

IR, X-ray and ultrasonic velocity of uranyl (II) stearate

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ABSTRACT

The infrared and X-ray diffraction techniques have been used to study the structure of uranyl (II) stearate in solid state, whereas the structural changes of the metal soap in the solvent-mixture of 50% dimethylformamide and 50% benzene(V/V) at 40°C have been studied by the ultrasonic method. The appearance of two absorption bands at 1570 and 1440 cm^{-1} which may be assigned to as $\nu_{\text{as}} \text{COO}^-$ and $\nu_{\text{s}} \text{COO}^-$ modes of carboxylate group of uranyl stearate indicate the ionic nature of this group in the soap. The XRD analysis reveals that uranyl soap has a single layer structure as proposed by vold and Hattiangdi for disoaps. Ultrasonic velocity measurement is employed to obtain various acoustic parameters and the critical micelle concentration, CMC (5.55×10^{-4} mol. dm^{-3}) for the soap solutions. The values of ultrasonic velocity and acoustic impedance are found to decrease while adiabatic compressibility and intermolecular free length increase with increasing soap concentration.

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While major developments have taken place in the study of alkali, alkaline earth and transition metal soaps, the studies on actinide soaps have remained almost untouched with the result that only a few references (1-5) are available in this relatively unexplored field. The physicochemical characteristics and structure of these soaps depend on the method and conditions of preparation. The information about the structure and properties of these soaps is of great significance for their use in industries under varying conditions. Therefore, the present investigation is aimed at the physicochemical characteristics of uranyl(II) stearate both in solid state and in solutions.

MATERIALS AND METHODS

Merck/BDH reagent grade chemicals were used. Stearic acid was purified by distillation under reduced pressure, The m.p. of the purified acid was 128°C. Uranyl distearate was prepared by the direct metathesis of potassium stearate with uranyl nitrate at 50-55°C under vigorous stirring. The precipitated soap was digested, filtered, washed with distilled water-ether and dried. The metal soap thus obtained was crystallized twice from benzene-dimethylformamide and dried under vacuum for atleast 48 h before use. The purity was checked up by the elemental analysis and determining the m.p. (118°C).

The infrared absorption spectra of stearic acid, potassium stearate and uranyl stearate were obtained with a Perkin-Elmer "577 Model" grating spectrophotometer in the region of 4000-400 cm^{-1} using

potassium bromide disc method. The X-ray diffraction patterns for the metal soap were obtained over the range of diffraction angle, $2\theta=3-65^\circ$ with Philips "PW-1730" X-ray diffractometer using $\text{Cu-K}\alpha$ radiations filtered by a nickel-foil. The XRD curves were recorded under the applied voltage of 40 kV-20 μA using scanning speed of 1° min^{-1} and chart speed of 1 cm min^{-1} . The wavelength of the radiation was taken as 1.542 A° . The ultrasonic velocity measurements of the solutions of uranyl soap were recorded on a single frequency (1 MHz) ultrasonic interferometer "Model F-81", Mittal Enterprises, New Delhi. The density measurements (± 0.0001) were made with the help of pycnometer. All the measurements were carried out at a constant temperature ($40.0 \pm 0.05^\circ\text{C}$) in a thermostat.

RESULTS AND DISCUSSION

The results obtained from the present investigation are below :

Ir Spectrum:

The infrared spectrum of uranyl stearate is depicted in Fig. 1. The characteristic absorption bands of carboxyl group of fatty acid (2650, 1700, 940, 690 and 550 cm^{-1}) are found completely absent in the spectra of both potassium (2960, 2920, 2850, 1430, 1380, 1325-1190, 1110, 720 and 530 cm^{-1}) and uranyl (2960, 2920, 2850, 1570, 1470, 1440, 1415, 1370, 1350-1170, 1120, 720, 520 and 440 cm^{-1}) stearates; whereas the absorption maxima characteristic of the aliphatic portion of stearic acid (2960,

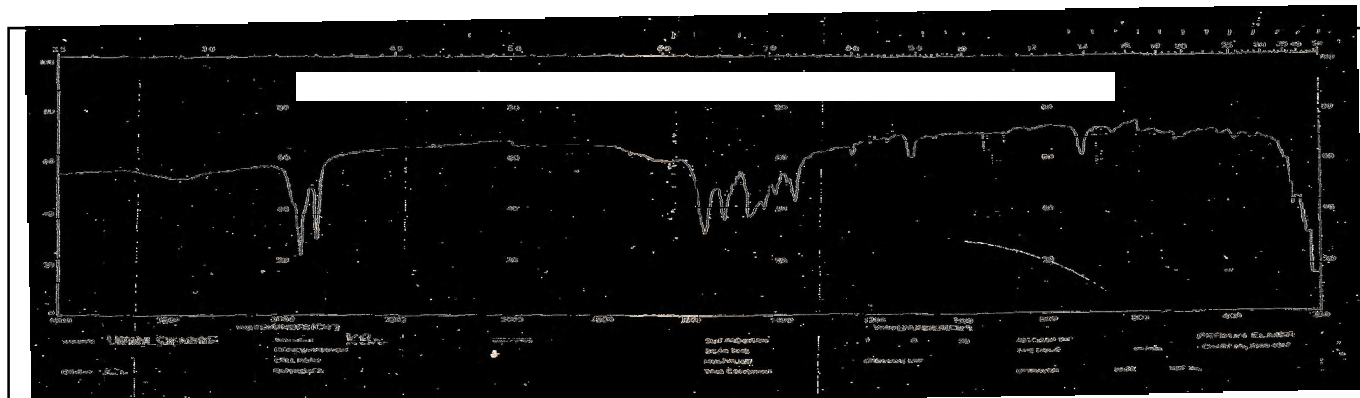


Fig. 1 : Infrared absorption spectrum of Uranyl stearate

2920 and 2850 cm^{-1}) remain essentially unchanged even when the acid is converted into either of these soaps (potassium/uranyl). The complete disappearance of the absorption band in the vicinity of 1700 cm^{-1} and the appearance of two absorption bands in carboxyl group corresponding to the asymmetric ($\nu_{\text{as}} \text{COO}^-$) and symmetric ($\nu_{\text{s}} \text{COO}^-$) vibrations at 1570, 1440 cm^{-1} (uranyl soap) and at 1560, 1430 cm^{-1} (potassium soap) indicate that there is a complete resonance in the two COO^- bands of carboxylic group of the soap molecule and the soap possesses ionic character. The progressive bands of medium intensity observed in the region of 1350-1170 cm^{-1} in the spectra of the soaps (uranyl/potassium) as well as fatty acid are due to wagging and twisting vibrations of the chains of successive methylene group in their molecules. The rocking vibrations of CH_3 (1120-1110 cm^{-1}) as well as CH_2 rocking vibrations (930-720 cm^{-1}) are also observed in the spectra of the fatty acid and the soaps (uranyl / potassium). The weak absorption band corresponding to U-O band is observed at 440 cm^{-1} in the spectrum of uranyl stearate. The spectra for soaps do not show any absorption maxima in the region of 3500-3300 cm^{-1} confirming the absence of any co-ordinated water molecules in the soap molecules. The frequencies are in agreement with previous results (6-8).

X-ray diffraction analysis :

Since it is not possible to prepare a large crystal of

metal soap sufficient for detailed single crystal examination, the X-ray diffraction patterns of uranyl stearate have, therefore, been investigated to characterise the structure of this soap in solid state. The intensities of diffracted X-rays as a function of diffraction angle 2θ for uranyl stearate are reproduced over the range of 3-65°. The interplanar spacings, d , have been calculated from the position of the intense peaks using well known Bragg's relationship. The calculated spacings together with relative intensities with respect to the most intense peaks are recorded in Table 1.

In X-ray diffraction patterns of uranyl stearate, numerous peaks are observed over the range of 3-65° of diffraction angle. These peaks are attributed to the diffraction of X-rays by the planes of metal ions (known as basal planes). The interplanar spacings calculated for 2nd, 4th, 6th, 7th, 11th and 13th order diffractions for uranyl stearate are recorded in Table 1. The appearance of the diffractions upto 13th order for uranyl stearate suggests good crystallinity for the soap. The average planar distance (long spacing) comes out to be 52.22 Å. Since this value of long spacing is almost equal to double the length of the stearic acid radical (stearate of the soap molecule), it is therefore suggested that the molecular axes are perpendicular to the basal plane. The uranyl ions, UO_2^{++} fit into spaces between oxygen atoms of the ionized carboxyl group without straining the bonds. Numerous diffractions peaks in the intermediate range of the

Table 1 : X-ray diffraction analysis of uranyl stearate

2θ	θ	$\text{Sin } \theta$	$\lambda/2 \text{ Sin } \theta$	d	n	I/I_0
3.372	1.686	0.0294	26.244	52.448	2	100.0
6.754	3.377	0.0589	13.089	52.356	4	56.01
10.831	5.060	0.0882	8.741	52.446	6	18.6
11.803	5.901	0.1082	7.500	52.500	7	20.4
19.021	9.570	0.1652	4.667	52.337	11	13.0
22.119	11.059	0.1918	4.020	52.260	13	39.3

Average value of $d = 52.244$

diffraction angles are also observed in the diffraction pattern of uranyl stearate and these are attributed to the diffraction of X-ray by planes of atoms of much smaller separation than the basal planes. The calculated spacings for 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 uranyl ions (UO_2^{++}) 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 (stearate) on both sides of each basal plane and that uranyl stearate possesses single layer structure as proposed by Vold and Hattiangdi (9).

Ultrasonic velocity measurement :

The solutions of uranyl stearate in a mixture of DMF and Benzene (50% V/V) exhibit a decrease in the ultrasonic velocity, v with increasing soap concentration (Table 2). Mathematically, this behavior can be explained. The variation of velocity with concentration, (dv/dc) depends on the concentration derivative of density, ρ and adiabatic compressibility, β as :

$$dv/dc = -v/2[1/\rho \gamma (d\rho/dc) + 1/\beta (d\beta/dc)] \dots\dots\dots (i)$$

The density and adiabatic compressibility are found to increase with increasing soap concentration (Table 2), the derivatives $d\rho/dc$ and $d\beta/dc$ are, therefore, positive with the result that the ultrasonic velocity according to the expression (i) must decrease with the increase in soap concentration (negative dv/dc). The results are in accordance with the data (10-12) reported for electrolytic

solutions involving heavy metal cations.

The plots of both density and ultrasonic velocity as a function of soap concentration, C (mole dm^{-3}) are characterized by an intersection of two straight lines at a point which corresponds to the critical micelle concentration, CMC (5.55×10^{-4} mol. dm^{-3}) of uranyl (II) stearate in DMF and Benzene mixture (50% V/V). The CMC is in agreement with the one obtained by conductance method. For dilute soap solutions (below the CMC), the variation of ultrasonic velocity with the soap concentration can be expressed (13): $v = v_0 + GC$, where v_0 is the ultrasonic velocity for the solvent and G is Garnsey's constant (13). The value of Garnsey's constant (-4.8×10^6) has been evaluated from v - C plot below the CMC. The v - c plot upon extrapolation to zero soap concentration gives the ultrasonic velocity, v_0 (1.368×10^5 cm sec^{-1}) for the solvent-mixture used in the present study. The extrapolated v_0 (1.368×10^5 cm sec^{-1}) is found to be consistent with the experimental value of ultrasonic velocity for the solvent-mixture (1.368×10^5 cm sec^{-1}).

The increase in adiabatic compressibility with increasing concentration of the soap solution may be attributed to the fact that the ions in the solutions furnished by the ionization of the metal soap (UO_2^{++} ; $\text{C}_{17}\text{H}_{35}\text{COO}^-$) are surrounded by a layer of solvent molecules having extremely poor interaction between them (solvent molecules and the ions), *i.e.* a lyophobic interaction (14). The adiabatic compressibility of the soap solutions is found to obey Bachem's relationship (15): $\beta = \beta_0 + AC + BC^{3/2}$; where β_0 is the adiabatic compressibility of the solvent, C is the molar concentration while A , B are constants. The plot of $\beta - \beta_0/C$ vs. $C^{1/2}$ is linear below the CMC and constants A and B as determined from the intercept and slope of the plot are 27.5 and 642.8, respectively.

The increase in intermolecular free length, L_f and

Table 2 : Ultrasonic velocity measurements of uranyl stearate in mixture of DMF-Benzene (50% V/V) at $40 \pm 0.05^\circ\text{C}$

Concentration $C \times 10^4$ (mol. dm^{-3})	Density, ρ (g.cm^{-3})	Velocity, v (cm.sec^{-1})	Adiabatic Compressibility $\beta \times 10^{10}$ ($\text{cm}^2 \text{dyne}^{-1}$)	Intermolecular free length, L_f (A_0)	Specific acoustic impedance $z \times 10^{-5}$ (C.G.S. Unit)	Apparent molar compressibility $\phi_k 10^5$ (CGS Unit)	Apparent molar volume $-\phi_v 10^{-3}$ ($\text{cm}^3 \text{mol}^{-1}$)
10	0.9131	1.3169	0.6315	0.509	1.2024	4.0804	4.3630
9	0.9122	1.3224	0.6268	0.508	1.2063	4.0836	4.8491
8	0.9116	1.3262	0.6237	0.507	1.2089	4.2371	3.6201
7	0.9108	1.3316	0.6192	0.505	1.2128	4.2650	3.0105
6	0.9102	1.3383	0.6134	0.502	1.2181	4.0658	2.5670
5	0.9098	1.3442	0.6083	0.500	1.2229	3.9190	2.3810
4	0.9095	1.3500	0.6033	0.498	1.2278	3.6590	2.3815
3	0.9092	1.3545	0.5994	0.497	1.2306	3.6260	2.3816
2	0.9089	1.3587	0.5951	0.495	1.2349	3.335	2.3860
1	0.9086	1.3641	0.5914	0.491	1.2390	3.0818	2.3864

decrease in acoustic impedance, z with increasing concentration (Table 2) can also be explained on the basis of lyophobic interaction between the ions (furnished by the ionization of the metal soap) and solvent molecules. The apparent molar volume increases ($-\phi_v$ decreases) for dilute soap solutions (below the CMC) while the same decreases ($-\phi_v$ increases) at higher concentrations (Table 2). Likewise, the apparent molar compressibility, ϕ_k is initially found to increase (upto $7.0 \times 10^{-4} \text{ mol dm}^{-3}$) while it decreases at higher soap concentration (Table 2). These facts also suggest that soap molecules in dilute solutions are ionized (weak ionization as confirmed by conductance method) into metal cations, UO_2^{++} and fatty acid anions, $\text{C}_{17}\text{H}_{35}\text{COO}^-$. These ions are surrounded by a thin film of solvent molecules bound and oriented towards the ions (weak ion-solvent interactions as inferred in the earlier part of the discussion). The orientations of solvent molecules around the ions is attributed to the influence of the electrostatic field of the ions and thus the internal pressure increases which reduces the compressibility for the soap solutions (Table 2), *i.e.* the solutions become harder to compress (16). For the solvent mixture of DMF-Benzene (50% V/V), the values of the parameters: $L_f^0(0.41 \text{ \AA}^3)$, $\beta_o(0.587 \times 10^{-10} \text{ cm}^2 \text{ dyne}^{-1})$, $\phi_k^0(2.39 \times 10^{-5} \text{ CGS Unit})$ and $\phi_v^0(-2.388 \times 10^3 \text{ cm}^3 \text{ mol}^{-1})$ have been evaluated by the extrapolation of the plots of these parameters versus soap concentration.

The significance of the present investigation lies in the fact that it succeeds in elucidating the structure of uranyl (II) stearate both in solid state and in solution which is so important for the assessment of the applied worth of the metal soap.

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