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Characterization of uranyl soaps by spectroscopic and thermal measurements

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Abstract. The infrared and visible spectrophotometric data of uranyl soaps showed that metal-oxygen bonds in uranyl soaps are not purely ionic but are partially covalent in character. The X-ray diffraction patterns confirmed the double-layer structure with molecular axes perpendicular to the basal plane. The thermal decomposition of these soaps was found to be kinetically of zero order and the energies of activation were found to lie between 14–58 kJ/mol.

Introduction

A survey of the literature[1-12] reveals that the physico-chemical properties and structure of lanthanide and actinide soaps have not yet been thoroughly investigated inspite of their considerable industrial application.

The present work deals with the studies of the structure of uranyl soaps (octanoate and decanoate) in solid state as well as in solutions using IR and VIS spectrophotometry, X-ray and thermal techniques. The lower soaps possess higher solubility and have therefore been chosen in order to study the behaviour of uranyl soaps in solutions. The IR spectra of sodium and uranyl soaps have been compared with a view to obtaining information about the ionic nature of uranyl soaps in the solid state.

Experimental

BDH-grade chemicals were used for the preparation of uranyl soaps.

The soaps (octanoate and decanoate) were prepared by the direct metathesis of the corresponding sodium soaps, using a slight excess over the required amount of aqueous solution of uranyl nitrate with vigorous stirring. The soaps were purified by recrystallization from dimethylformamide. The purity of the soaps was checked by elemental analysis and metal contents.

The infrared absorption spectra of uranyl and sodium soaps, together with corresponding fatty acids, were recorded on a Perkin-Elmer Grating spectrophotometer "Model 577" in the region 4000–400 cm^{-1}, using the potassium bromide disc method.

The visible spectrophotometric measurements of the solutions of uranyl soaps in dimethylformamide were carried out in the region 340–950 nm using a Toshniwal visible spectrophotometer "Model CL10A3" having a wavelength reproducibility of ± 1 nm.

The nephelauxetic ratio[13], B, and percentage covalency, δ, are calculated using the relationships:

$$B = \frac{\nu_c}{\nu_f} \quad \text{and} \quad \delta = \frac{(1 - B)}{B} \cdot 100$$

where ν_c and ν_f are the energies (in cm^{-1}) for the transition in the complex and free ion, respectively. The values of ν_c have been obtained from the plots of optical density *vs.* wavelength and are found to be 22730 cm^{-1} (440 nm) for both octanoate and decanoate. The value of ν_f 24107 cm^{-1} (415 nm) for uranyl ion has been taken from the spectrum of an aqueous solution of uranyl ions[14].

Another bonding parameter, $b^{1/2}$, suggested by *Henrie* and *Choppin*[15], is given by the relationship:

$$b^{1/2} = \left(\frac{1 - B}{2}\right)$$

The X-ray diffraction patterns of uranyl soaps were obtained using a Philips PW 1730 diffractometer using Cu-K_α radiations filtered through a nickel foil. The wavelength of radiations was taken as 1.542 Å.

The thermogravimetric analysis of uranyl soaps was carried out at a constant rate of heating in a thermobalance (Mettler TG50, U.S.A.) by maintaining similar conditions throughout the investigations.

Results and discussion

Infrared absorption spectra

The IR spectra of uranyl soaps (octanoate and decanoate) were reported and compared with the results of the corresponding sodium soap and fatty acid (Table I).

The absence of water of crystallization in sodium and uranyl soaps was confirmed by the absence of a band near 3500 cm^{-1} in their spectra. The absorption maxima, characteristic of the aliphatic portion of the fatty acid molecules, remained unchanged on the formation of the salt from the corresponding acid. The absorption bands near 2650, 1700, 940, 690 and 550 cm^{-1}, observed in the spectra of fatty acids, are associated with the carboxylic group of the acid molecules. The absorption band near 1700 cm^{-1} revealed that the fatty acids exist in a dimeric structure with hydrogen bonding between the two molecules of the fatty acid. These characteristic vibrations of the fatty acid were found to be completely absent in the spectra of the sodium and uranyl soaps.

Table I Infrarted absorption spectral frequencies (cm^{-1}) together with their assignments.

Absorption	Octanoic acid	Sodium octanoate	Uranyl octanoate	Decanoic acid	Sodium decanoate	Uranyl decanoate
CH_3, C–H asymmetric stretching	2950 w	2960 w	2960 w	2960 vw	2940 vw	2960 vw
CH_2, C–H asymmetric stretching	2920 s	2920 vs	2930 w	2920 vs	2910 m	2920 vw
CH_2, C–H symmetric stretching	2850 s	2860 m	2860 m	2855 s	2840 ms	2840 vs
OH, stretching	2580 m	–	–	2660 vw	–	–
C=O, stretching	1700 vs	–	–	1680 s	–	–
COO^-, C–O asymmetric stretching	–	1550 m	1530 br	–	1550 vs	1540 vw
CH_2, deformation	1460 m	1460 w	1465 br	1470 m	1460 w	1500 ms
COO^-, C–O symmetric stretching	–	1410 s	1430 m	–	1390 br	1440 vs
C–O stretching, O–H in-plane deformation	1430 m	–	–	1430 ms	–	–
CH_2 (adjacent to COOH gp.), deformation	1370 s	–	1400 s	1405 vs	–	1390 w
CH_3, symmetric deformation	1340 s	1340 m	1320 vw	1350 w	1330 w	1360 s
Progressive bands (CH_2 twisting and wagging)	1320–1040 m	1300–1050 w	1305-1010 vw	1270–1220 w	1300–1050 w	1240–1130 vw
CH_3 rocking	1100 vs	1110 w	1120 vs	1110 w	1100 vw	1110 m
OH, out-of-plane deformation	930 s	–	–	940 vs	–	–
CH_2 rocking	720 ms	730 ms	730 m	720 vs	720 vs	710 s
COOH bending mode	690 m	–	–	690 vs	–	–
COOH wagging mode	550 ms	–	–	550 m	–	–

Key to abbreviation: vw = very weak, vs = very strong, s = strong, m = medium, ms = medium strong, w = weak, br = broad.

The infrared spectra of acids in the carboxylic region showed considerable changes on salt formation. In general, carboxylic acid, on complexation with metal, showed two important bands, one due to the asymmetric stretching vibration and the other due to the symmetric vibration of the carboxylate ion. These vibrations were observed near 1560–1550 cm^{-1} and 1410–1390 cm^{-1}, respectively, in the spectra of sodium soaps and near 1540–1530 cm^{-1} and 1440–1430 cm^{-1}, respectively, in the spectra of uranyl soaps. The appearance of two absorption bands in the spectra of sodium and uranyl soaps, instead of one band observed near 1700 m^{-1} in the spectra of fatty acids, indicates that the two C–O bonds of the carboxyl group of the soap molecule are identical. It is therefore concluded that the resonance character of the ionised carboxyl group is retained in these metal soaps. It should be pointed out that the metal–oxygen bonds in the ionised structure of these soaps should have ionic character.

Spectrophotometry

The ionic character of metal–oxygen bonds in uranyl soaps has also been confirmed by visible spectrophotometric measurements. The calculated value of the nephelauxetic ratio, B (0.94), which is slightly less than unity, together with the small value of percentage covalency, confirm that the metal–oxygen bonding in these soaps has a very small covalent character and further that these soaps are almost ionic in nature.

X-ray analysis

The X-ray diffraction patterns of uranyl soaps (octanoate and decanoate) were investigated in order to characterise their structure.

The intensities of diffracted X-rays as a function of diffraction angle, 2θ for uranyl soaps, were recorded. The interplanar spacings, d, have been calculated from the position of the intense peaks using *Bragg*'s relationship, $n \cdot \lambda = 2 \cdot d \cdot \sin(\theta)$, where λ is the wavelength of radiation. In the X-ray diffraction patterns of uranyl soaps, numerous peaks were observed over the range of 6–65° of the diffraction angle which were attributed to the diffraction of X-rays by planes of metal ions (known as basal planes). The good crystallinity of uranyl soaps was confirmed by the appearance of the diffractions upto 13th and 9th orders for octanoate and decanoate, respectively. The interplanar spacings calculated for 3rd, 4th, 5th, 6th, 7th, 8th, 9th, 12th and 13th order diffractions for uranyl octanoate were 27.37, 27.24, 27.19, 26.25, 26.40, 26.42, 27.16, 27.12 and 27.29 Å, respectively. The average planar distance, *i.e.* the long spacing for uranyl octanoate, was 26.93 Å.

The interplanar spacings calculated for 2nd, 3rd, 4th, 5th, 6th, 8th and 9th order diffractions for uranyl decanoate were 31.60, 32.76, 31.34, 31.63, 31.30, 32.77 and 31.70 Å, respectively. The average planar distance for uranyl decanoate was 31.87 Å. The difference in the observed values of long spacings of uranyl decanoate (31.87 Å) and octanoate (26.93 Å) was 4.94 Å, which corresponds to double the length of additional methylene ($-CH_2-$) groups in the fatty acid radical constituent of the soap molecule. It is therefore suggested that the zig-zag chains of the fatty-acid radical extend forward on both sides of each basal plane. The observed values of long spacings for octanoate (26.93 Å) and decanoate (31.87 Å) of uranyl soaps were almost equal to twice the calculated dimensions of octanoate (27 Å) and decanoate (32 Å) ions obtained from *Pauling*'s values of atomic radii and bond angles. This suggests that the molecular axes of these soaps are perpendicular to the basal planes. The metal ions fit into spaces between the oxygen atoms of the carboxyl group without significantly straining the bonds.

On the basis of the long and short spacings, it is proposed that the metal ions in uranyl soaps are arranged in a parallel plane, *i.e.* a basal plane equally spaced in the crystal with fully extended zig-zag chains of fatty-acid radicals on both sides of each basal plane, with the uranyl soaps having the double-layer structure as proposed by *Vold* and *Hattiangdi*[16].

Thermal analysis

The results of thermogravimetric analysis of uranyl soaps showed that the final residue was the metal oxide and the weight of residue was in agreement with the theoretically calculated weight of uranium oxide, using the molecular formula of corresponding soaps. A white crystalline powder was found, condensed at the cold part of the tube surrounding the sample, and it was identified as 8-pentadecanone (m.p. 40 °C) and 10-nonadecanone (b.p. 228 °C) in the case of octanoate and decanoate, respectively. The thermal decomposition of uranyl soaps can be expressed as:

$$(RCOO)_2UO_2 \longrightarrow R{-}CO{-}R + UO_3 + CO_2$$

where R is C_7H_{15} and C_9H_{19} for octanoate and decanoate, respectively.

It was found that the order of reaction for the decomposition of uranyl soaps is zero and that the values of energy of activation obtained from *Freeman–Carroll*'s[17], *Horowitz–Metzger*'s[18] and *Coats–Redfern*'s[19] equations were 32.8 and 36.1, 44.9 and 57.5 and 19.7 and 14.3 kJ/mol for octanoate and decanoate, respectively.

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