Binding Ability of Acetamide Oxime with Proton, Copper(II), and Dioxouranium(VI) in Aqueous Solutions

Takahiro Hirotsu,* Shunsaku Katoh, and Kazuhiko Sugasaka
Government Industrial Research Institute, Shikoku, 2-3-3 Hananomiya-cho, Takamatsu 761, Japan
Manabu Senō
Institute of Industrial Science, The University of Tokyo, 7-22-1 Roppongi, Minato-ku, Tokyo 106, Japan
Takaharu Itagaki
Central Research Laboratory, Mitsubishi Chemical Industry, Ltd., 1000 Kamoshida-cho, Midori-ku, Yokohama 227, Japan

The equilibrium constant of acetamidoxime (acetamide oxime) with proton in aqueous solutions was determined using the potentiometric method. The compositions and stability constants of the complexes of this ligand with Cu^{II} and $U^{VI}O_2$ in aqueous solutions were also determined. Acetamidoxime forms 1 : 1 and 1 : 2 complexes with Cu^{II} and $U^{VI}O_2$. Furthermore, the $U^{VI}O_2$ complexes were found to be more stable than those of Cu^{II}; these characteristic properties of the ligand are discussed in relation to the recovery of uranium from sea water.

It has been demonstrated that some polymers bearing amidoxime groups show high selective adsorptivity for uranium in sea water.[1] The adsorptive property of the chelating polymers is assumed to principally depend on the metal-complexing nature of ligands. Therefore, our interest has been focussed on the metal-chelating behaviour of amidoxime compounds in aqueous solutions, especially stoicheiometric compositions, and stabilities of the relevant chemical species.

A considerable number of metal complexes with amidoximes have been prepared and their structures have been determined by *X*-ray crystallography. Diaminoglyoxime forms complexes with Co^{II},[2] Ni^{II},[3] and Cu^{II},[4] in which the oxime nitrogen is co-ordinated to the metal ions. Interestingly, acetamidoxime forms a 1:4 complex with $U^{VI}O_2$, which is equatorially surrounded by the four oxime oxygens of the monodentate amidoxime groups.[5] On the other hand, Pearse and Pflaum[6] showed that the dissociation constants (pK_{a1}) of some amidoximes were 3—5 in aqueous solutions by the potentiometric method and that benzamidoxime (benzamide oxime) formed a 1:2 complex with Co^{II} in alkaline medium, by the method of continuous variation. Manoussakis and Kouimtzis[7] reported that benzanilidoxime (*N*-phenylbenzamide oxime) formed a 1:1 and a 1:2 complex with $U^{VI}O_2$ in aqueous dioxane solutions. However, little investigation of the stoicheiometric compositions and stabilities of metal complexes of amidoximes in aqueous solutions has been carried out. This situation is probably due to the poor solubility and low molar absorptivity of the metal complexes with amidoximes.[6]

Accordingly, the complexing behaviours of acetamidoxime with Cu^{II} and $U^{VI}O_2$ have been examined and the stoicheiometric compositions and stability constants of the species in aqueous solutions are reported herein.

Experimental

Reagents.—Acetonitrile and hydroxylamine hydrochloride obtained from Wako Co. were used without further purification to prepare acetamidoxime. A standard HNO_3 solution was prepared from concentrated HNO_3 (Merk, suprapur). Standard solutions of Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, and $U^{VI}O_2$ were prepared from the corresponding nitrates (uranyl salt, Wako; others, Merk GR). A carbon dioxide-free KOH standard solution was prepared from KOH (Merk GR) by the ion-exchange method.[8] All the above solutions were adjusted to an ionic strength of 0.1 mol dm^{-3} with KNO_3 (Merk, suprapur). Water used for the preparation of all the solutions was deionized by an ion-exchange column and then twice distilled.

Preparation of Acetamidoxime.—A solution of hydroxylamine (1 mol) in methyl alcohol (200 cm^3) was obtained by treatment of hydroxylamine hydrochloride with metallic sodium. A solution of acetonitrile (1 mol) in methanol (50 cm^3) was added dropwise to the solution of hydroxylamine, and then stirred at room temperature for 48 h. The solution was filtered, concentrated to *ca.* 50 cm^3 and cooled to −15 °C. The colourless precipitates were collected. Recrystallization from methanol four times gave colourless needles (Found: C, 32.0; H, 8.30; N, 37.9; Cl, 0.00. Calc. for $C_2H_6N_2O$: C, 32.45; H, 8.15; N, 37.8; Cl, 0.00%).

Potentiometric Equilibrium Measurements.—The potentiometric equilibrium measurements of acetamidoxime in the absence and the presence of the metal ions were carried out with an Orion research 801 ion analyser using a Beckman Futura glass electrode and a Beckman Futura double-junction type calomel electrode. All titrations were performed in a double-walled titration cell of 100 cm^3 capacity. The temperature of all solutions was maintained at 25.0 ± 0.05 °C by circulating thermostatted water through the outer jacket of the cell. The cell was fitted with glass and calomel electrodes, a microburet delivery tube, and a nitrogen inlet tube. Ionic strengths of all the solutions were maintained at 0.1 mol dm^{-3} with KNO_3. All titrations were performed under an atmosphere of nitrogen gas which had been bubbled through an aqueous solution having the same ionic strength as the solution being titrated.

The calibration of the potentiometer was made with N.B.S. standard buffer solutions (pH 4.008, 6.863, and 9.183 at 25 °C). Conversion of pH meter reading, pH_M, to $-\log [H]$ was made by correcting the difference between pH_M and $-\log [H]$ obtained on titrating 0.01 mol dm^{-3} HNO_3 with 0.1 mol dm^{-3} KOH at the ionic strength of 0.1 mol dm^{-3} (KNO_3): $-\log [H] = pH_M - 0.063$. The hydroxide ion concentration was calculated from the apparent ionic product of water, pK_W', determined by titrating 0.1 mol dm^{-3} KNO_3 with 0.1 mol dm^{-3} KOH: $pK_W' = pH_M - \log [OH] = 13.94$. The ligand concentration of sample solutions was arranged to be 2×10^{-3} mol

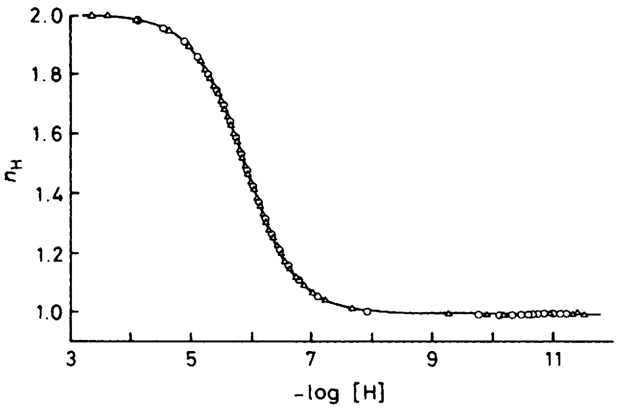

Figure 1. Average number of protons bound to acetamidoxime as a function of $-\log$ [H] at 25 °C and $I = 0.1$ mol dm^{-3} (KNO_3). [HL] = 1.983×10^{-3} (○) and 3.868×10^{-3} mol dm^{-3} (△). The solid curve was calculated using a pK_{a1} value of 5.90

Table. Stability constants, β_{pqr}, of the complexes, $M_p(HL)_qH_r$, at 25 °C and $I = 0.1$ mol dm^{-3} (KNO_3)

	Complex			
M	p	q	r	$\log \beta_{pqr}$*
	0	1	1	5.900(0.001)
Cu^{II}	1	1	−1	−3.14(0.02)
Cu^{II}	1	2	−2	−7.66(0.03)
$U^{VI}O_2$	1	1	−1	−0.97(0.02)
$U^{VI}O_2$	1	2	−2	−4.42(0.07)

* Values in parentheses are estimated standard deviations.

dm^{-3} in most cases, being four times higher than that of the metal ions. The free ligand was first titrated by 0.1 mol dm^{-3} HNO_3 and then back-titrated with 0.1 mol dm^{-3} KOH. In the presence of metal ions, the titrations with 0.1 mol dm^{-3} KOH were performed by starting from solutions containing the same molar quantity (for all the metal ions except $U^{VI}O_2$) and a two-fold excess (for $U^{VI}O_2$) of acid with respect to the ligand.

Determination of Concentrations of Metal Ions in the Solutions.—The concentration of Cu^{II} was determined electrogravimetrically as copper metal, and those of Co^{II}, Ni^{II}, and Zn^{II} were determined by titration with ethylenediaminetetra-acetic acid. The concentration of $U^{VI}O_2$ was determined gravimetrically as U_3O_8.

Calculation of Equilibrium Constants.—The equilibrium between acetamidoxime, metal ion, and proton, and the relevant stability constant, β_{pqr}, are conveniently represented by equations (1) and (2) respectively; p, q, and r are the

$$pM + q(HL) + rH \rightleftharpoons M_p(HL)_qH_r \qquad (1)$$

$$\beta_{pqr} = [M_p(HL)_qH_r]/[M]^p[HL]^q[H]^r \qquad (2)$$

numbers of moles of metal ion (M), ligand (HL), and proton (H) in the complex $M_p(HL)_qH_r$, respectively, and charges of respective species are omitted. A negative value of r denotes the deprotonation from the complex. Calculation of β_{pqr} was carried out using MINIQUAD.[9] For each system at least two titrations were performed, and each of the titration curves contains more than 50 experimental points.

Results and Discussion

The dissociation equilibrium of amidoxime (HL) may be represented by equations (3) and (4) (charges are omitted),

$$H_2L \rightleftharpoons HL + H \qquad pK_{a1} \qquad (3)$$

$$HL \rightleftharpoons L + H \qquad pK_{a2} \qquad (4)$$

where pK_{a1} and pK_{a2} are the relevant dissociation constants.[7] The potentiometric titrations of acetamidoxime solutions containing no metal ions were carried out in the ligand concentration range 1.983×10^{-3} to 13.75×10^{-3} mol dm^{-3}. From the potentiometric equilibrium curves obtained the average number of protons bound to an acetamidoxime molecule, n_H, was calculated (Figure 1). From Figure 1, pK_{a1} of acetamidoxime was found to be 5.90, whereas deprotonation of the oxime group [equation (4)] was not observed at $-\log$ [H] < 12. Therefore, the proton–acetamidoxime stability constant, β_{011}, was calculated by MINIQUAD using equation (1); the results are given in the Table. The value of β_{011} was found to be 5.900 in the ligand concentration range 1.983×10^{-3} to 13.75×10^{-3} mol dm^{-3}. The experimental points of n_H fell well on the theoretical curve which was derived by using a pK_{a1} value of 5.90, as shown in Figure 1.

The pK_{a1} value of acetamidoxime is higher than those of R–C(NH_2)NOH (R = phenyl, benzyl, 2-tolyl, or 4-tolyl).[6] The amino group of acetamidoxime is presumed to exhibit higher basicity because the methyl group has a larger Taft value. On the other hand, the pK_a values of oximes (R^1R^2C=NOH)[10] can be estimated by equation (5), where σ^* are the Taft values of R^1

$$pK_a = 12.35 - 1.18\,\Sigma\,\sigma^* \qquad (5)$$

and R^2, which are not acyl groups. From this equation the pK_{a2} value of acetamidoxime is estimated to be 11.6, but the oxime group seems to behave as a weaker acid, as mentioned above.

In the Co^{II}–acetamidoxime system, the potentiometric equilibrium curves hardly deviated from that in the absence of Co^{II} at $-\log$ [H] < 8, whereas precipitates were formed at $-\log$ [H] > 8. Similar phenomena were also observed in the Ni^{II}– and Zn^{II}–acetamidoxime systems. Accordingly, the stability constants of the Co^{II}, Ni^{II}, and Zn^{II} complexes were not obtained in this study.

In the Cu^{II}–acetamidoxime system, the potentiometric equilibrium curves were obtained over the range of $-\log$ [H] = 3—12 without precipitation. On the other hand, in the $U^{VI}O_2$–acetamidoxime system, the titrations were carried out at a range of $-\log$ [H] < 6, beyond which precipitates were formed. The stability constants were calculated from these results as shown in the Table. The hydrolyses of Cu^{II} and $U^{VI}O_2$ were considered in the calculation. Acetamidoxime was found to form 1:1 and 1:2 complexes with both Cu^{II} and $U^{VI}O_2$. The $U^{VI}O_2$ complexes were more stable than the Cu^{II} complexes. Figures 2 and 3 show the distributions of the complexes of Cu^{II} and $U^{VI}O_2$ respectively as a function of $-\log$ [H]. In the Cu^{II} complexes, the 1:1 complex is formed at $-\log$ [H] 5—9, while at higher $-\log$ [H] values it is converted to the 1:2 complex. On the other hand, for $U^{VI}O_2$, the 1:1 complex is formed at lower $-\log$ [H] values, and the 1:2 complex is formed at $-\log$ [H] > 5.5.

From the above results, these acetamidoxime complexes were found to have stabilities in following order: Co^{II}, Ni^{II}, Zn^{II} < Cu^{II} < $U^{VI}O_2$. This result would be explained well from the hard–soft acid–base concept. According to this concept, $U^{VI}O_2$ is a hard acid, whereas Co^{II}, Ni^{II}, Cu^{II}, and Zn^{II} are less hard acids. In general, hard acids show higher affinity toward the donor atoms of N and O than do soft ones. This suggests that acetamidoxime forms more stable complexes with metal ions of the more hard acids. In fact, the oxygen atom of acetamidoxime (HL) was reported to co-ordinate to $U^{VI}O_2$ in a monodentate mode from an *X*-ray crystal structure determination of $[UO_2(HL)_4][NO_3]_2$.[5]

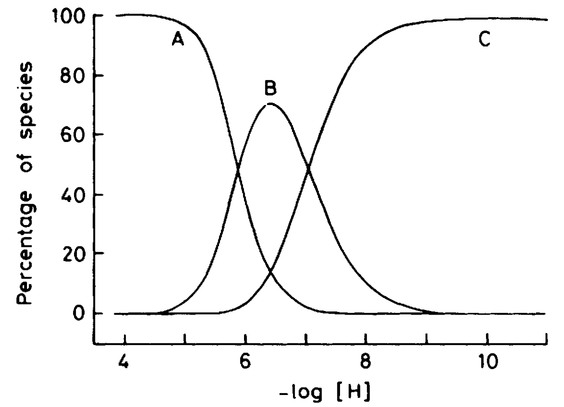

Figure 2. Distribution of species as a function of $-\log$ [H] in a system containing a 8:1 molar ratio of acetamidoxime to Cu^{II} at 25 °C and $I = 0.1$ mol dm^{-3} (KNO_3). $[HL] = 4 \times 10^{-3}$, $[Cu^{II}] = 0.5 \times 10^{-3}$ mol dm^{-3}. Species (*p*, *q*, *r*): A, 1, 0, 0; B, 1, 1, -1; C, 1, 2, -2

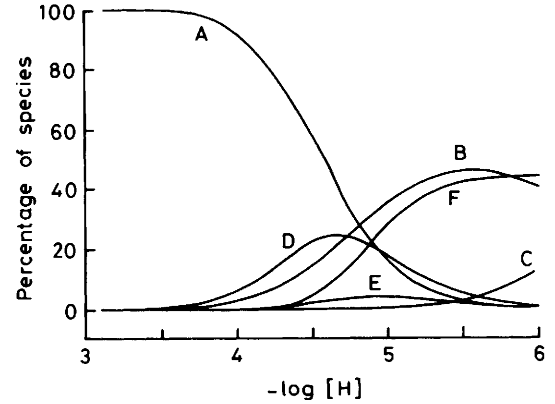

Figure 3. Distribution of species as a function of $-\log$ [H] in a system containing a 4:1 molar ratio of acetamidoxime to $U^{VI}O_2$ at 25 °C and $I = 0.1$ mol dm^{-3} (KNO_3). $[HL] = 2 \times 10^{-3}$, $[U^{VI}O_2] = 0.5 \times 10^{-3}$ mol dm^{-3}. Species $[(UO_2)_p(HL)_qH_r]$: A, 1, 0, 0; B, 1, 1, -1; C, 1, 2, -2. Species $[(UO_2)_p(OH)_r]$: D, 2, -2; E, 3, -4; F, 3, -5

Conclusions

The concentration of uranium in sea water (pH 8.1—8.3) is as low as 1.4×10^{-8} mol dm^{-3}, although alkali metal ions and alkaline-earth metal ions are present in much higher concentrations. The first row transition metal ions (Mn^{II}, Fe^{III}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}), which are also the main cationic elements in sea water besides the above metal ions, are present in almost the same concentration as uranium.[11] In this study, acetamidoxime was found to exist as a neutral species at pH 8.1—8.3 because the oxime group has a very low acidity, suggesting very low complexing affinity to alkali and alkaline-earth metal ions through ionic bonding. Furthermore, it was found that acetamidoxime forms a much more stable complex with $U^{VI}O_2$ than with Co^{II}, Ni^{II}, Zn^{II}, and Cu^{II}. These characteristic properties of acetamidoxime seem to be responsible for the high selective adsorptivity of polymers bearing amidoxime groups to uranium in sea water.

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