Infrared Spectroscopic Studies of Uranyl(VI) Species adsorbed from Aqueous $[UO_2(CO_3)_3]^{4-}$ Solutions on to a Polymer bearing Amidoxime Groups

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Infrared spectra of uranyl(VI) species adsorbed from aqueous $[UO_2(CO_3)_3]^{4-}$ solutions on to a polymer having amidoxime groups were examined in order to obtain information on the adsorption mechanism. The subtraction spectra in a region of 500—1 500 cm^{-1} exhibit only a distinct band at 886 cm^{-1} ascribed to the ν_3 mode of the O=U=O moiety and no band assigned to carbonato ligands, suggesting the existence of a carbonato-free uranyl(VI) complex; this is consistent with the adsorption equilibrium reported previously.

A most attractive feature of a polymer bearing amidoxime groups is its high selectivity to uranium[1] which is assumed to be present as a tricarbonatouranate(VI) ion, $[UO_2(CO_3)_3]^{4-}$, in sea-water (pH 8.1—8.3).[2] On the basis of a potentiometric investigation on the binding abilities of acetamidoxime to several metal ions, it has been shown that the selectivity toward uranium is principally due to the ligand forming more stable complexes with 'hard' metal ions.[3] In a previous paper,[4] the adsorption equilibrium on an amidoxime polymer of uranium from aqueous $[UO_2(CO_3)_3]^{4-}$ solutions was examined at pH 8—9 and a mechanism of uranium adsorption was proposed: the adsorption proceeds by ligand exchange of three carbonate ions on the central uranyl(VI) ion with two amidoxime groups, accompanied by two deprotonations. The uranyl(VI) complex with the amidoxime polymer is more stable than that with acetamidoxime $[CH_3C(NH_2)NOH]$ as a ligand, and this is supposed to be due to an entropy effect analogous to the case of chelation. However, a more direct investigation is necessary to confirm the nature of the chemical species of uranyl(VI) adsorbed on the amidoxime polymer.

Infrared studies of various uranyl(VI) complexes have been reported. A linear O=U=O moiety of $D_{\infty h}$ symmetry possesses three vibrational modes, of which the antisymmetric stretching mode, ν_3, is significantly susceptible to perturbations by other ligands, leading to a wide wavenumber range of 850—940 cm^{-1}.[5] The ν_3 mode of uranyl(VI) diperchlorate occurs at 965 cm^{-1},[6] whereas the very stable sodium tricarbonatouranate(VI) exhibits a very low ν_3 frequency at 843 cm^{-1}.[7,8] It is, therefore, expected that the ν_3 mode of uranyl(VI) species adsorbed on the amidoxime polymer will provide significant information on ligand groups participating in complex formation.

In the present study, the i.r. spectra of uranyl(VI) species adsorbed on an amidoxime polymer from aqueous $[UO_2(CO_3)_3]^{4-}$ solutions were examined in order to obtain definite information on the adsorption mechanism of uranium; the result serves to confirm the adsorption equilibrium of uranium presented previously.[4]

Experimental

Materials.—An amidoxime polymer cross-linked with divinylbenzene (ligand content: 1.14 mmol g^{-1}) was prepared by the method reported previously.[9] A given amount of the polymer was immersed in a 2.10×10^{-4} mol dm^{-3} uranium solution (100 cm^3) under the conditions described previously.[4] The concentration of sodium hydrogencarbonate and pH of the solution were adjusted to 0.1 mol dm^{-3} and 8.2, respectively.[4] Under these conditions, the chemical species of uranium in the solution phase can be assumed to be $[UO_2(CO_3)_3]^{4-}$.[10] After the uranium adsorption, the polymer was washed thoroughly with distilled water until no sodium ions were detected in the washings by means of atomic absorption spectrometry, and dried at 40 °C *in vacuo*. By this procedure three samples were obtained, the amounts of uranium adsorbed being 4.9×10^{-5}, 7.3×10^{-5}, and 9.9×10^{-5} mol g^{-1}.

Infrared Spectra.—All i.r. spectra were measured on a Nicolet model 7199A FT-IR spectrophotometer using a TGS detector. The atmosphere in all chambers of the spectrometer was replaced by air free from water and carbon dioxide. After the i.r. bands due to water and carbon dioxide had disappeared completely, the spectra of amidoxime polymer samples in KBr pellets were recorded by 10^4 cumulative scans at a resolution of 2 cm^{-1}. The spectra were obtained over a range of 500—1 500 cm^{-1} by subtracting the spectrum of the original polymer from that of the polymer loaded with uranium to eliminate the absorption at 710 cm^{-1}.

Results and Discussion

The adsorption of uranium from aqueous $[UO_2(CO_3)_3]^{4-}$ solutions at pH 8—9 on to an amidoxime polymer is tentatively assumed to obey equilibrium (1), where HL is a neutral amidoxime group.[4]

$$[UO_2(CO_3)_3]^{4-} + 2HL \rightleftharpoons [UO_2(HL)_2H_{-2}] + 3CO_3^{2-} + 2H^+ \quad (1)$$

This equation is in accord with the experimental data and means that the uranium adsorption proceeds by ligand exchange of all carbonate ions on the central uranyl(VI) ion with two amidoxime groups, accompanied by deprotonations. Thus, it is suggested that the uranyl(VI) species adsorbed on the amidoxime polymer is a carbonate ion-free complex, $[UO_2(HL)_2H_{-2}]$.

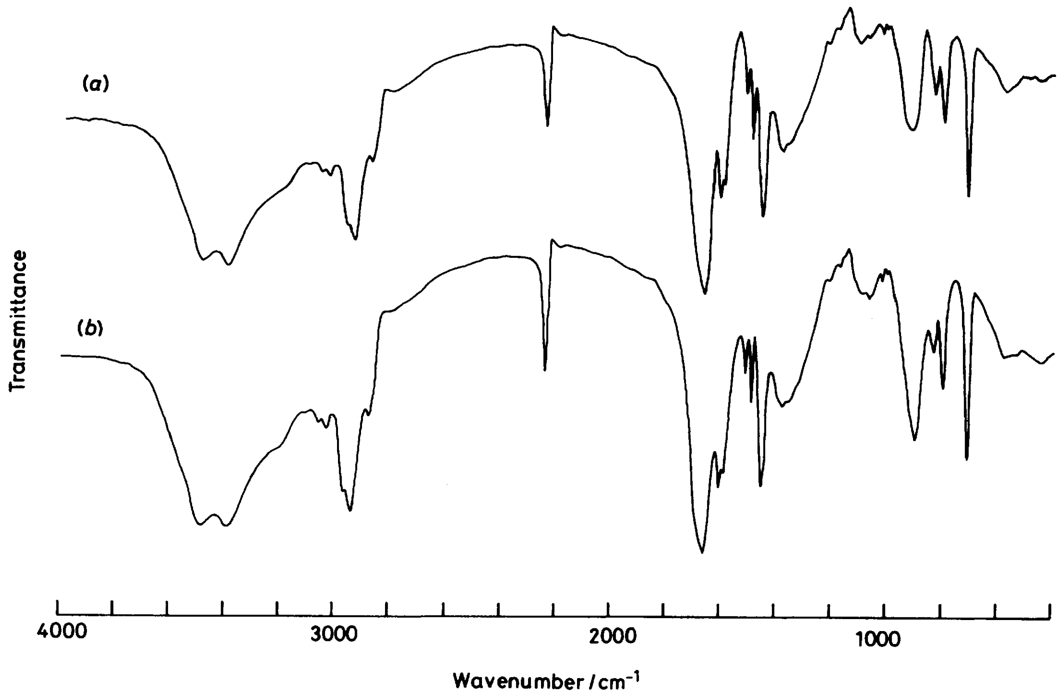

Figure 1. Infrared spectra of the amidoxime polymer before (*a*) and after uranium adsorption (*b*). Amount of uranium adsorbed: 9.9 × 10^{-5} mol g^{-1}

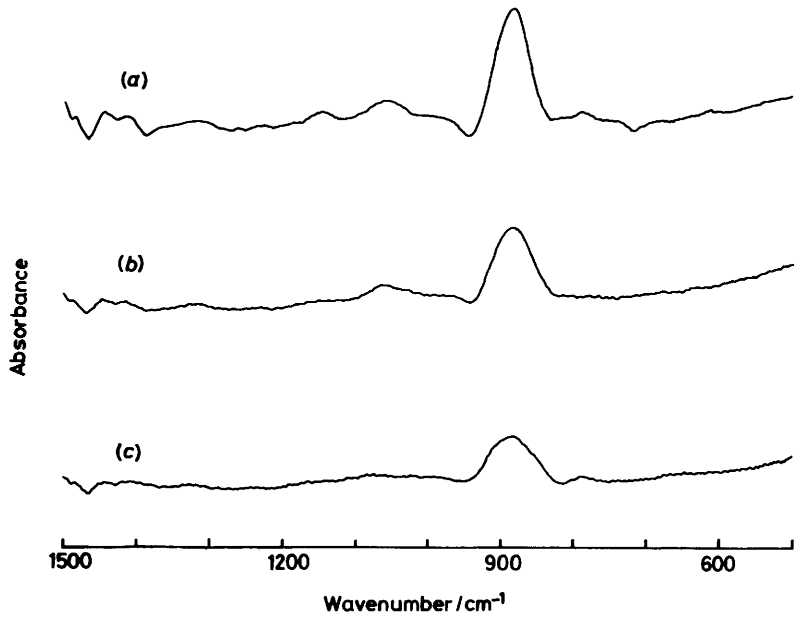

Figure 2. Subtraction spectra for various amounts of uranium adsorbed: (*a*) 9.9 × 10^{-5}, (*b*) 7.3 × 10^{-5}, and (*c*) 4.9 × 10^{-5} mol g^{-1}

Infrared spectra of amidoxime polymer samples before and after the uranium adsorption are shown in Figure 1. In Figure 1(*a*) the bands at 3 390 and 3 480 cm^{-1} are assigned to a symmetric and an antisymmetric stretching mode of NH_2, respectively. The bands at 915 and 1 660 cm^{-1} are assigned to N–O and C=N stretching modes of the oxime group, respectively, in good agreement with literature data.[9,11] The band at 2 240 cm^{-1} is ascribed to unreacted nitrile groups. In comparison with this spectrum, there exists a distinct difference near 900 cm^{-1} in Figure 1(*b*). This may be ascribed to the ν_3 mode of the O=U=O moiety, which may appear over a wide range of wavenumbers (850—940 cm^{-1}).[5a] On the other hand, no band ascribed to carbonate ions, which possess four normal modes in the range of 700—1 500 cm^{-1},[12] is apparently observed. To confirm these observations, the spectra obtained upon subtraction of the spectrum for the original amidoxime polymer from that upon uranium adsorption were examined.

The subtraction spectra are shown in Figure 2. A distinct band is observed at 886 cm^{-1} in every case, which increases in intensity with increasing amount of uranium adsorbed;

therefore, this band is ascribed to the ν_3 mode of the O=U=O moiety adsorbed on the amidoxome polymer. No other significant bands are observed at 500—1 500 cm^{-1}. The i.r. spectrum of sodium tricarbonatouranate(VI) shows that the bands assigned to the carbonato ligand appear at 1 062 (ν_1, A_1'), 821 (ν_2, A_2''), 1 342 and 1 560 (ν_3, E), and 700 and 732 cm^{-1} (ν_4, E'), and that the intensities of these bands are almost equal to that at 843 cm^{-1} due to the O=U=O moiety.[8] Thus, even when possible frequency shifts are taken into account, no bands ascribable to the carbonato ligand are observed in the subtraction spectra. This is consistent with the observation of the ν_3 mode of the O=U=O moiety at 886 cm^{-1}, because the ν_3 frequency of tricarbonatouranate(VI) is shifted to a lower wavenumber, 843 cm^{-1}.[8] It is, therefore, suggested that the present i.r. spectra are consistent with the adsorption mechanism expressed by equation (1), in which the uranyl(VI) species are adsorbed as $[UO_2(HL)_2H_{-2}]$.

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Received 14*th November* 1986; *Paper* 6/2200