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Comparative UV−Vis Studies of Uranyl Chloride Complex in Two Basic Ambient-Temperature Melt Systems: The Observation of Spectral and Thermodynamic Variations Induced via Hydrogen Bonding

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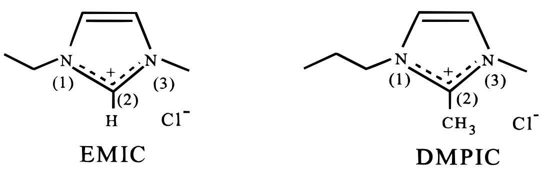
Extensive studies have been made of the absorption spectra of dilute solutions of uranium(IV,VI) compounds in various solvent media.[1−5] These studies provide structural information concerning the coordination environment of a uranium species in different solvent systems. It is known that the electronic f−f and charge-transfer transitions of uranium(IV) hexahalide and uranyl halide complexes are very sensitive to variations in the properties of a solvent system.[1c,6] Since these electronic transitions are electric-dipole forbidden in nature,[4] the observed electronic absorption bands arise from (a) magnetic-dipole transitions; (b) electric-multipole transitions; and/or (c) relaxation of the selection rule for electric-dipole transitions. Relaxation of the selection rule can be thought of as either a static or a vibronic interaction. Hydrogen bonding between uranium(IV) and -(VI) halide complexes and solvent is an example of the static interaction, which can induce a distortion of the symmetry of the uranium ion thereby resulting in the relaxation of the selection rule. Relaxation of the selection rules as described above is considered to be one rationale for the sensitivity of the vibronic absorption bands of uranium(IV,VI) compounds to variation in the hydrogen-bonding properties of different solvents.

In the case of uranyl halide complexes, the linear oxo group (UO_2^{2+}) is directly involved in the hydrogen bonding via the uranyl group (U═O) with H−X groups (e.g., H−O; H−N) of the solvent.[1c] The high oxidation state of the uranium center (+6) makes these hydrogen bonds derive appreciable thermodynamic stability. Recently, H−N hydrogen bonding has been employed in the design of new ligands which are capable of discriminating and sequestering the uranyl ion from other metal ions in solution.[7] The oxo group is "recognized" using an intramolecular hydrogen bond from the ligand to the uranyl oxo group. This new ligand-design principle has been described as stereognostic coordination chemistry by Raymond and coworkers.[7]

Scheme 1



The importance of hydrogen bonding in an ambient-temperature melt composed of aluminum chloride and 1-ethyl-3-methylimidazolium chloride (EMIC) has been described in the literature.[8] On the basis of IR measurements, Osteryoung *et al.*[8a] proposed that two-species, ion-pair interactions occur in the basic melt, possibly involving distortion of the imidazolium ring with hydrogen bonding between the hydrogen on the C(2) carbon atom (Scheme 1) of the ring and the counteranions. The strong hydrogen-bonding capability of the hydrogen covalently bonded to the C(2) is due to the formal positive charge of C(2).[9] The first objective of the present work is to verify the importance of the hydrogen on C(2) of EMIC in hydrogen-bond formation between the room-temperature melt and uranyl solutes. The substitution of this hydrogen with a CH_3 group should significantly reduce the hydrogen-bonding capability of the melt. This variation in the hydrogen-bonding capability should influence the optical spectrum of uranyl ion dissolved in the melt. Accordingly, we propose to use the optical spectrum of uranyl ion to probe the variation of the hydrogen-bonding capability of the different ambient-temperature melts. Our second objective is to investigate what effect this variation of the hydrogen-bonding capability has on the thermodynamic properties of melts (in our case, the solubility of UO_3 in melts). We seek to demonstrate the use of hydrogen bonding to tailor the solubility of the uranyl compounds in nonaqueous molten salts. The melts chosen for our investigations are composed of either EMIC or 1,2-dimethyl-3-propylimidazolium chloride (DMPIC, Scheme 1) mixed with $AlCl_3$.

Uranium trioxide was prepared according to a standard literature procedure.[10] $AlCl_3$ was purified as described previously.[11] 1-Ethyl-3-methylimidazolium chloride (EMIC) was synthesized according to the procedure of Smith *et al.*[12] DMPIC was synthesized according to the procedure of Peirsma and Wilkes[13a] and Gifford and Palmisano.[13b] All molten salt solutions were prepared under a helium atmosphere in a drybox with <1 ppm moisture. All melt solutions were evacuated under

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(1) (a) Gruen, D. M.; McBeth, R. L. *J. Inorg. Nucl. Chem.* **1959**, *9*, 290. (b) Morrey, J. R. *Inorg. Chem.* **1963**, *2*, 163. (c) Ryan, J. L. *Inorg. Chem.* **1964**, *3*, 211. (d) Dewaele, R.; Heerman, L.; D'Olieslager, W. *J. Electroanal. Chem.* **1982**, *142*, 137. (e) Toth, L. M.; Felker, L. K.; Hunt, R. D.; Brunson, R. R.; Loghry, S. L. *Sep. Sci. Technol.* **1993**, *28*, 781.

(2) Anderson, C. J.; Deakin, M. R.; Choppin, G. R.; D'Olieslager, W.; Heerman, L.; Pruett, D. J. *Inorg. Chem.* **1991**, *30*, 4013.

(3) Clark, D. L.; Hobart, D. E.; Neu, M. P. *Chem. Rev.* **1995**, *95*, 25.

(4) (a) Denning, R. G. Electronic Structure and Bonding in Actinyl Ions. *Struct. Bonding* **1992**, *79*, 216. (b) Rabinowitch, E.; Belford, R. L. *Spectroscopy and Photochemistry of Uranyl Compounds*; Macmillan: New York, 1964.

(5) (a) Dai, S.; Xu, W.; Metcalf, D. H.; Toth, L. M. *Chem. Phys. Lett.* **1996**, *262*, 315. (b) Dai, S.; Toth, L. M.; Del Cul, G. D.; Metcalf, D. H. *J. Phys. Chem.* **1996**, *100*, 220. (c) Dai, S.; Toth, L. M.; Del Cul, G. D.; Metcalf, D. H. *Inorg. Chem.* **1995**, *34*, 412. (d) Metcalf, D. H.; Dai, S.; Del Cul, G. D.; Toth, L. M. *Inorg. Chem.* **1995**, *34*, 5573.

(6) Dai, S.; Toth, L. M.; Del Cul, G. D.; Metcalf, D. H. In *Proceedings of the Ninth International Symposium on Molten Salts*; Hussey, C. L., Newman, D. S., Mamantov, G., Ito, Y., Eds.; Electrochemical Society: Pennington, NJ, 1994; p 308.

(7) (a) Franczyk, T. S.; Czerwinski, K, R.; Raymond, K. N. *J. Am. Chem. Soc.* **1992**, *114*, 8138. (b) Walton, P. H.; Raymond, K. N. *Inorg. Chim. Acta* **1995**, *240*, 593.

(8) (a) Tait, S.; Osteryoung, R. A. *Inorg. Chem.* **1984**, *23*, 4352. (b) Fannin, A. A.; King, L. A.; Levisky, J. A.; Wilkes, J. S. *J. Phys. Chem.* **1984**, *88*, 2609.

(9) Dymek, C. J.; Stewart, J. J. P. *Inorg. Chem.* **1989**, *28*, 1472.

(10) Hoekstra, H. R.; Siegel, S. *J. Inorg. Nucl. Chem.* **1961**, *18*, 154.

(11) Marassi, R.; Chambers, J. Q.; Mamantov, G. *J. Electroanal. Chem. Interfacial Electrochem.* **1976**, *69*, 345.

(12) Smith, G. P.; Dworkin, A. S.; Pagni, R. M.; Zingg, S. P. *J. Am. Chem. Soc.* **1989**, *111*, 525.

(13) (a) Peirsma, B. J.; Wilkes, J. S. Frank J. Seiler Laboratory Technical Report FJSRL-TR-82-0004, ADA 122, 840 (September 1982). (b) Gifford, P. R.; Palmisano, J. B. *J. Electrochem. Soc.* **1987**, *134*, 611.

S0020-1669(97)00251-6 CCC: $14.00

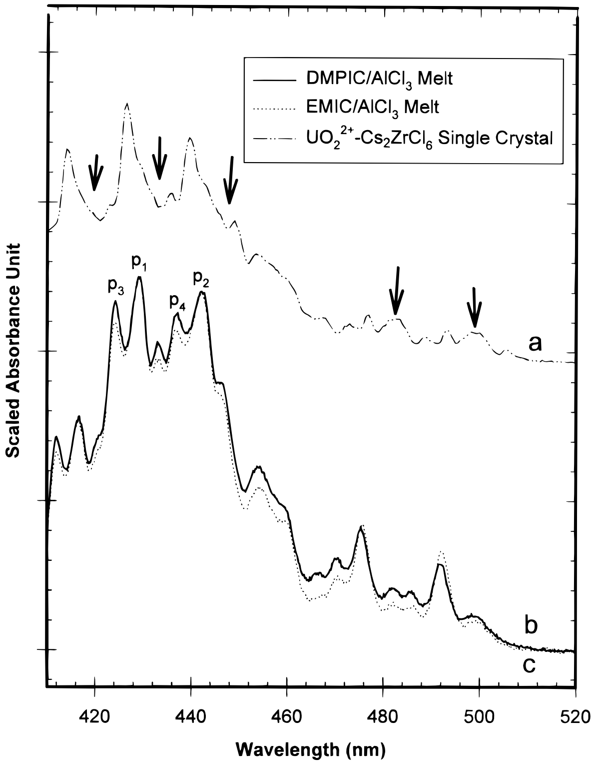

Figure 1. UV−vis electronic absorption spectra of $UO_2Cl_4^{2-}$ in (a) a Cs_2ZrCl_6 single crystal, (b) an $AlCl_3$/EMIC melt, and (c) an $AlCl_3$/DMPIC melt.

vacuum overnight to remove potential proton impurities.[14a] There were no differences between the spectrum measured using the melt with phosgene pretreatment and that without phosgene pretreatment.[14b] Crystals of Cs_2ZrCl_6 doped with $UO_2Cl_4^{2-}$ were grown by the Bridgeman technique from melts at 850 °C containing a stoichiometric mixture of $ZrCl_4$ and CsCl with 1 mol % of $Cs_2UO_2Cl_4$.[5c] UV−visible spectra were measured at room temperature with a Cary 14H scanning spectrophotometer interfaced to a PC for data collection and analysis via On-Line Instrument Systems (OLIS) software and hardware. Samples were loaded into a quartz cuvette (1 cm path length) with a threaded glass cap.

Figure 1 shows the UV−visible spectra obtained by dissolving UO_3 into basic melts composed of EMIC/$AlCl_3$ ($AlCl_3$:EMIC = 48:52) and DMPIC/$AlCl_3$ ($AlCl_3$:DMPIC = 48:52), along with that of $UO_2Cl_4^{2-}$ doped in a Cs_2ZrCl_6 single crystal (Figure 1a). The spectra obtained by dissolving UO_3 into the two basic melts are normalized to the same maximum intensity and overlaid together in order to highlight the differences between them.

A basic melt is defined as one containing a molar excess of the organic salt relative to $AlCl_3$ while an acidic melt contains a molar excess of $AlCl_3$.[15] Excess chloride ion in melts acts as a Lewis base. The spectra obtained by dissolving UO_3 in either melt (Figure 1b,c) are independent of the pCl as long as the mole ratio of $AlCl_3$/EMIC or $AlCl_3$/DMPIC is less than 1. Furthermore, the general band patterns observed in the two spectra (Figure 1b,c) are very similar to that of $UO_2Cl_4^{2-}$ in polar solvents such as concentrated HCl solution.[1c] Accordingly, we assign the spectra in Figure 1b,c to those of uranyl chloride species in these basic melts.

Although the spectra for the melts are similar to that of $UO_2Cl_4^{2-}$ doped into Cs_2ZrCl_6 (Figure 1b,c vs 1a), the relative intensity of the vibronic bands changes greatly between the two sets of spectra. $UO_2Cl_4^{2-}$ is located in perfect octahedral sites in the Cs_2ZrCl_6 crystal and experiences only weak Coulombic interactions with its surroundings. The intensities of vibronic transitions involving the simultaneous excitation of the uranyl symmetric stretch during electronic transitions are expected to be weak due to the forbiddenness of electric-dipole transitions.[4a] The observed intensities are mostly induced by magnetic-dipole transitions.[4a] However, these groups of vibronic transitions can become electric-dipole allowed via a symmetry distortion (static coupling) induced by intermolecular interactions such as hydrogen bonding.[4a,6,16] Accordingly, they are very sensitive to the local environment of the uranyl ion.[1b] The selection rule concerning electric-dipole transitions can also be relaxed via intramolecular vibronic coupling (dynamic coupling) through simultaneous excitation of unsymmetric vibrations during electronic transitions.[17,18] The intensities of the corresponding vibronic transitions are relatively insensitive to the variation of solvents because of the intramolecular nature of the dynamic mechanism. Thus, the intensity *ratios* of vibronic bands involving excitation of the uranyl *symmetric* stretch to those involving *unsymmetric* stretches in the single crystal should be much smaller than vibronic bands in melt systems where the interaction is expected to be much stronger and to involve not only Coulombic interactions but also interactions with solvent molecules. As is clearly seen in Figure 1, this assertion is consistent with the experimental observation that the spectrum of $UO_2Cl_4^{2-}$ in the single crystal has a group of vibronic transitions (marked with arrows in Figure 1) with lower relative intensities than those in the spectra of $UO_2Cl_4^{2-}$ in the room-temperature melts. Accordingly, the above comparison between the spectrum of the single crystal where no strong intermolecular interactions exist and those of the melts where strong interaction may exist identifies the vibronic bands associated with the simultaneous excitations of the symmetric (e.g., p_1 and p_2 in Figure 1) and unsymmetric vibrations (p_3 and p_4 in Figure 1). Due to the broad line width and overlaps of several electronic transitions, it is very difficult to identify the origins of the transitions in these room-temperature spectra. However, we can assign the bands in the range from 22 000 to 25 000 cm^{-1} to transitions $\Sigma_g^+ \rightarrow \Phi_g$ and $\Sigma_g^+ \rightarrow \Delta_g$, while the bands lower than 22 000 cm^{-1} can be attributed to the transitions of $\Sigma_g^+ \rightarrow \Pi_g$ and $\Sigma_g^+ \rightarrow \Delta_g$. These assignments are based on detailed low-temperature spectral studies by Denning.[4a]

The intensity ratios of vibronic bands involving only simultaneous excitation of symmetric vibrations to those involving unsymmetric vibrations can be used as a gauge to measure the strength of the interaction of $UO_2Cl_4^{2-}$ with its surroundings.[1c] This interaction scale is, to some extent, analogous to the PY scale used to probe solvent polarity in organic chemistry.[18,19] The greater the values of the ratios, the stronger the interaction of $UO_2Cl_4^{2-}$ with its surroundings. Accordingly, a qualitative measure of the difference in hydrogen bonding between $AlCl_3$/

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(14) (a) Noel, M. A. M.; Rrulove, P. C.; Osteryoung, R. A. *Anal. Chem.* **1991**, *63*, 2892. (b) Sun, I. W.; Ward, E. H.; Hussey, C. L. *Inorg. Chem.* **1987**, *26*, 4309.

(15) (a) Osteryoung, R. A. In *Molten Salts Chemistry*; Mamantov, G., Marrassi, R., Eds.; NATO ASI Series C: Mathematical and Physical Science, Vol. 202; Reidel: Dordrecht, 1987; p 329. (b) Hussey, C. L. In *Advances in Molten Salt Chemistry*; Mamamtov, G., Mamantov, C. B., Eds.; Elsevier: Amsterdam, 1983; Vol. 5, p 185.

(16) (a) Liehr, A. D.; Ballhausen, C. J. *Phys. Rev.* **1957**, *106*, 1161. (b) Hitchman, M. A. In *Transition Metal Chemistry*; Melson, G. A., Figgis, B. N., Eds.; 1985; Vol. 9.

(17) Dai, S.; Toth, L. M.; Del Cul, G. D.; Metcalf, D. H. *Chem. Phys.* **1995**, *200*, 271.

(18) Karpovich, D. S.; Blanchard, G. J. *J. Phys. Chem.* **1995**, *99*, 3951.

(19) Sun, Y. P.; Ma, B.; Bunker, C. B. *J. Chem. Soc., Chem. Commun.* **1994**, 2099.

EMIC and $AlCl_3$/DMPIC melts can be determined by a defined parameter which is a function of these ratios. Since the origin of the intensity variation in our uranyl spectra is the same as that of the PY scale in organic chemistry,[18,19] we use the similar intensity ratio formula I_{p1}/I_{p3} or I_{p2}/I_{p4} as the PY scale to measure the degree of the interaction, where I_{p1}, I_{p2}, I_{p3}, and I_{p4} are adsorption intensities of bands p_1, p_2, p_3, and p_4. The parameter determined from intensity ratios of the band p_1 to p_3 and band p_2 to p_4 for spectrum b in Figure 1 are 1.088 and 1.084, which are larger than the corresponding values (1.002 and 1.031) for spectrum c. This indicates that $UO_2Cl_4^{2-}$ interacts much more strongly with EMI^+ than $DMPI^+$. The enhancement in the interaction for EMI^+ can be attributed to its ability to form hydrogen bonds through the hydrogen at C(2).

The UV−visible spectrum of $UO_2Cl_4^{2-}$ can also be used to quantitatively determine the solubility of UO_3 in $AlCl_3$/EMIC and $AlCl_3$/DMPIC melts. Molar absorption extinction coefficients for UO_3 dissolved in these melts were measured for samples made to ensure complete dissolution of the solute. With the absorption coefficients thus determined, the solubilities of UO_3 in the melt at various temperatures can be accurately determined via the Lambert−Beer law and are listed in Table 1. The solutions used in the solubility determination were equilibrated with solid UO_3 for 48 h before measurement. As seen from Table 1, the solubility of UO_3 in the DMPIC/$AlCl_3$ melt is much smaller than that in the EMIC/$AlCl_3$ melt at all temperatures investigated. This difference in solubility of UO_3 correlates well with the difference in hydrogen-bonding capabilities for these two melt systems. Enhancement of the solubility of a solute through tailoring of the hydrogen-bonding properties of solvents is, to some extent, identical to the strategy used by Raymond and co-workers[7] to increase the complexation constants of ligands via the introduction of hydrogen bonding. The above countercation effect on the solubility of the anionic solute species in the room-temperature melts is a further extension of our recent observation that the solubilities of oxides in inorganic high-temperature ionic chloride melts strongly depend on the interaction between the solute chloride complex and the solvent cation.[5b]

Table 1. Solubilities of UO_3 in $AlCl_3$/EMIC (48/52) and $AlCl_3$/DMPIC (48/52) Melts at Two Temperatures

	solubility (M)	
temp, °C	$AlCl_3$/EMIC	$AlCl_3$/DMPIC
55	1.716×10^{-2}	nondetectable
65	2.458×10^{-2}	1.010×10^{-2}

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