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Preparation and Chelating Properties of 8-Hydroxyquinoline–Formaldehyde Polymers

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Synopsis

Condensation of 8-hydroxyquinoline with formaldehyde in acid solution yielded a polymer of molecular weight ~3300. Modification of this polymer with resorcinol resulted in improved physical properties of this material. 8-Hydroxyquinoline–formaldehyde polymers can be used as selective chelating ion-exchange resins which permit separation of various cations. The polymeric metal chelates are thermally less stable than the unchelated polymer.

DISCUSSION

Previous work on chelating polymers[1-5] showed that unusual selectivity for various metal ions can be achieved by polymerizing ligands capable of chelate formation. Salicylic acid–formaldehyde polymers (SFP),[1-3] for instance, showed selectivity towards UO_2^{+2} in contrast to the monomer, and polythiosemicarbazide showed extraordinary selectivity for Cu^{+2}.[4,5] We wished to investigate the selectivity of polymers prepared from the well known 8-hydroxyquinoline ligand. The thermal stability of some metal chelates of 8-hydroxyquinoline–formaldehyde polymer (8-HQF) were also of interest to us.

The Menasse reaction of 8-hydroxyquinoline and formaldehyde is known to produce polymers of relatively low molecular weight.[6,7] The copolymerization of 8-hydroxyquinoline with resorcinol has been described.[8] The preparation of high molecular weight 8-hydroxyquinoline formaldehyde polymers by acid catalysis has not been described previously. We prepared polymers of 8-hydroxyquinoline by this method. The structure of these polymers can be varied by introduction of resorcinol or phenol to achieve some degree of crosslinking.

When 8-hydroxyquinoline was reacted with formaldehyde in the presence of strong acid only a very small amount of condensation polymer was formed. This may have been due to salt formation between the tertiary nitrogen of 8-hydroxyquinoline, resulting in deactivation of the molecule. In view of this fact it seemed to be best to attempt copolymerization of 8-

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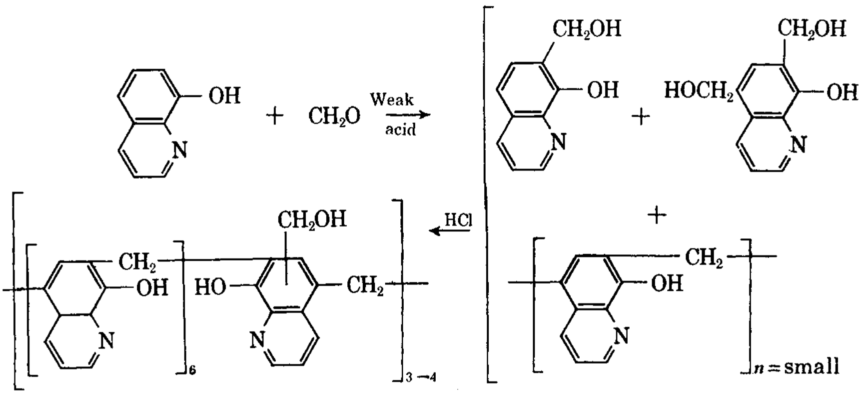
hydroxyquinoline and formaldehyde by employing a weak acid such as oxalic acid and allowing the reaction to continue until most of the formaldehyde had reacted. It was then possible to obtain higher molecular weight materials from the hydroxymethylated amine and any oligomer by the addition of strong acid. A strong acid such as HCl tends to form carbonium ions with hydroxymethylated derivatives of 8-hydroxyquinoline and thus facilitates aromatic substitution resulting in an increase of molecular weight of the polymer.



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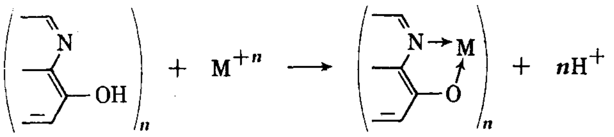
8-HQF prepared in this fashion had a molecular weight of 3340 ± 10% and was soluble in DMF and dilute mineral acids.

Polymerization of 8-hydroxyquinoline with formaldehyde can also be accomplished by using basic catalysts. The polymers obtained in this fashion appeared to be of higher molecular weight. These products were insoluble in all solvents except boiling DMF and mineral acids.

The 8-HQF polymers described above were capable of chelate formation with metal ions in a fashion similar to the monomeric ligand.



For steric reasons imposed by the polymer chains, only di- and trivalent metal ions were chelated completely by the ligand, while the ionic and coordinate valencies of tetravalent metal ions were only partially satisfied by the polymeric ligand, and the metal ions retained some of their original gegen ions.

Steric hindrance as well as a tendency to form different hybrids contribute to the selectivity of the chelating polymer towards various metal ions. Selectivity of 8-HQF is expressed herein in distribution ratios of various metal ions between their aqueous solution and the solid polymer in contact with them. These distribution ratios were calculated on the basis of

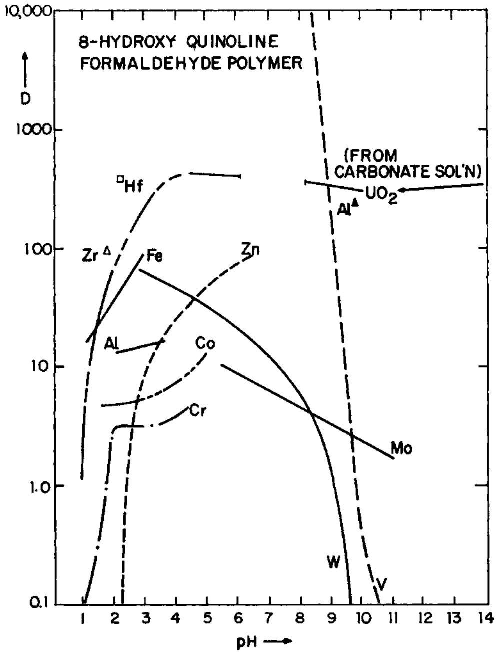


Fig. 1. Distribution ratios of metal ions in contact with 8-hydroxyquinoline–formaldehyde polymer (5 meq. metal ion in 200 ml. 1*M* $NaNO_3$).

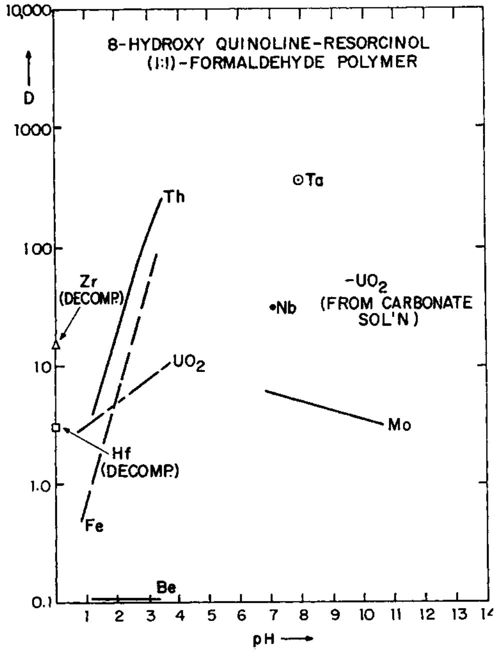


Fig. 2. Distribution ratios of metal ions in contact with 8-hydroxyquinoline–resorcinol (1:1)–formaldehyde polymer (5 meq. metal ion in 200 ml. 1*M* $NaNO_3$).

experiments described for other chelating polymers in earlier publications.[2,5] Figures 1 and 2 show these distribution ratios for various metal ions as a function of pH. 8-Hydroxyquinoline formaldehyde polymer (Fig. 1) could be used for a separation of UO_2^{+2} from Cr^{+3}, Co^{+2}, and Al^{+3} at pH 3 and of UO_2^{+2} from Zn^{+2} at pH 2. In basic solution, it should be possible to separate vanadium and tungsten at pH = 10.8 from molybdenum. There also seems to be a possibility of separating tungsten from vanadium. The pH range for this separation, however, is very narrow (9.8–10.2). At pH 10.8–11.2 uranium could be adsorbed from carbonate ore leaches.

The 8-HQF copolymer with resorcinol had, as expected, generally lower capacities (Fig. 2) and did not lend itself readily to metal separation although its physical properties (e.g., hardness, attrition) were superior to 8-HQF.

Thermal Stability of Metal Chelates of 8-Hydroxyquinoline–Formaldehyde Polymers

Metal chelates of 8-HQF were prepared from Zn^{+2}, Ni^{+2}, Al^{+3}, Fe^{+3}, Th^{+4}, and U^{+4}.

Because of the nonstoichiometric composition of other polymeric chelates, a valid comparison of the influence of the metal on the thermal stability of the polymeric chelate could only be made between the Zn^{+2}, Fe^{+3}, and the Al^{+3} compounds.

Figure 3 shows the thermograms of 8-HQF, $Al(8\text{-}HQF)_3$, and $Fe(8\text{-}HQF)_3$. The most obvious difference between the thermograms of the polymer and its metal chelates was that the polymer decomposed in two steps while the chelates had one sharp decomposition point. Decomposi-

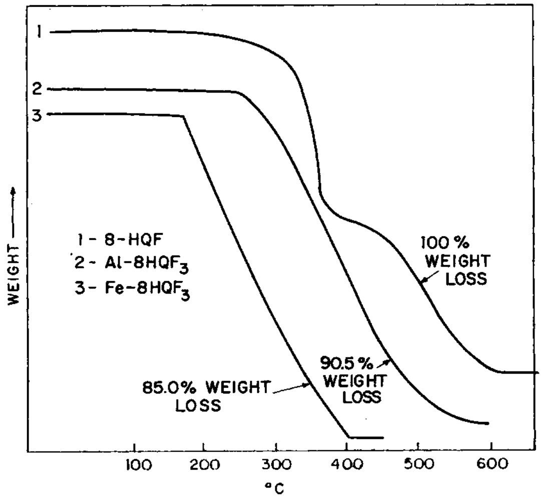


Fig. 3. Thermal decomposition of 8-hydroxyquinoline–formaldehyde polymer (8-HQF) and its chelates with aluminum and iron(III): (*1*) 8-HQF; (*2*) $Al(8\text{-}HQF)_3$; (*3*) $Fe(8\text{-}HQF)_3$.

tion of the polymer started near 270°C. Around 400°C. the decomposition slowed for a short period and became rapid again at about 455°C. The polymer was completely decomposed at 605°C. The decomposition of the aluminum and iron chelate occurred in one step starting sharply at 180°C. for the $Fe(8\text{-}HQF)_3$ and at 250°C. for the $Al(8\text{-}HQF)_3$. The zinc chelate (Fig. 4, curve *2*) decomposed at 260°C., and constant weight was attained at approximately 600°C. The zinc chelate was therefore somewhat more stable than the aluminum chelate. The thermogram of the nickel compound (Fig. 4, curve *3*) was very similar in its pattern to the iron chelate (Fig. 3, curve *3*). For the non-stoichiometric Ni–8HQF decomposition began at approximately 230°C. Since the nickel chelate decomposed in one step although its composition was not stoichiometric, it can be assumed that this decomposition was catalytically induced by the metal. This is probably the mechanism of decomposition for the iron chelate also. Both of these metals are able to change their ionic valency whereas Al^{+3} and Zn^{+2} cannot be converted to other oxidation states.

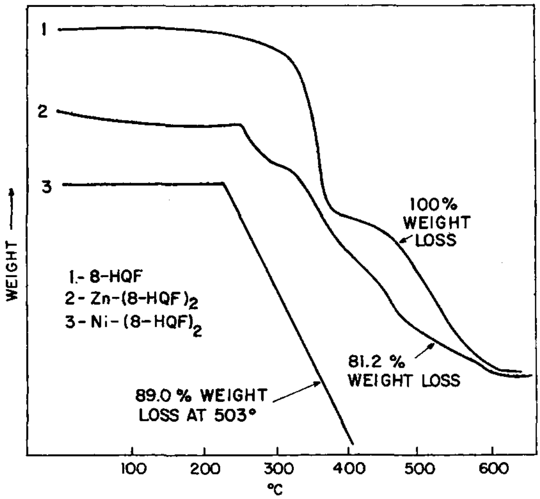


Fig. 4. Thermal decomposition of 8-hydroxyquinoline–formaldehyde polymer (8-HQF) and its chelates with zinc and nickel: (*1*) 8-HQF; (*2*) Zn(8-HQF); (*3*) $Ni(8\text{-}HQF)_2$.

The U^{+4} and Th^{+4} chelates, both of which contained an excess of metal were not investigated. It seems likely, as in the case of SFP[1] with tri- and tetravalent ions, that the polymer is not able to surround the metal ions completely to form the required d^5sp^2 hybrids. The polymeric chelates probably contained U^{+4} and Th^{+4} ions which retained some of their original gegenions (or hydroxyl ions or DMF).

Fe^{+3} and Al^{+3}, which form d^2sp^3 hybrids, and Zn^{+2}, which forms sp^3 hybrids, chelates had close to the theoretical metal content. These arrangements seem more favorable for the polymeric ligand than the dsp^2 hybrid formed by nickel and the ligand.

The chelation of hexacoordinated metal ions such as Fe^{+3} and Al^{+3} by the polymer should impose considerably more strain on the ligand chain than that which results from chelation of tetracoordinate metals such as Zn^{+2} and Ni^{+2}. It was therefore conceivable that due to this strain all chelates decomposed at a lower temperature than the ligand, and furthermore, comparing ions which cannot change their ionic valency (Zn^{+2}, Al^{+3}) with those which do (Fe^{+3}, Ni^{+2}), the Zn^{+2} chelate probably was more stable than the Al^{+3} chelate, and the Ni^{+2} chelate more stable than that of Fe^{+3}.

EXPERIMENTAL

Polymerization of 8-Hydroxyquinoline with Formaldehyde in the Presence of Acid

8-Hydroxyquinoline (29 g., 0.2 mole), 20 g. (0.24 mole CH_2O) of 37% formaldehyde solution, and 1 g. of oxalic acid were mixed and heated 2 hr. with good agitation on a steam bath. To this, 1 ml. of 37% hydrochloric acid in 10 ml. of water was added, and the heating continued overnight. A solid was obtained which was filtered, washed with water, and extracted 16 hr. with ethanol in a Soxhlet extractor. The dry product weighed 23 g. and melted at 250–254°C., with softening starting at 238°C. The resin was soluble in dimethylformamide (DMF) and insoluble in benzene and chloroform. Large amounts of benzene, chloroform, alcohol, or acetone did not precipitate the polymer from the dilute DMF solution. The molecular weight of the purified polymer was determined by light scattering measurements in DMF to be 3.340 ± 10%. Infrared spectral measurements, neutralization equivalents, and elemental analysis were consistent with the proposed structure of the average molecule (I).

ANAL. Calcd. for I: C, 75.44%; H, 4.55%; N, 8.68%. Found: C, 75.15%; H, 4.91%; N, 9.17%.

Identical polymerizations were carried out with the use of 3 hr. reflux with oxalic acid followed by only 2 hr. reflux with hydrochloric acid and refluxing overnight with only oxalic acid. The yield and quality of the resin did not seem to be altered by changing these variables.

Acid-Catalyzed Polymerization of 8-Hydroxyquinoline, Resorcinol, and Formaldehyde

8-Hydroxyquinoline (14.5 g., 0.1 mole), 11 g. (0.1 mole) of resorcinol and 30 g. (0.37 mole CH_2O) of 37% aqueous formaldehyde solution were heated on a steam bath with stirring until a homogeneous melt was formed. Then, 2 g. of oxalic acid was added. The mixture was heated until it solidified. Water (50 ml.) was added and the mixture further heated for 1 hr. To this was added 1 ml. of 37% HCl and the mixture heated another hour to yield a brown-orange resin. After the same work-up as described above, 16 g. of polymer was obtained which softened at 225°C.

Another experiment was run in which 14.5 g. (0.1 mole) of 8-hydroxyquinoline, 3.3 g. (0.03 mole) of resorcinol, and 12 g. (0.15 mole CH_2O) of 37% formaldehyde were polymerized with 2 g. of oxalic acid as described in preceding experiments. The product was not significantly different from the other products.

Base-Catalyzed Polymerization of 8-Hydroxyquinoline with Formaldehyde and Resorcinol

A mixture of 14.5 g. (0.1 mole) of 8-hydroxyquinoline, 10 g. (0.12 mole CH_2O) of 37% aqueous formaldehyde solution, and 150 ml. of water were heated in the presence of 60 g. of sodium hydroxide for 17 hr. At the end of this time the crude product was brought to pH 6, removed by filtration, and extracted overnight with ethanol in a Soxhlet extractor. The yield of dry product was 15 g. The product did not melt but darkened at 245°C. The product was totally soluble in 10% hydrochloric acid.

The above described experiment was repeated three times except that resorcinol was added to the polymerization recipe. Polymerizations were carried out by using 0.05, 0.1, or 0.2 mole of resorcinol/mole of 8-hydroxyquinoline. The product containing 0.05 mole of resorcinol/mole of 8-hydroxyquinoline was totally soluble in 10% hydrochloric acid. Products containing 0.1 and 0.2 mole of resorcinol/mole of 8-hydroxyquinoline were not totally soluble in 10% HCl. These products were washed with 10% HCl in a flask with strong agitation, removed by filtration, rewashed in the same manner, removed by filtration again, suspended in water and the pH brought to 5–6 by the addition of sodium acetate. The products were washed with water and dried. The yields were in the range of 15–17 g. None of the products melted up to 300°C. All of them darkened somewhat at 250°C. or slightly above. Crosslinking experiments of 8-hydroxyquinoline with resorcinol were carried out up to a 1:1 molar ratio.

Metal Chelates of 8-Hydroxyquinoline–Formaldehyde Polymer

Several ways to prepare metal chelates of 8-HQF were tried in order to obtain stoichiometric compositions. Since the polymer was practically insoluble in all solvents but DMF, solutions of 8-HQF in this solvent at various concentrations were therefore precipitated by addition of solutions of the desirable metal ions, as chlorides in DMF with and without addition of base (triethylamine) to attain pH values between 3 and 12. The sequence of combination of these solutions was varied and so was the temperature. Neither of these procedures gave completely satisfactory results. The best results were obtained using the following procedures.

Zn(8-HQF)$_2$. A 0.02 mole portion of 8-HQF (on basis of $^1/_7$ of the weight of I) (3.2 g.) was dissolved in 100 ml. of DMF. To this solution which was stirred by a magnetic stirrer, a solution of 0.02 mole of $ZnCl_2 \cdot 6H_2O$ (2.7 g.) in 100 ml. of DMF were added. The apparent pH of the slurry was adjusted to 11.7 by addition of triethylamine. The greenish-yellow precipitate was filtered by suction 24 hr. after precipitation was complete. It was washed with 20 ml. DMF and then extracted with ethanol for 24 hr. in a Soxhlet extractor. After being dried *in vacuo* at the temperature of refluxing ethanol for 24 hr., the precipitate contained 16.40% zinc (theory 16.92%).

$Ni(8\text{-}HQF)_2$. 8-HQF (0.01 mole, 1.6 g.) was dissolved in 60 ml. DMF. To this solution, a solution of 0.01 mole of $NiCl_2 \cdot 6H_2O$ (1.78 g.) in 50 ml. DMF was added. A green precipitate formed immediately. The apparent pH of the slurry was 2.5. The precipitate was treated as described for the zinc chelate. It contained 8.8% nickel (theory 15.47%).

$Al(8\text{-}HQF)_3$. 8-HQF (0.01 mole, 1.6 g.) in 50 ml. DMF and 0.0033 mole of $AlCl_3 \cdot 6H_2O$ (0.08 g.) dissolved in 25 ml. DMF were combined. A yellow precipitate formed immediately. The apparent pH of the slurry was 3. The precipitate was treated as described for the zinc chelate. It contained 5.07% Al (theory 5.30%).

$Fe(8\text{-}HQF)_3$. 8-HQF (0.01 mole, 1.6 g.) was dissolved in 50 ml. of DMF. To this solution, a solution of 0.0033 mole of $FeCl_3 . 6H_2O$ (0.09 g.) dissolved in 25 ml. DMF was added. A green precipitate formed immediately. The apparent pH of the slurry was 3. The precipitate was treated as described above. It contained 10.45% Fe (theory 10.40%).

Th(8-HQF). 8-HQF (0.01 mole, 1.6 g.) was dissolved in 50 ml. DMF and combined with a solution containing 0.0025 mole of anhydrous thorium chloride in 25 ml. DMF. A green precipitate formed immediately. The apparent pH of the slurry was 3. The precipitate was treated as described above. It contained 30.40% Th (theory 26.56%).

U^{+4}(8-HQF). 8-HQF (0.01 mole, 1.6 g.) was dissolved in 100 ml. DMF and combined with a solution of 1.9 g. of UCl_4 (33.4% uranium) dissolved in 25 ml. DMF. A dark brown preicpitate formed after some standing. The apparent pH of the slurry was 3. The precipitate was treated as described above. It contained 43.50% uranium (theory 27.06%).

Samples (150–250 mg.) of these polymeric metal chelates were heated from room temperature to constant weight at a rate of 5°C./min. on a thermogravimetric balance (system Chevenard) which measures and registers the weight continually as the temperature of the material is raised.

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Résumé

La condensation de 8-hydroxyquinoléine avec le formaldéhyde fournit un polymère de poids moléculaire d'environ 3300. La modification de ce polymère avec la résorcine améliorait les propriétés physiques du matériau. On peut employer les polymères de 8-hydroxyquinoléine et formaldéhyde comme résines échangeuses d'ions sélectives formant des chélates, qui permettent la séparation de divers cations. Les chélates polymère-métal sont moins stables thermiquement que le polymère non-chelaté.

Zusammenfassung

Kondensation von 8-Hydroxychinolin mit Formaldehyd in saurer Lösung liefert ein Polymeres von Molekulargewicht ~3300. Modifikation dieses Polymeren mit Resorcin führt zu verbesserten Eigenschaften des Materials. 8-Hydroxychinolin-Formaldehydpolymere können als selektive Chelat-bildende Ionenaustauscherharze verwendet werden, welche die Trennung verschiedener Kationen gestattet. Die Polymermetallchelate sind thermisch weniger Stabil als das Nicht-Chelat-Polymere.

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