

SHORT COMMUNICATIONS

Imidedioxime as a Significant Component in So-Called Amidoxime Resin for Uranyl Adsorption from Seawater

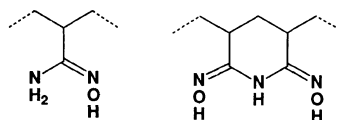
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The recovery of uranyl dissolved homogeneously, but highly diluted (3.3 ppb) in the ocean is a challenging possibility to obtain an exhaustless energy source. Among adsorbents hitherto developed, the so-called "amidoxime" polymer may share the position closest to the desired characteristics. This polymer was introduced first in 1957.¹ Later, this functional group was incorporated into macroporous resin² or in fiber³ to exhibit much superior adsorption characteristics than the previously developed hydrous titania⁴ and extensive efforts have been made for the realization of uranyl recovery from seawater.⁵ In this adsorbent, "amidoxime" is claimed primarily responsible for the uranyl adsorption. In spite of the significant contributions, structural analysis has unfortunately been based on limited experimental information from pH titration, IR measurement, and other indirect methods.^{2,3,6} In this report, we analyzed the polymer structure for the first time by ¹³C NMR spectroscopy and obtained structural evidences that *the main functional group responsible for the uranyl binding is not "amidoxime," but cyclic "imidedioxime."* According to the revised concept, the "imidedioxime" polymer with a greatly improved adsorption rate of uranyl from seawater has been successfully developed.



Amidoxime

Imidedioxime

EXPERIMENTAL

Polyacrylonitrile fiber ($\Phi = 12 \mu\text{m}$) is a product of Japan Exlan. The hollow fiber, PAN-15, was obtained from Asahi Medical. This was treated with hydroxylamine under two different conditions: Condition A, A methanolic solution of hydroxylamine was prepared by adding a methanolic KOH solution (4.98 g KOH in 55 ml of methanol) to a methanolic $\text{NH}_2\text{OH} \cdot \text{HCl}$ solution (5.25 g of $\text{NH}_2\text{OH} \cdot \text{HCl}$ in 55 ml of methanol) under ice cooling followed by filtration. Polyacrylonitrile hollow fiber (3.98 g) was heated in the methanolic NH_2OH solution thus prepared under reflux for 17 h. Condition B, Polyacrylonitrile hollow fiber (0.76 g) was heated in the presence of $\text{NH}_2\text{OH} \cdot \text{HCl}$ (1.9 g) and Na_2CO_3 (1.4 g) in 10 ml of $\text{EtOH-H}_2\text{O}$ (1:1) at 90°C overnight. Authentic dimethylpropan-, methylpropan-, and propanamidoximes as well as tetraoxatetradecanedicarbamidoxime were

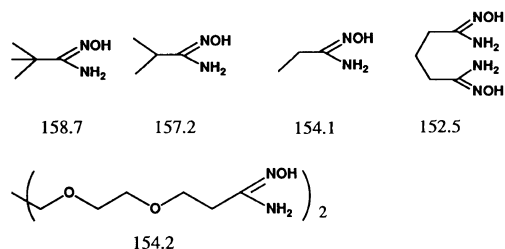
prepared by treatment of corresponding cyano compounds with a methanolic NH_2OH solution. All these compounds gave satisfactory ^{13}C and ^1H NMR spectra and elemental analyses. Glutar-bisamidoxime, -imidedioxime and -imide-monoxime were prepared according to the literature method.⁷ ^1H and ^{13}C NMR spectra were obtained in $\text{DMSO}-d_6$ solution using JEOL PMX 90. Chemical shifts are given by downfield shifts from ^1H and ^{13}C of tetramethylsilane.

RESULTS AND DISCUSSION

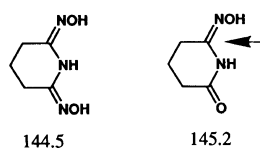
A typical procedure to prepare the uranyl adsorbent is as follows: "Polyacrylonitrile is treated with 3% NH_2OH solution in methanol. The polymer is then treated with an alkaline solution, *e.g.*, 1 *N* NaOH at room temperature for 1 day." In this procedure, two different types of chemical processes are involved inherently, *i.e.*, a conversion of nitrile and transformation by alkaline treatment. In the first conversion, the "amidoxime" group is possibly generated. Although compounds having an isolated cyano group afford the amidoxime group by treatment with NH_2OH ,⁸ the situation is not so simple in polyacrylonitrile, which is extremely susceptible to neighboring group participation toward attack of external nucleophiles to cyano grouping.⁹ In fact, when glutaronitrile, a simplest model of the 1,3-dicyano disposition in polyacrylonitrile, is treated with $\text{NH}_2\text{OH} \cdot \text{HCl}$ in the presence of a half molar equivalent of sodium carbonate in 50% aqueous ethanol under reflux, imidedioxime can be isolated.⁷

In order to get information on possible amidoxime and imidedioxime structural units in the polymer, we prepared several authentic samples of amidoxime and imide-oxime structures whose ^{13}C NMR data are illustrated in Scheme I. These two functional groups were easily recognizable by chemical shift difference, since the amidoxime carbon appeared in the range 153 to 159 ppm and the imide-oxime

Amidoxime



Imidoxime



Scheme 1.

near 145 ppm. Alkyl substitution α to the amidoxime carbon tends to give a shielding effect, as shown by the uniform decreasing order of chemical shifts:



Polyacrylonitrile hollow fiber was treated with

(A) methanolic NH_2OH solution prepared from $\text{NH}_2\text{OH} \cdot \text{HCl}$ by the addition of an equimolar KOH in methanol, under reflux (sample 1) and

(B) $\text{NH}_2\text{OH} \cdot \text{HCl}$ in the presence of a half molar equivalent of Na_2CO_3 in 50% aqueous ethanol under reflux (sample 2).

For both samples, complete disappearance of the cyano group was confirmed by IR spectrum. Figure 1 shows the ^{13}C NMR spectra in $\text{DMSO}-d_6$ solution of these polymer samples which gave two signals at 155 and 148 ppm in relative intensity ratios 3:1 and 2:3 for samples 1 (Figure 1a) and 2 (Figure 1b), respectively. The reaction appeared clean and a small peak was detected only for sample 2 in the carbonyl region 170–180 ppm. If one considers the chemical shift data along with the substitution patterns shown in Scheme 1, the

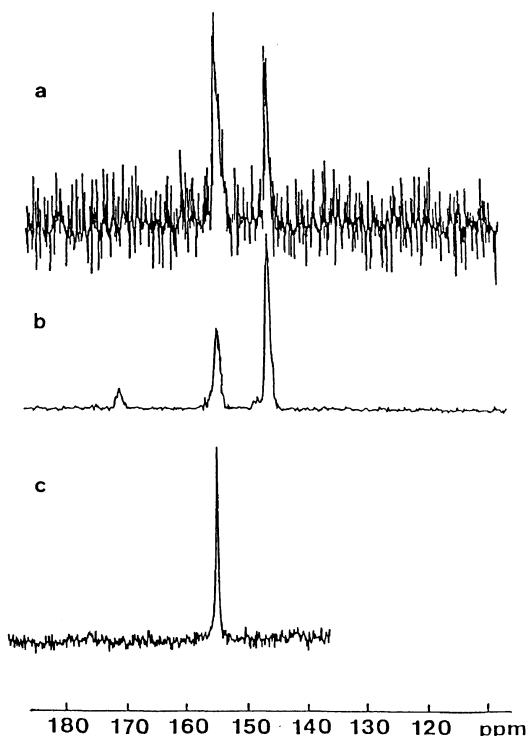


Figure 1. Polyacrylonitrile hollow fiber treated with NH_2OH under condition A (NH_2OH in MeOH) (a) and condition B ($\text{NH}_2\text{OH} \cdot \text{HCl} - \text{Na}_2\text{CO}_3$ in $\text{EtOH} - \text{H}_2\text{O}$) (b) in addition to alternating copolymer of butadiene-acrylonitrile treated with NH_2OH (c). See the text for details.

peak at 155 ppm in samples 1 and 2 is unequivocally assigned to amidoxime, while the peak at 148 ppm to imidedioxime. This assignment is supported further by the following observation:

The alternating copolymer of butadiene and acrylonitrile¹⁰ was treated with a methanolic NH_2OH solution. The resulting polymer gave a single peak at 155 ppm without any other in the range 140–150 ppm (Figure 1c). In this case, no imidedioxime formation is expected because two adjacent cyano groups are separated far from each other by the intervening 2-butenyl unit in the polymer chain. The peak at 155 ppm may thus be assigned to the amidoxime.

The so-called “amidoxime” polymer was

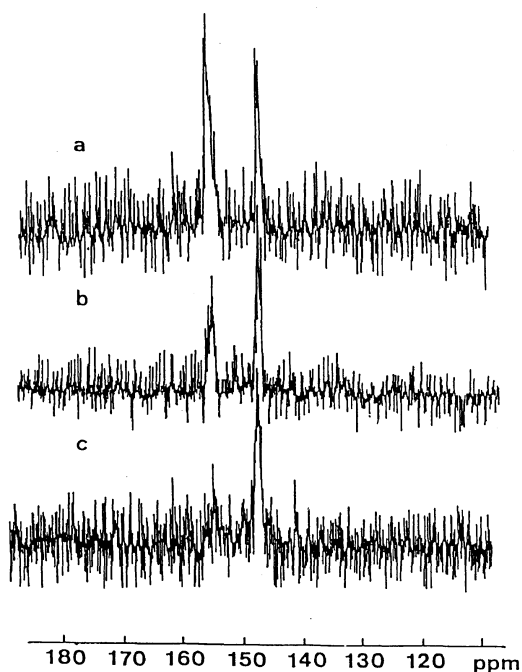


Figure 2. Effect of alkaline treatment on the polymer structure. Polyacrylonitrile hollow fiber treated with methanolic NH_2OH , before alkaline treatment (a), alkaline treatment with 1 N NaOH at 25°C for 10 h (b) and 24 h (c).

elucidated to be by no means the pure amidoxime structure, but a mixture of amidoxime and imidedioxime. Condition B seems to favor the formation of imidedioxime structure, in agreement with the finding that it was the sole isolated product under this condition in the case of glutaronitrile as described above.¹¹

Activation by the alkaline treatment is not fully understood in terms of chemical structural changes, but attributed to increased micropore in the adsorbent.¹² The most contributing factor to the micropore formation may be conversion of the cyano group partially remaining in the polymer in the first controlled nitrile conversion to amide and/or carboxylic acid. Structural information on the polymer adsorbent is limited,^{13,14} and no direct methods to trace further possible transformations during the alkaline treatment are available. ¹³C NMR spectroscopy provided definite in-

formation on this important point, as shown in Figure 2. "Amidoxime" at 155 ppm in the sample 1 decreased gradually by alkaline treatment and almost no amidoxime remained after 24 h. Thus the "activated" adsorbent contains only a small amount of amidoxime, but predominantly the imidedioxime group.¹⁵

Since the above findings on polymer structure indicate that imidedioxime is prepared more favorably by condition B and that most of amidoxime, even formed in the initial hydroxylamine treatment, is lost during alkaline treatment, polyacrylonitrile fiber ($\Phi = 12 \mu\text{m}$) was treated with $\text{NH}_2\text{OH} \cdot \text{HCl}$ in the presence of Na_2CO_3 in 50% aqueous ethanol under reflux for 3 h (sample 3). Only half the cyano groups was designed to be converted, so that micropores would be obtained by later alkaline treatment. Sample 3 was then "activated" by treatment with 1 N NaOH at 25°C for 1 (sample 4) and 3 days (sample 5). These samples (20 mg each) were immersed separately in 5 l of seawater for a day. The amounts of uranium recovered were 30, 500, and 650 $\mu\text{g g}^{-1} \cdot \text{Ads}$ for samples 3, 4, and 5, respectively. The data clearly show the effect of alkaline treatment on adsorption efficiency. More importantly, a comparison of these data with maximum adsorption data so far attained, ca. 150–200 $\mu\text{g g}^{-1} \cdot \text{Ads}$,¹⁶ using fibers of considerable mechanical strength indicated significant improvement in the adsorption rate. It is worthwhile commenting that the economical line of uranyl recovery from seawater may be drawn near 500 $\mu\text{g g}^{-1} \cdot \text{Ads}$ per day.^{17,18} The establishment of a reliable and direct method for elucidating the structure and proposal for a new efficient functional candidate may lead to further improvement in adsorption characteristics, on the basis of which an inexhaustible energy source from seawater may be obtained.

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