O_3}}\,.$$

The thermogravimetric data have been used to calculate the energy of activation and to find the order of reaction for the decomposition of samarium soaps using

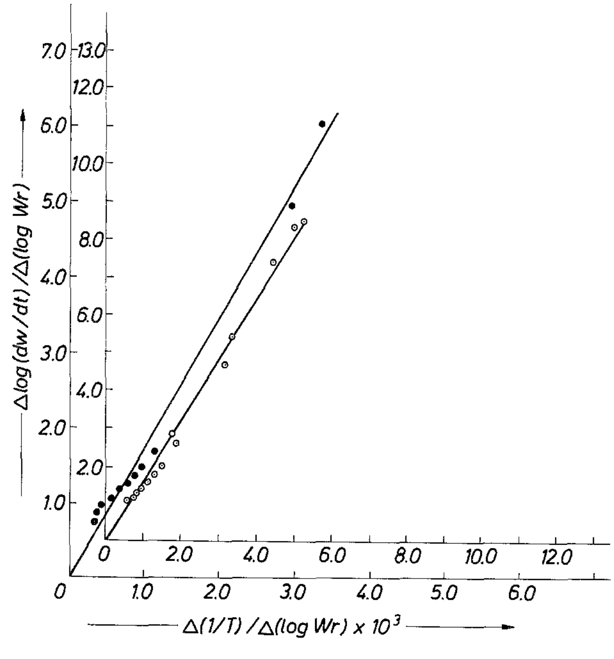

Fig. 1. Freeman Carroll's type plot for caproate and caprate

the equation of Freeman Carroll [19] which may be written as

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

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 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 in weight vs. time curves at appropriate times.

The plots of $[\log(dw/dt)/\log W_r]$ vs. $[(1/T)/\log W_r]$ have been found to be linear with an intercept equal to zero (Fig. 1). It is, therefore, concluded that the order of reaction for the decomposition of samarium soaps is zero and the values of energy of activation from the slope $(-E/2.303\,R)$ of the plots (Fig. 1) are 8.0 and 7.8 kcal mol^{-1} for caproate and caprate, respectively.

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