Thermochimica Acta, 131 (1988) 79–90
Elsevier Science Publishers B V , Amsterdam – Printed in The Netherlands

THERMAL AND SPECTRAL CHARACTERISATION OF COMPOUNDS OF THE URANYL ION WITH SURFACTANTS

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(Received 24 November 1987)

ABSTRACT

Compound formation was observed when acidic solutions of uranyl chloride were mixed with cationic alkyl pyridinium chloride surfactants above their critical micellar concentrations The compounds with dodecyl and hexadecyl pyridinium chlorides (LPC or CPC) were isolated in crystalline form, analysed for elemental composition, and IR and fluorescence spectra recorded The compounds have a molecular formula $S_2UO_2Cl_4$, where S is the alkyl pyridinium group X-ray diffraction showed the $(CP)_2UO_2Cl_4$ crystals to be triclinic TG, DTA and DSC studies show that $(CP)_2UO_2Cl_4$ melts reversibly at ~ 395 K and loses ligand at ~ 563 K The heat of fusion of the compound was found to be 60 94 ± 0 33 kJ mol^{-1} with a corresponding entropy change of 38 eu mol^{-1} Thermal decomposition studies in vacuo show that the uranyl ions sensitise the decomposition of the compound $(CP)_2UO_2Cl_4$ A probable mechanism by which the micellar environment may induce chlorocomplexation of the uranyl ion is discussed

INTRODUCTION

During an experimental study on micellar interactions in solutions containing uranyl ions, we noticed precipitation and crystallisation of some uranium-bearing compounds Experimental conditions have been standardised to obtain such compounds using cationic surfactants—dodecyl and hexadecyl pyridinium chlorides To our knowledge, this is probably the first time that surfactants containing large molecules of uranyl have been prepared The compounds have a general formula $S_2UO_2Cl_4$ (S = alkyl pyridinium). Their thermal and fluorescent properties have also been investigated, and results are presented in this paper.

EXPERIMENTAL

E Merck (puriss. grade) hexadecyl (cetyl) pyridinium chloride (CPC) was used as received Dodecyl (lauryl) pyridinium chloride (LPC) was obtained

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from HICO Industries (Bombay, India) and was purified as described in ref. 1. Triple-distilled water and reagent grade HCl were used for preparing the aqueous solutions of UO_2Cl_2 and the surfactants at appropriate acidities.

Optical absorption and fluorescence spectra were obtained using a Hitachi 330 recording spectrophotometer and Aminco Bowman spectrophotofluorimeter. The IR spectra in KBr pellets and Nujol mull were measured on a Perkin-Elmer 577 IR spectrophotometer.

Combustion techniques were used for the elemental analysis of C, H, N in the compounds. Their uranium content was determined by precipitating ammonium diuranate from aqueous solutions and igniting the precipitate to give U_3O_8 gravimetrically.

Since uranium interferes with the estimation of chloride ion, an aqueous solution of the compound was passed through Dowex 50 X cation exchange resin which retains both the alkyl pyridinium and uranyl cations. The eluate contains the chloride ion which was estimated by titration with standard $AgNO_3$ solution using K_2CrO_4 as an indicator. The chloride content of neat surfactant and UO_2Cl_2 solutions were also determined similarly.

The X-ray diffraction patterns were recorded on a Philips X-ray diffractometer Model PW 1010 using Cu *Kα* radiation. Thermogravimetric (TGA), differential thermal (DTA) and differential scanning calorimetric (DSC) analyses were carried out in argon and air atmospheres on instruments described in ref. 2. DSC studies were done on a Perkin-Elmer DSC 1B unit.

RESULTS

Compatibility studies

The compatibility of UO_2Cl_2 and the alkyl pyridinium chloride surfactant to remain in aqueous solution was first investigated over a range of component concentration at different acidities. At [HCl] < 1 M, the solutions are stable and the uranium is contained in aqueous micellar solutions for a considerable period. As the HCl concentration is increased and the surfactant concentration is kept above its critical micellar concentration (CMC) [3], phase separation of a yellow compound is observed. (CMC is the narrow range of concentration at which the surfactant starts aggregating to form micelles.) The entire amount of uranium could be precipitated in 2 M acid solutions containing 1:2 or higher UO_2^{2+}:surfactant stoichiometries. Even at low acidities, [HCl] < 1 M, slow crystallisation of the compound takes place over a period of several days. The crystals used in the present studies were obtained from solutions containing 0.1 M HCl, 0.02 M UO_2Cl_2 and 0.002 M CPC or 0.03 M LPC which were kept aside for 10 days. The surfactant concentrations chosen are marginally higher than their CMC

TABLE 1

Elemental analysis of synthesised compounds

Constituent	$(CP)_2UO_2Cl_4$		$(LP)_2UO_2Cl_4$	
	% Expected	% Found	% Expected	% Found
Carbon	49 4	50 19	43 22	45 32
Hydrogen	7 43	7 60	5 70	5 75
Nitrogen	2 73	2 94	6 30	6 43
Chloride	13 90	14 20	15 60	15 40
Uranium as U_3O_8	27 50	26 60	30 80	29 40

values, (CMC values for CPC $\cong 8 \times 10^{-4}$ M, LPC $\cong 1\ 5 \times 10^{-2}$ M [4]) but are deliberately lower than the stoichiometric requirements for complete extraction of uranium from the solution This was done in order to have high Poisson distribution, i e U/micelle, and thus encourage a slow crystallisation process at the micellar pseudophase

Elemental composition

The crystals obtained from low acid solutions as well as the precipitates obtained from molar acid solutions have the same composition for the same surfactant (Table 1) The elemental composition corresponds to a molecular formula $(CP)_2UO_2Cl_4$ and $(LP)_2UO_2Cl_4$ for the hexadecyl and dodecyl compounds

IR spectra

The IR absorption spectra of the precipitates and the crystals in KBr pellets and Nujol mull are identical, the salient features are summarised in Table 2 The spectra show typical absorption bands due to uranyl and alkyl pyridinium groups. The respective spectral bands are not much shifted (< 10 cm^{-1}) compared with their band position in neat reactant, viz CPC, LPC or UO_2Cl_2 [5] The O–U–O antisymmetric stretching frequency at 910 cm^{-1} is split into a doublet in the surfactant uranyl compound

Fluorescence spectra

Figure 1 shows the fluorescence spectra of the crystals of the compounds along with those of UO_2Cl_2 and $S_2UO_2Cl_4$ The sharp vibronic features of the crystals compare well with those of $K_2UO_2Cl_4$, in contrast with the structureless fluorescence from UO_2Cl_2 [6]

TABLE 2

Infrared frequencies of the synthesised compounds (cm^{-1})

UO_2Cl_2	LPC	$(LP)_2UO_2Cl_4$	$(CP)_2UO_2Cl_4$	Assignments [5]
In KBr pellets	2900	2900	2900	n-Alkyl residue
	2830	2830	2830	n-Alkyl residue
	1615	1615	1615	Ring stretching
	1505	1500(sh)	1505(sh)	Ring vibrations
	1470	1475	1474	Deformation vibr of pyridinium ring
	1450	1455	1455	n-Alkyl residue
	1360	1360	1370	
	1310	1305	1315	Deformation vibr of pyridinium ring
	1255	1255	1260	
	1200	1205	1210	
	1160	1165	1170	Deformation vibr of pyridinium ring
		1150(sh)	1160(sh)	
	1110	1110	1110	H-deformation in the plane of pyr ring
	1060	1060	1055	
	1055			
	1040	1045	1045	
	1020	1015	1015	
	910	905–915 (doublet)	905–915 (doublet)	O–U–O asym stretch
	760	765	775	CH out of stretch of pyr ring
	705	705	715	n-Alkyl residue
	675	675	680	CH out of plane deformation of pyr ring
In Nujol mull	252	250	250	O–U–O bending

Aqueous solutions of the surfactant–uranyl compound show no fluorescence. The UV/VIS absorption spectra of the aqueous solutions of the compounds show characteristic features due to alkyl pyridinium group in the UV (~ 260 nm) and UO_2^{2+} in the visible While no marked changes in either peak positions or the molar extinction coefficients have been observed, an enhancement in the uranyl absorption peaks was observed in methanolic solutions of the compound compared with the methanolic solutions of neat UO_2Cl_2 at the same 0 02 M concentrations ($\varepsilon = 20$) The two surfactant–uranyl compounds we prepared are insoluble in [HCl] > 2 M and solvents like acetone and ether, but are soluble in alcoholic solvents like methanol

The small IR shifts (< 10 cm^{-1}) indicate that the uranyl moiety is not bound directly to the CP or LP moiety From the above results the most likely formula for the compounds obtained is $(CP)_2UO_2Cl_4$ or $(LP)_2UO_2Cl_4$, and the compound can be looked upon as a double salt or adduct of CPC or LPC with UO_2Cl_2. Similar organic compounds of UO_2 with trialkylammonium salts are known, e g. $[(CH_3)_3N]_2[UO_2Cl_4]$ [7].

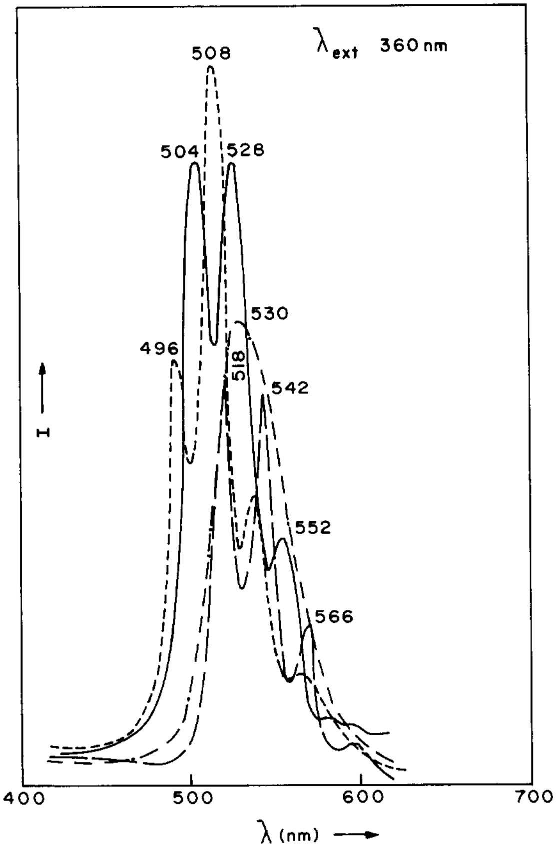

Fig 1 Fluorescence spectra of uranyl compounds (uncorrected) — — —, $(CP)_2UO_2Cl_4$, ——, $(LP)_2UO_2Cl_4$, - - , UO_2Cl_2, - - - - - -, UO_2SO_4

Thermal studies on $(CP)_2UO_2Cl_4$

Melting point studies show that neither CPC nor $(CP)_2UO_2Cl_4$ has a sharp melting point (355–363 K for CPC and 390–413 K for $(CP)_2UO_2Cl_4$) Thermogravimetric analyses (TGA) of the compound performed in argon and dry air yielded (Fig. 2) the following information The compound did not lose any weight in argon below 483 K. Between 483 and 613 K, however, a rapid weight loss was observed which corresponded to the complete loss of two CPC molecules, thus giving UO_2Cl_2 as a solid residue On further heating a small gradual weight loss was observed The corresponding thermogram recorded in air under identical conditions was much different from that recorded in argon (Fig. 2). The weight loss in air commenced earlier at ~ 458 K, but was complete only at ~ 698 K. There was no further gradual weight loss as had been observed in the thermogram recorded in argon The total and percentage weight losses were larger in air than in argon and corresponded to the formation of U_3O_8 An interesting feature of this curve

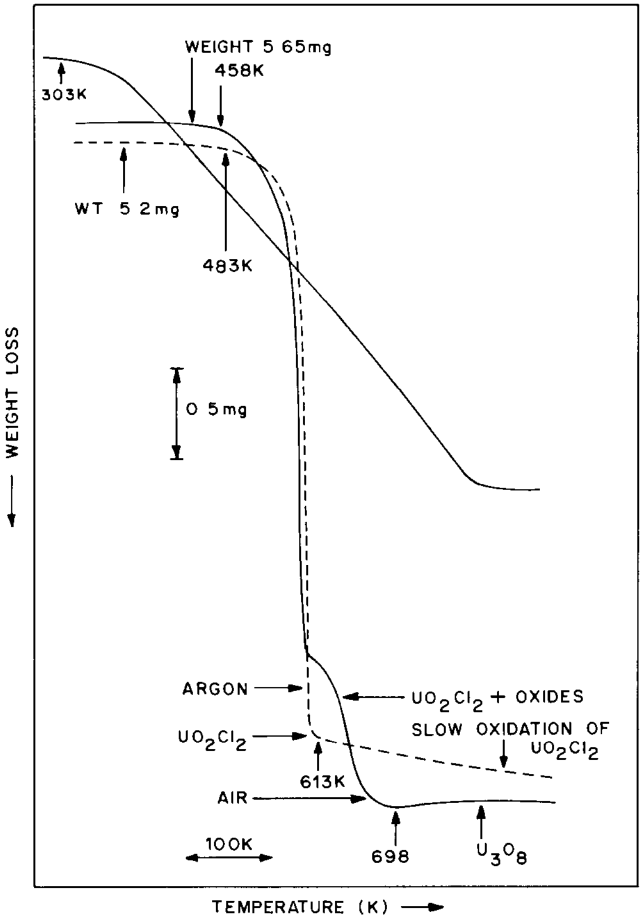

Fig 2 Thermogravimetric studies on $(CP)_2UO_2Cl_4$ ———, in argon, - - - - - -, in air

was an apparent intermediate step at 593 K which could not be assigned to the formation of any compound of definite molecular formula Attempts were made to stop the reaction isothermally at ~ 523 K and isolate the intermediate The black solid obtained at ~ 523 K when dissolved in 2 M HNO_3 showed only traces of Cl^- indicating that intermediary UO_2Cl_2 has transformed into a mixture of uranium oxides [8]

Differential thermal analysis (DTA) curves recorded on $(CP)_2UO_2Cl_4$ in argon and in air (Fig 3) differed in several aspects DTA curves recorded for argon yielded two endothermic peaks The first, in the region 383–443 K, corresponds to the melting of the solid and is reversible The peak is broad because the compound does not have a sharp melting point This was followed by another broad endothermic peak (~ 563 K) which could be attributed to the loss of ligand, i e CPC

The corresponding DTA trace for air showed an endothermic peak followed by two exothermic peaks While the endothermic peak was reversi-

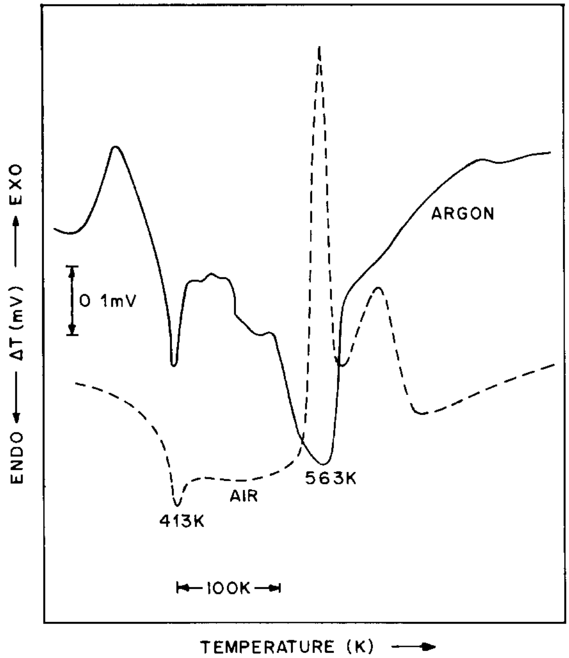

Fig 3 Differential thermal analysis studies on $(CP)_2UO_2Cl_4$ ———, in argon, - - - - - -, in air

ble and could be attributed to the melting of the compound in air, the nature of the exothermic peaks is quite complex The two peaks appear to result from a combination of decomposition and the concurrent oxidation of the liberated ligand and subsequent oxidation of UO_2Cl_2 to U_3O_8

It is interesting to note that the first exothermic peak in air occurs at about the same temperature (~ 563 K) as the second endothermic peak in argon The temperature of the second exothermic peak is found to be 593 K in the TG curve (Fig 3) in air These results therefore suggest that the thermal decomposition of the compound is accompanied by ligand oxidation (first exothermic peak) in air, and is followed by a successive oxidation of UO_2Cl_2 to U_3O_8 at 593 K

No peaks attributable to water of crystallisation were found, whereas compounds like $[(CH_3)_3N]_2[UO_2Cl_4]$ have 0 25 moles of water of crystallisation [7]

Differential scanning calorimetry studies showed that the heat of fusion of the compound is $60\,94 \pm 0\,33$ kJ mol^{-1} The corresponding entropy change at the melting point was 38 eu mol^{-1} The large change essentially arises from the surfactant moiety The DSC data for neat CPC showed that the heat of fusion of CPC is $65\,20 \pm 0\,33$ kJ mol^{-1}

A few experiments were done heating the compound in vacuo (10^{-3} torr) $(CP)_2UO_2Cl_4$ melted reversibly at 393–413 K, and around 563 K a white solid sublimed and was collected This white solid was found to be air- and moisture-sensitive, and its Nujol solution made from fresh material and transferred in a dry box gave IR peaks due to the pyridinium ring alone This solid is probably pyridinium hydrogen chloride, which itself is very hygroscopic The IR pattern of the residue displayed peaks due to uranyl and alkyl groups. Similar experiments with CPC alone showed that it melts at ~ 363 K, but no decomposition was noticed even on heating up to 598 K. These results indicate that uranyl ions sensitise the decomposition of $(CP)_2UO_2Cl_4$

X-ray studies

X-ray diffraction patterns of $(CP)_2UO_2Cl_4$ show that the material is crystalline and is different from both CPC and UO_2Cl_2 The *d*-spacings obtained from the diffraction pattern could be indexed on the basis of the

TABLE 3

d-Spacings, intensities and *h*, *k*, *l* values for $(CP)_2UO_2Cl_4$

d (obs) (Å)	(*h k l*)	I/I_0
10 05	0 1 0	100
7 69	1 0 0	8
6 73	1 0 1	36
6 33	$\bar{1}$ 0 1	8
5 22	$\bar{1}$ $\bar{1}$ 1	13
5 07	1 $\bar{2}$ 2	15
4 63	1 0 2	18
4 13	1 $\bar{2}$ 3 0 2 1 2 $\bar{1}$ 1	10
3 66	$\bar{2}$ 2 0	8
3 507	$\bar{1}$ 3 0 $\bar{1}$ 0 3	13
3 363	2 $\bar{2}$ 3 2 0 2 0 3 0 0 1 3	15
3 132	$\bar{1}$ 1 3	8
3 038	$\bar{1}$ 3 1	10
2 734	3 $\bar{1}$ 1	10
2 515	0 4 0 3 $\bar{3}$ 3	13
2 442	$\bar{1}$ $\bar{3}$ 4 $\bar{3}$ 3 0	8

triclinic unit cell with $a = 8.299 \pm 0.014$, $b = 11.744 \pm 0.053$, $c = 13.570 \pm 0.0310$ and $\alpha = 115.45 \pm 0.25°$, $\beta = 77.55 \pm 0.25°$ and $\gamma = 111.73 \pm 0.22°$. The cell volume was estimated to be 1107 Å^3. The observed *d*-values and the corresponding indices are listed in Table 3.

DISCUSSION

The above results show that well-defined crystalline compounds are obtained by the interaction of uranyl chloride with the alkyl pyridinium chloride surfactants. At the surfactant concentrations higher than their CMC values (LPC ~ 1.5×10^{-2} M, CPC ~ 8×10^{-4} M), the surfactants aggregate as micelles, with aggregation numbers 40 and 80 for LPC and CPC, respectively [2]. Since no discernible compound formation at surfactant concentrations below CMC was observed, it is concluded that compound formation is initiated at the micellar pseudophase, the bulk uranyl concentration (0.02 M typically) acting as a reservoir of uranium to the micellar interface. The micelles themselves are aggregates (80 molecules for CPC and 40 for LPC), with alkyl chains forming the non-polar core and the polar pyridinium groups projecting out in the aqueous phase (Fig. 4). The cationic micelle is surrounded by a Stern layer of Cl$^-$ anions. The localised concentration of Cl$^-$ ions in the Stern layer is quite high, despite being

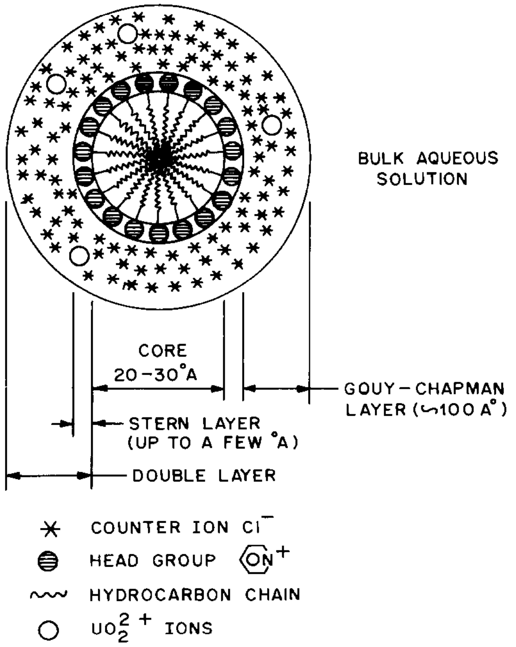

Fig. 4. Schematic representation of cationic micelle–UO_2^{2+} interactions.

somewhat diffuse compared with the micelle itself. For example, at [S] = 0 04 M we have an average concentration of micelles $[M] \cong 5 \times 10^{-4}$ M The concentration of CPC within a spherical micelle of mean diameter ~ 2 5 nm is ~ 16 M, and the chloride concentration in the vicinity of the Stern layer is < 5 M We consider that the abundant availability of chloride ions in the ionic double layer provides a means of chlorocomplexion of uranyl ions in the vicinity of the cationic micelle The random diffusion of uranyl ions in the bulk aqueous phase brings the uranyl ion to the double layer

$$UO_2^{2+} + n\ Cl^- \underset{2}{\overset{1}{\rightleftharpoons}} UO_2^{2+}\text{-}Cl_n^- \xrightarrow{3} [UO_2Cl_4]^{2-}$$

The forward entry and reverse escape rates provide a residence time for the uranyl ion in the domain of the ionic double layer During this residence time the chlorocomplexion of step 3 becomes possible, and the anionic complex is exposed to the coulombic interaction of the cationic micelle Since the cationic micelle–anionic Stern layer is a complementary composite, the lifetime for the Coulombic interactions is sufficiently large for the $[UO_2Cl_4]^{2-}$ complex to be stabilised as $(CP)_2UO_2Cl_4$ or transform itself as adduct $(CPCl)_2UO_2Cl_2$.

Although the ionic double layer is relatively rich in chloride ions, compared with the bulk aqueous phase, it is not sufficiently so to discourage the escape rate (step 2) At low HCl concentrations uder such conditions, only a very small fraction of the uranyls undergo complexation These provide nucleation sites for slow crystallisation of the uranyl–surfactant compound over several days

At higher [HCl] > 1 M concentrations, a more favourable distribution of Cl^- between ionic double layer and bulk aqueous phase occurs, promoting rapid formation of the stabilised complex via step 3 In other words, the relative dynamics of escape (step 2) and complexation (step 3) are determined by how "loose" is the $UO_2^{2+}\text{-}Cl_n^-$ intermediate The greater is the Cl^- concentration in the double layer, the closer will be the distance between Cl^- and UO_2^{2+} ions, and the higher will be its survival rate for undergoing inner sphere complexation

It must be mentioned that the conventional chlorocomplexation of uranyl requires high HCl concentration (> 12 M) In this work we have demonstrated that the availability of a micellar double layer facilitates complexation at much lower bulk HCl concentrations (0 5–2 M)

The presently reported $(CP)_2UO_2Cl_4$ and $(LP)_2UO_2Cl_4$ compounds are probably akin to known dialkali tetrauranates The compounds are highly fluorescent with a vibronic structure similar to that of $K_2UO_2Cl_4\ H_2O$ It is interesting to note that with the lower alkali cations (e g Na, K), the chlorouranates have some water of crystallisation With bulkier alkali cation (like Cs) the compounds stabilise without any water of crystallisation [4] The bulky hexadecyl or dodecyl pyridinium cations provide sufficient stability since our compounds have no water of crystallisation, as shown by TG experiments The $(CP)_2UO_2Cl_4$ is triclinic like the caesium compound, and we have plans to further determine its optical properties

CONCLUSIONS

Cationic surfactants (alkyl pyridinium chlorides) form yellow compounds with uranyl ions in aqueous solution above their CMC values From the IR spectra, elemental analysis and fluorescence behaviour we conclude that their chemical formula is $S_2UO_2Cl_4$ The compounds have no water of crystallisation X-ray studies have been done on $(CP)_2UO_2Cl_4$ the compound is triclinic and the cell constants are given Thermal studies show that $(CP)_2UO_2Cl_4$ has no sharp melting point but the melting is reversible On subsequent heating the ligand is lost and oxides of uranium are obtained as products When heated in the presence of air, oxygen facilitates the burning of ligand to yield U_3O_8 and the intermediate step is probably the formation of UO_2Cl_2 The heat of fusion of $(CP)_2UO_2Cl_4$ is found to be 60 94 ± 0 33 kJ mol^{-1}, and the corresponding entropy change at the melting point is 38 eu mol^{-1} Bulk heating studies in vacuo suggest that uranyl ions catalyse the decomposition of $(CP)_2UO_2Cl_4$, one of the products being pyridinium hydrogen chloride The probable mechanism of chlorocomplexation of uranium at the micellar interface is discussed

ACKNOWLEDGEMENTS

The authors thank Dr R M Iyer, Director, Chemical Group BARC, Dr. J P Mittal and Dr K S Venkteswarlu for their interest in this work Thanks are also due to The Head, Analytical Chemistry Division BARC, for providing elemental analyses and to Shri K V Muralidharan for help in X-ray work

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