Co-ordination Behaviour of Dioxouranium(VI) Nitrate in Water–Acetone Mixtures

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Potentiometry using nitrate ion-selective electrodes, Raman, ^{1}H n.m.r. and u.v.–visible absorption spectroscopy have been used to study the co-ordination behaviour of dioxouranium(VI) nitrate in water–acetone mixtures over the complete solvent composition range. At the concentrations studied (up to 0.14 mol dm^{-3}) there was no evidence of UO_2^{2+}–NO_3^- complexing in pure water, and the co-ordination species is believed to be $[UO_2(H_2O)_5]^{2+}$. Complexing starts to occur above 60% (v/v) acetone–water, probably *via* a two-step equilibrium, and at high acetone concentrations the only significant complex species present is suggested to be $[UO_2(NO_3)_2(H_2O)_2]$.

Dioxouranium(VI) nitrate hexahydrate is, perhaps, the compound most frequently chosen to study the chemistry, photochemistry, and electrochemistry of the dioxouranium(VI) (uranyl) ion in solution. In large part this stems from its solubility in water and various organic solvents, and from the relatively high degree of purity available. Its structure in the solid state is well established by both *X*-ray[1] and neutron[2] diffraction to consist of an axial O–U–O system surrounded in the equatorial plane by two bidentate nitrate ligands and two water molecules. However, perhaps surprisingly, rather less is known about the co-ordination species present in solutions of this compound.

In an extensive series of studies on the electrical conductivity of uranyl nitrate in a variety of organic solvents, Jezowska-Trzebiatowska and co-workers[3,4] demonstrated that the nitrate ions were normally bonded to UO_2^{2+}. Infrared[5] and Raman[6] spectroscopic studies of relatively concentrated aqueous solutions of $UO_2(NO_3)_2 \cdot 6H_2O$ also suggest co-ordination of dioxouranium(VI) by the NO_3^- ion. Dynamic and static fluorescence studies on aqueous solutions have provided further evidence for such complexing.[7,8] In contrast, a relatively low degree of UO_2^{2+}–NO_3^- binding in water is suggested by the values of the stability constants (typically log K between -0.5 and -1).[9] In addition, spectroscopic evidence has recently been presented to support the presence of different co-ordination species in aqueous and alcoholic solutions of this compound.[10]

In connection with our studies on the photochemistry of the dioxouranium(VI) ion in aqueous solution,[11] we have been interested in its solvent exchange rate. This requires a knowledge of the co-ordination species. We report here the application of a variety of techniques to the determination of the complexes present in solutions of $UO_2(NO_3)_2 \cdot 6H_2O$ in various acetone–water mixtures.

Results and Discussion

A potentiometric study of solutions of uranyl nitrate (0.07—0.14 mol dm^{-3}) in pure water using a nitrate ion-selective electrode gave a free nitrate ion concentration exactly twice the uranyl salt concentration. Thus under these conditions there was no evidence for any significant UO_2^{2+}–NO_3^- complexing, in agreement with published formation constants for this system.[9] In contrast, potentiometric studies of uranyl nitrate (0.14 mol dm^{-3}) in 96.7% (v/v) acetone–water revealed a free nitrate ion concentration of 5.3 ($\pm$3.8) $\times$ 10^{-4} mol dm^{-3}, indicating that virtually all the NO_3^- is complexed by UO_2^{2+}. The large error limits in this value are probably associated with the degradation of the polymer membrane of the ion-selective electrode. However, the magnitude compares favourably with the value $[NO_3^-]_{free}$ = 8.3 $\times$ 10^{-4} mol dm^{-3} calculated for this system from the stability constant determined conductometrically in pure acetone.[3] Potentiometric measurements were also made on solutions of dioxouranium(VI) nitrate in various acetone–water mixtures (Table). These show that complex formation starts to occur above about 60% (v/v) acetone.

Table. Potentiometric measurements of the free nitrate ion concentration for solutions of dioxouranium(VI) nitrate (0.14 mol dm^{-3}) in acetone–water

Acetone (%, v/v)	$[NO_3^-]_{free}$/mol dm^{-3}
0	0.28
60.0	0.28
65.0	0.10
70.0	6.5 $\times$ 10^{-2}
75.0	7.0 $\times$ 10^{-2}
96.7	5.3 $\times$ 10^{-4}

Indications of the type of co-ordination were obtained from Raman spectral studies. Spectra were recorded of solutions of uranyl nitrate (0.14 mol dm^{-3}) in water, acetone, and various mixtures of these solvents. Typical spectra are shown in Figure 1. Comparison of the spectrum in water with that of nitric acid (0.28 mol dm^{-3}) indicated no detectable complexing of NO_3^-, the only difference being the presence of a band at 872 cm^{-1} in the former case assigned to the ν_1 mode of the UO_2^{2+} group.[5,6] Similarly, spectra in 60% (v/v) acetone–water support the potentiometric result that there is no significant UO_2^{2+}–NO_3^- co-ordination. However, the spectra in 96.7% (v/v) acetone–water show a number of changes, with a slight decrease in the ν_1 stretching frequency of UO_2^{2+} to 866 cm^{-1}, replacement of the free nitrate peak at 1 048 cm^{-1} by a band at 1 035 cm^{-1} assigned to the ν_1 vibration of co-ordinated nitrate, and the appearance of a band at 1 540 cm^{-1} and a shoulder at 750 cm^{-1}, which are attributed to the ν_3 and ν_4 vibrations of bidentately bound NO_3^-.[6] These values are close to those observed with molten uranyl nitrate hexahydrate,[6] and, taken with the potentiometric data, are consistent with UO_2^{2+} being bound to two bidentate NO_3^- groups.

If solvent exchange is sufficiently slow, ^{1}H n.m.r. spectroscopy provides a convenient method for determining cation hydration numbers, and 60- and 100-MHz n.m.r. spectra of solutions of uranyl nitrate at low temperature and high salt and acetone concentrations suggest a hydration number of *ca.* 2.[12,13] We

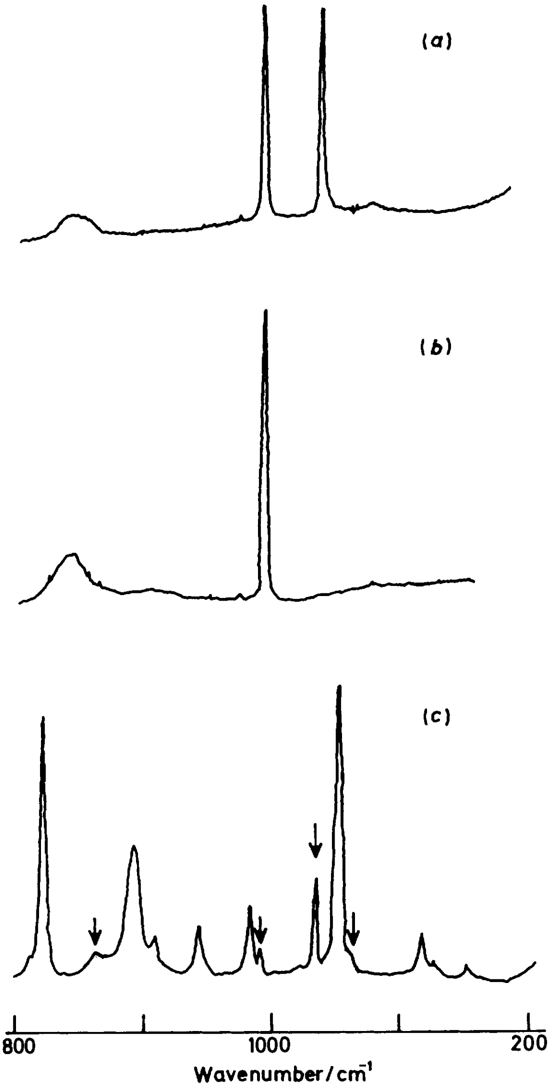

Figure 1. Raman spectra of (*a*) dioxouranium(VI) nitrate (0.14 mol dm^{-3}) in water, (*b*) nitric acid (0.28 mol dm^{-3}) in water, and (*c*) dioxouranium(VI) nitrate (0.14 mol dm^{-3}) in 96.7% (v/v) acetone–water. In spectrum (*c*) the bands resulting from the dioxouranium(VI) species are indicated with arrows

have repeated these experiments using 200-MHz ^{1}H n.m.r. spectroscopy and for solutions of $UO_2(NO_3)_2$ (0.14 mol dm^{-3}) in 93.6% (v/v) [$^2H_6$]acetone–water at −83 to −88.5 °C observed similar spectra[14] to those reported by Fratiello *et al.*,[12] with the signal of co-ordinated water appearing 9.4 p.p.m. downfield from that of the acetone internal standard. From the integrals of the co-ordinated and bulk water signals we confirm that an average of 1.9 ($\pm$0.2) water molecules are co-ordinated per dioxouranium(VI) complex. It is worthy of note that this value is slightly higher than that reported previously for this salt concentration (1.3).[12] However, we favour our value, and concord with Shcherbakov and Shcherbakova[13] that this low value reflects the lower sensitivity of the spectrometer used in that study. These results all suggest that at high acetone concentrations the salt exists as $[UO_2(NO_3)_2(H_2O)_2]$, in agreement with conductometric studies.[3] Magnetic circular dichroism (m.c.d.) measurements[15] also favour this structure, which is likely to have a co-ordination geometry similar to that observed in the solid state.[1,2]

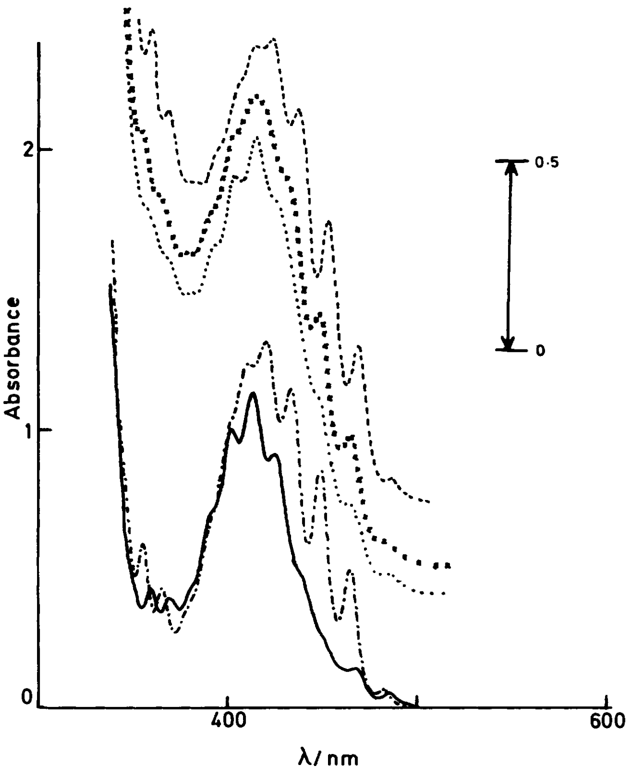

Figure 2. Ultraviolet absorption spectra of solutions of dioxouranium(VI) nitrate (0.14 mol dm^{-3}, 1-cm cells) in water (——), 70% (v/v) acetone–water (· · · ·), 80% (v/v) acetone–water (× × × ×), 90% (v/v) acetone–water (– – – –), and acetone (– · – · –). For convenience, the spectra in 70—90% acetone–water have been offset, and the absorbance scale expanded

At the concentrations studied (up to 0.14 mol dm^{-3}) there was no evidence of UO_2^{2+}–NO_3^- complexing in aqueous solution, although this undoubtedly does occur at higher concentrations.[6] Whilst the hydration number of UO_2^{2+} in aqueous solution has been the subject of controversy, with values from 4[12] to 6[13,16] being reported, recent studies using m.c.d.,[17] *X*-ray diffraction and ^{1}H n.m.r. spectroscopy[18] strongly favour the predominance of $[UO_2(H_2O)_5]^{2+}$. This same co-ordination has previously been indicated in i.r.[19] and *X*-ray diffraction[20] studies of crystalline uranyl perchlorate hydrates. The u.v.–visible absorption spectrum of the dioxouranium(VI) ion is strongly dependent upon its equatorial co-ordination geometry,[15,21] and is thus expected to be informative on changes in complexation resulting from variations in the solvent composition. Electronic absorption spectra were run of solutions of dioxouranium(VI) nitrate (0.14 mol dm^{-3}) over the complete acetone–water concentration range (Figure 2). The spectra in acetone and water are in good agreement with those reported previously,[15,22] and analysis using the criteria of Görller-Walrand and DeJaegere[21] supports the idea of different co-ordination symmetries and geometries in the two solvents. Whilst the resolution of our solution spectra is, naturally, inferior to that of the low-temperature spectra reported by these workers,[21] the data are consistent with symmetry groups D_{2h} and D_{5h}, and equatorial co-ordination numbers of 6 and 5, respectively, in these two solvents. The absorption spectrum of the UO_2^{2+} ion starts to show changes in both band intensities and absorption maxima above about 60% (v/v) acetone–water, in agreement with Raman and potentiometric data. No clear isosbestic points are observed on variation of the spectra with solvent composition. Whilst changes in both co-ordination and solvent polarity are involved, the big differences observed between 70 and 90% (v/v) acetone–water, which do not appear to reflect large changes in dielectric constant,[23] support a two-step equilibrium for nitrate complexation [equations (1) and (2)] as suggested previously from n.m.r. studies.[12]

$$[UO_2(H_2O)_5]^{2+} + NO_3^- \rightleftharpoons [UO_2(NO_3)(H_2O)_x]^+ + (5 - x)H_2O \quad (1)$$

$$[UO_2(NO_3)(H_2O)_x]^+ + NO_3^- \rightleftharpoons [UO_2(NO_3)_2(H_2O)_2] + (x - 2)H_2O \quad (2)$$

Experimental

Solutions of uranyl nitrate (pro-analysis) were prepared using triply distilled water and pro-analysis grade acetone, or 99.5% hexadeuterioacetone (for n.m.r. measurements). Potentiometric studies were made using a Philips PW 9416/20/24 ion-selective analyser fitted with an IS 561-NO_3^-/SP nitrate-selective electrode and RH-44/2-SD-1 double-junction calomel reference electrode. The electrode was calibrated in each acetone–water mixture using sodium nitrate solutions; good linear response of the electrode potential *vs.* the logarithm of the nitrate concentration was observed over the range 10^{-3}—0.3 mol dm^{-3}.[14] At high acetone concentrations, stabilization of the electrode was not possible due to degradation of the polymer membrane. However, relatively reproducible results were obtained by always measuring the potential after the same time (60 s) of contact of the electrode with the solution. Raman spectra were recorded on samples in 4.5 × 1 cm glass cells using a Cary 82 spectrometer with a Spectra-Physics argon-ion laser (model 164) emitting at 514.5 nm. The output was adjusted to provide 300 mW at the sample, and scattered light was collected at 90° to the laser beam. Proton n.m.r. spectra were run on a Varian XL-200 spectrometer fitted with a variable-temperature (−150 to +220 °C) probe. Spectra were recorded using the deuterium resonance of the solvent as a heteronuclear lock and acetone as internal reference. Ultraviolet–visible absorption spectra were recorded in 1-cm quartz cells using a Shimadzu UV-240 double-beam spectrometer.

Acknowledgements

We are grateful to Professors C. F. G. C. Geraldes, V. M. S. Gil, and J. J. C. Teixeira-Dias for access to the n.m.r. and Raman spectrometers, and for valuable discussions. We thank the Instituto Nacional de Investigagão Cientifica for financial support.

References

1 D. Hall, A. D. Rae, and T. N. Waters, *Acta Crystallogr.*, 1965, **19**, 389.
2 J. C. Taylor and M. H. Mueller, *Acta Crystallogr.*, 1965, **19**, 536.
3 B. Jezowska-Trzebiatowska and M. Chmielowska, *J. Inorg. Nucl. Chem.*, 1961, **20**, 106.
4 S. Ernst and B. Jezowska-Trzebiatowska, *J. Inorg. Nucl. Chem.*, 1966, **28**, 2885 and refs. therein.
5 M. Gál, P. L. Goggin, and J. Mink, *J. Mol. Struct.*, 1984, **114**, 459.
6 M. H. Brooker, C. H. Huang, and J. Sylwestrowicz, *J. Inorg. Nucl. Chem.*, 1980, **42**, 1431.
7 M. D. Marcantonatos, M. Deschaux, and F. Celardin, *Chem. Phys. Lett.*, 1980, **69**, 144.
8 A. F. Leung, *J. Phys. Chem. Solids*, 1982, **43**, 467.
9 'Stability Constants of Metal-Ion Complexes,' compiled by L. G. Sillen and A. E. Martell, *Special Publ.* No. 17, Chemical Society, London, 1964, pp. 170—171.
10 M. da Graça Miguel, S. J. Formosinho, and M. L. P. Leitão, *J. Photochem.*, 1986, **33**, 209.
11 S. J. Formosinho and M. da Graça Miguel, *J. Chem. Soc., Faraday Trans. 1*, 1985, 1891 and earlier papers in this series.
12 A. Fratiello, V. Kubo, R. E. Lee, and R. E. Schuster, *J. Phys. Chem.*, 1970, **74**, 3726.
13 V. A. Shcherbakov and L. L. Shcherbakova, *Sov. Radiochem. (Engl. Transl.)*, 1976, **18**, 188.
14 M. E. D. G. Azenha, M.Sc. Thesis, Universidade de Coimbra, 1987.
15 P. Brint and A. J. McCaffery, *J. Chem. Soc., Dalton Trans.*, 1974, 51.
16 I. I. Lipilina and O. Ya. Samilov, *Dokl. Akad. Nauk SSSR*, 1954, **98**, 99; *Chem. Abstr.*, 1955, **49**, 8670e.
17 C. Görller-Walrand and W. Colen, *Chem. Phys. Lett.*, 1982, **93**, 82.
18 A. Åberg, D. Ferri, J. Glaser, and I. Grenthe, *Inorg. Chem.*, 1983, **22**, 3986.
19 V. M. Vdovenko, L. G. Mashirov, and D. N. Suglobov, *Sov. Radiochem. (Engl. Transl.)*, 1964, **6**, 289.
20 N. W. Alcock and S. Esperas, *J. Chem. Soc., Dalton Trans.*, 1977, 893.
21 C. Görller-Walrand and S. DeJaegere, *Spectrochim. Acta, Part A*, 1972, **28**, 257.
22 L. Kaplan, R. A. Hildebrandt, and M. Ader, *J. Inorg. Nucl. Chem.*, 1956, **2**, 153.
23 G. Åkerlof, *J. Am. Chem. Soc.*, 1932, **54**, 4125.

Received 7th March 1988; *Paper* 8/00930I