Poly-(4- and 5-Acrylamidosalicylic Acids). Part IV. Selectivity in the Extraction of Metal Cations from Aqueous Solution

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4- and 5-Aminosalicylic acids have been converted into their *N*-acryloyl derivatives which underwent polymerisation in the presence of sodium and borate ions to give poly-(4- and 5-acrylamidosalicylic acids). These polymers act as solid-state chelating agents capable of selectively extracting specific cations from aqueous solution. Thus the polymers show appreciable selectivity for Fe^{3+} in the pH range 2·0—2·7, and for Cr^{3+}, UO_2^{2+}, and Cu^{2+} in the pH range 4·5—5·5; nearly 100% of each of these ions was extracted when a stoicheiometric quantity of polymer was used. A maximum of *ca.* 30% of the ions Ni^{2+}, Co^{2+}, Zn^{2+}, and Mn^{2+} were extracted in the pH range 4·5—6·0. Cd^{2+} was extracted to *ca.* 50% in the pH range 4·5—5·5.

METAL cations may be removed from aqueous solutions either by absorption onto an ion-exchange resin, or by solvent extraction. The former technique is normally non-selective in its absorption whilst the latter is usually very selective but is more complex to use because it involves a liquid–liquid phase exchange with a subsequent physical separation of the two liquids. Solvent-extraction procedures are, however, gaining acceptance especially in the recovery of copper, uranium, and certain of the noble metals, because of improved selectivity of the reagents used. It has long been thought,[1] however, that combination of the ion-specificity of solvent extraction with the insolubility of an ion-exchange resin would give a superior reagent. Polymers are obvious candidates for such a role, and several types have been considered,[1] amongst them being modifications of polymerised salicylic acid.[2-4]

Among the first of such materials reported were copolymers of salicylic acid–resorcinol–formaldehyde and a polystyrene–azosalicylic acid which were tested for their hydrogen and copper ion capacities.[5] Lastovsky *et al.*[6] discussed the pH dependence of the equilibrium exchange capacity of a *p*-aminosalicylic acid–resorcinol copolymer, but both the pH ranges and the cations used were restricted. Paris [7] has described uranium extraction with a salicylic acid–formaldehyde polymer used in slurry form, and Donaruma [8] has used polymers with repeating units containing hydroxy- and carboxy-groups in an *ortho* relationship both in slurry and solvent extraction applications. Kruse [9] has claimed selective extraction of uranium with chelating agents based on salicylic acid and its derivatives, selectivity being achieved by control of pH in the range 3·5—5·5; Baker [10] has described applications of similar materials. Greiger [11] has described a polymer containing ' at least one phenolic hydroxy-group esterified with a non-polymerisable acid ' with an acryloyl grouping to provide the polymerisable function.

DeGeiso and his co-workers [12-14] described a water-insoluble salicylic acid–formaldehyde polymer of average molecular weight 6700 $\pm$ 15% which complexed with Zn^{2+}, Ni^{2+}, and UO_2^{2+} in the ratio 2 monomer units per cation, and with Fe^{3+} and Al^{3+} in a 3 : 1 ratio. This polymer extracted uranium preferentially at pH 4, after removal of the iron, and was appreciably selective for UO_2^{2+} over the range of pH values tested.

These investigations demonstrate that salicylic acid–formaldehyde polymers show selectivity and good complexing powers. It may be argued, however, that the presence of an aromatic ring in the polymer chain could cause steric hindrance, and so lessen their effectiveness. Such a decrease in complexing ability could best be countered by the presence of a more flexible polymer chain, in which the aromatic nucleus is present as a side chain. Studies have shown the feasibility of polymerising 4- and 5-acrylamidosalicylic acids,[15] and polymers so made have exhibited good complexing powers with respect to borate and antibiotics [16] and, as their titanium complexes, with enzymes.[17] Here we describe both the synthesis of such polymers and an initial assessment of their extraction capabilities for a number of cations in acid media under conditions approximating to those encountered in industrial processes. The cation : polymer ratios were chosen to lie close to the stoicheiometric values given by DeGeiso.[12]

EXPERIMENTAL

Acryloyl chloride was prepared from acrylic acid and benzoyl chloride in the presence of hydroquinone; [15] the final product (64%) distilled at 73—75 °C.

4-Acrylamidosalicylic acid was prepared by treatment

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[1] J. R. Millar, *Chem. and Ind.*, 1957, 606.

[2] U.S.P. 2,144,101/1939.

[3] Dutch P. 63,636/1950.

[4] U.S.P. 2,565,418/1951.

[5] R. V. Davies, J. Kennedy, E. S. Lane, and J. L. Williams, *J. Appl. Chem.*, 1959, **9**, 368.

[6] R. P. Lastovsky, N. M. Djatlova, V. J. Tjomkina, I. D. Kolpakova, and O. V. Lavrova, Analyt. Chem., Proc. Intern. Symp., Birmingham University, 1962, 165.

[7] Swiss P. 318,201/1957.

[8] U.S.P. 3,035,022/1962.

[9] U.S.P. 3,052,515/1962.

[10] U.S.P. 3,089,885/1963.

[11] South African P. 67 00,783/1968.

[12] R. C. DeGeiso, L. G. Donaruma, and E. A. Tomic, *J. Org. Chem.*, 1962, **27**, 1424.

[13] R. C. DeGeiso, L. G. Donaruma, and E. A. Tomic, *Analyt. Chem.*, 1962, **34**, 845.

[14] R. C. DeGeiso, L. G. Donaruma, and E. A. Tomic, *Ind. Eng. Chem. Process Design Devel.*, 1963, **2**, 43.

[15] J. F. Kennedy, S. A. Barker, J. Epton, and G. R. Kennedy, *J.C.S. Perkin I*, 1973, 488.

[16] J. F. Kennedy, J. Epton, and G. R. Kennedy, *Antimicrobiol Agents and Chemotherapy*, 1973, **3**, 29.

[17] J. F. Kennedy and J. Epton, *Carbohydrate Res.*, 1973, **27**, 11.

of sodium 4-aminosalicylate with acryloyl chloride [15] (70% yield, m.p. 227 ± 2°). 5-Acrylamidosalicylic acid was similarly prepared (50% yield, m.p. 218 ± 2°).

Preparation of Poly-(4- *and* 5-*acrylamidosalicylic acids*) *in the Absence of Borate*.—The polymers were prepared by a method based on those previously described.[15] 4- or 5-Acrylamidosalicylic acid (15 g) was added to distilled water (180 cm^3) and the pH was adjusted to 9 by the addition of 10M-sodium hydroxide. The resulting solution was heated to 80 °C and azobisisobutyronitrile (0·15 g) in ethanol (50 cm^3) was added to it; the mixture was maintained at 80 °C for 48 h. Water (200 cm^3) was added to the resulting solution, which was pale yellow for the 4-amido-polymer and deep purple for the 5-amido-form. The acid forms of the polymers formed flocculant precipitates upon reduction of the pH to *ca.* 2 with 5M-hydrochloric acid. The poly-(4- and 5-acrylamidosalicylic acids) [(I) and (II) respectively] were washed with water by decantation and stored as suspensions in water at 4 °C.

Details of cation solutions and extractabilities

Polymer	Metal cation	Salt used	pH Range covered	Maximum extraction %	Optimum pH for maximum extraction
(I)	UO_2^{2+}	$UO_2(C_2H_2O_2)_2,2H_2O$	2·5—10·0	30	4·7—5·5
(II)	UO_2^{2+}	$UO_2(C_2H_2O_2)_2,2H_2O$	2·5—10·0	52	4·7—5·5
(III)	UO_2^{2+}	$UO_2(C_2H_2O_2)_2,2H_2O$	1·3—9·0	93	4·7—5·5
(IV)	UO_2^{2+}	$UO_2(C_2H_2O_2)_2,2H_2O$	1·5—6·5	90	4·7—5·5
(III)	Fe^{3+}	$Fe(NO_3)_3,9H_2O$	0·7—2·7	87	2·7 *
(IV)	Fe^{3+}	$Fe(NO_3)_3,9H_2O$	0·7—2·7	91	2·7 *
(III)	Cu^{2+}	$Cu(NO_3)_2,6H_2O$	1·0—6·0	85	4·8—5·2
(IV)	Cu^{2+}	$Cu(NO_3)_2,6H_2O$	1·0—6·0	76	4·8—5·2
(III)	Ni^{2+}	$Ni(NO_3)_2,6H_2O$	1·0—6·2	38	5·5 *
(IV)	Ni^{2+}	$Ni(NO_3)_2,6H_2O$	1·0—6·2	29	5·0 *
(III)	Co^{2+}	$Co(NO_3)_2,6H_2O$	1·2—6·2	27	5·1 *
(IV)	Co^{2+}	$Co(NO_3)_2,6H_2O$	1·9—6·1	25	5·2 *
(III)	Cr^{3+}	$CrCl_3,6H_2O$	1·5—5·7	92	5·0 *
(IV)	Cr^{3+}	$CrCl_3,6H_2O$	1·6—5·8	90	4·5 *
(III)	Zn^{2+}	$Zn(C_2H_3O_2)_2$	1·7—6·3	24	5·1 *
(IV)	Zn^{2+}	$Zn(C_2H_3O_2)_2$	1·7—6·3	25	5·1 *
(III)	Mn^{2+}	$MnSO_4,4H_2O$	1·7—6·0	30	5·0 *
(IV)	Mn^{2+}	$MnSO_4,4H_2O$	1·7—6·0	28	5·1 *
(III)	Cd^{2+}	$CdCl_2$	1·6—6·3	45	5·0—6·0
(IV)	Cd^{2+}	$CdCl_2$	1·6—6·3	52	4·5—5·5

* pH Values greater than these could not be achieved due to the precipitation of the hydroxide.

Preparation of Poly-(4- *and* 5-*acrylamidosalicylic acids*) *in the Presence of Borate*.—4- and 5-Acrylamidosalicylic acids were polymerised as described above, but $Na_2B_2O_7,10H_2O$ (9·39 g) was added to the reaction mixture before adjustment of the pH to 9. The resulting 4- and 5-amido-polymers [(III) and (IV) respectively)] were washed with water and then stored as above.

Both samples of the 4-amido-polymer were white, whereas the samples of the 5-amido-polymer were bluish-pink. Polymers (I) and (II) showed appreciable solubility at pH values above 6.

Determination of Acidic Hydrogen Equivalents of the Poly-(4- *and* 5-*acrylamidosalicyclic acids*).—Polymer suspensions were prepared by diluting and agitating the required amount of the stock suspensions to 110 cm^3, to give *ca.* 0·003 g cm^{-3} of polymer.

Aliquots (2 × 10 cm^3) of each polymer, when dried slowly at 20 °C *in vacuo* (over P_2O_5) to constant weight, gave an amorphous brown or a purple bead which failed to reform a suspension with water.

Similar aliquots (10 cm^3) were back titrated against standard 0·01M-sodium hydroxide solution. The base (30 cm^3) was added to the polymer aliquot and allowed to equilibrate; the excess was then titrated against 0·01M-nitric acid. End points were determined from plots of d(pH)/dV against V, (V = volume of acid added). Estimated equivalent weights of the repeat units of the polymers were as follows (theoretical value 207): (I) 207, (II) 196, (III) 215, and (IV) 210.

Metal Complex Formation by Poly-(4- *and* 5-*acrylamidosalicylic acids*).—Since initial tests showed that the complexing behaviour of the polymers was unaffected by the anions present, the cation solutions were made up using simple salts of known stoicheiometry (see Table).

To suspensions of the polymer (20—30 mg) in water (10 cm^3) were added 0·5M-sodium sulphate, 0·2M-sulphuric acid or 0·05M-sodium carbonate, and a solution of the cation, in such amounts that, after dilution of the mixture to 25 cm^3, the final concentration of the cation was in the range 100—1000 p.p.m., the final sulphate concentration was ten times the molarity of the cation, and the pH lay within the range 0·5—6·5. The suspensions were stirred for 30 min; the final pH was then measured and the suspension centrifuged, the supernatant liquid being retained for analysis for its residual metal content.

The amount of metal cation taken up by each polymer at a given pH was estimated by measuring the concentration of unchelated metal remaining in solution after equilibration.

Uncomplexed uranyl ion was determined by the method of Nietzel and De Sesa.[18] The pH of the supernatant was lowered to 3, a large excess of aluminium nitrate was added, and the uranium extracted into isobutyl methyl ketone (20 cm^3). After shaking to complete the extraction, an aliquot of the organic layer (10 cm^3) was added to a solution of ammonium thiocyanate and ascorbic acid in a butylcellosolve/water mixture (11 : 4 v/v, 15 cm^3) to develop the required colour. Optical densities were measured at 375 and 420 nm against a water blank, in a Unicam SP500 spectrophotometer. The amount of uranium present was calculated by reference to a calibration curve derived from standard solutions of uranyl acetate.

Uncomplexed manganous ion was determined by flame

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[18] O. A. Nietzel and M. A. De Sesa, *Analyt. Chem.*, 1957, **29**, 756.

photometry by aspiration of an appropriately diluted aliquot of the supernatant liquid into an acetylene–air flame. Emission values were determined at 403·3 nm, using a Unicam SP900 flame photometer, and estimates of the concentrations were derived by interpolation from values obtained for standard solutions of manganous sulphate.

Uncomplexed Cd^{2+}, Cr^{3+}, Co^{2+}, Cu^{2+}, Fe^{3+}, Ni^{2+}, and Zn^{2+} were determined by atomic absorption spectrophotometry. Appropriately diluted samples were aspirated into an acetylene–air flame in a Perkin-Elmer 303 spectrophotometer, and percentage absorption values were converted into absorbances from which the unknown concentrations were estimated by interpolation in the usual manner.

RESULTS

The percentages of the various cations extracted by polymers (III) and (IV) at various pH values are shown in Figures 1 and 2 respectively. The pH value used is that determined at the end of the equilibration period, prior to the centrifugation and determination of the cation concentration in the supernatant liquid. The percentage extraction values were obtained by subtracting the residual concentration in the supernatant from the original concentration determined by the methods as listed above. The pH ranges covered, maximum degrees of extraction, and pH values at which maximum extraction occurred are also listed in the Table.

The cations were easily desorbed from the polymer at a pH slightly less than 2, with the exception of iron where a pH close to 1 was required.

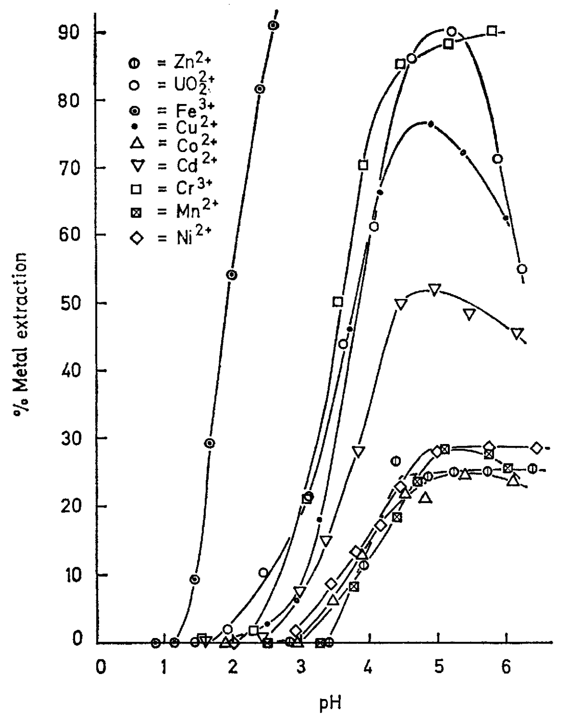

FIGURE 1 Percentage of metals independently extracted from solutions by poly(4-acrylamidosalicylic acid) at various pH values

DISCUSSION

As described above, all four polymers had equivalent weights corresponding to the presence of a free acid group in each repeating unit. This indicates that the polymers are both pure and have a carbon–carbon backbone with the salicylic groups attached *via* an amide link.

Whilst polymers (I) and (II) showed appreciable solubility at all pH values, and were completely soluble above pH 6, polymers (III) and (IV) were considerably less soluble. Moreover, the suspensions of (I) and (II) were cloudier than those of (III) and (IV) and appeared to contain more fine material. These observations together with the similarity in the equivalent weights indicate that, whilst the molecular weight of the polymer formed is dependent on the presence or otherwise of borate, the mode of polymerisation is not. Since (1) both the hydroxy- and carboxy-functions of salicylic acid are involved in complex formation with borate,[15] and (2) acidic salicylyl residues prevent the polymerisation from occurring (acrylamidosalicylic acid monomers were not polymerised in the absence of sodium ions or of borate [15]), the present work indicates that complex formation between borate and the monomer gives rise to polymers of longer chain length.

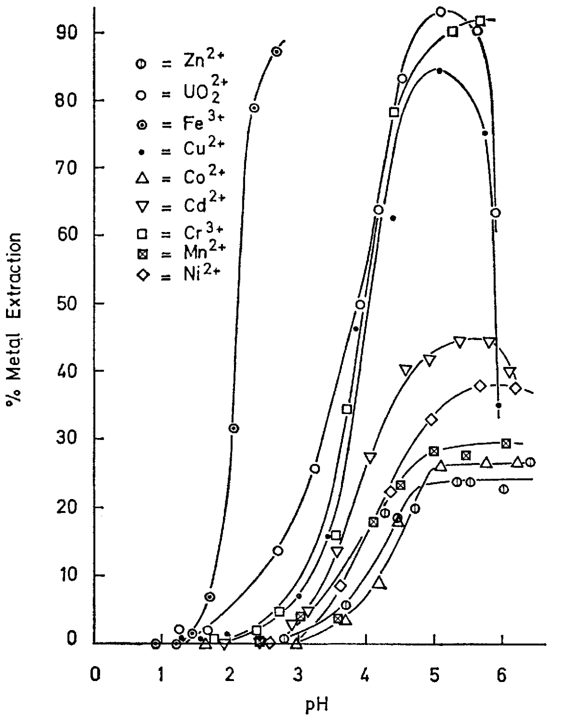

FIGURE 2 Percentage of metals independently extracted from solutions by poly-(5-acrylamidosalicylic acid) at various pH values

Variation of the time allowed for complex formation between polymer and UO$_2^{2+}$ showed that the system had reached equilibrium within 30 min; this time was therefore chosen for all subsequent investigations.

Since polymers (I) and (II) gave more soluble complexes with UO$_2^{2+}$ than did (III) and (IV) the former polymers were less efficient extractants in terms of the amount of complex which was recoverable by centrifugation (see Table); the latter complexes were therefore used in all subsequent work.

Since sulphuric acid is commonly used in mineral processing plants, all equilibrations were carried out in the presence of a large excess of sulphate ion. Cation concentrations were chosen such that they lay in the range 100—1000 p.p.m. during the equilibration of the complex formation, again to correspond to the majority of hydrometallurgical conditions.

With the exception of cadmium and nickel the degree of extraction of metal ions by the polymers at various pH values (Figures 1 and 2) shows that the 4- and 5-amido-polymers behave similarly. For both polymers the maximum extraction of UO_2^{2+}, Cu^{2+}, and Cd^{2+} occurred at *ca.* pH 5, whilst for other cations the degree of extraction reached a maximum at this pH and remained constant for higher pH values. Raising the pH of the metal solutions above the values of the discontinuities of the curves resulted in the precipitation of the metal ions as hydroxides or as basic salts.

For a given percentage of metal ion extracted, the 5-amido-polymer achieved the required degree of complexing at a marginally lower pH than did the 4-isomer. Although differences in the orientations of the carboxyl and the hydroxyl groups on the aromatic residues relative to the main chain may account for this behaviour, it is more likely that the effect is due to differences in the acid dissociation constants of the two acids.

The cations employed fall into two major groups by virtue of the extent to which they are extracted. One group comprises UO_2^{2+}, Cr^{3+}, and Cu^{2+} which show maximum extraction values approaching 100% in the pH range 4·5—5·5, and the other includes Mn^{2+}, Co^{2+}, Zn^{2+}, and Ni^{2+} which extract only to *ca.* 30% above pH 5. Iron is another strongly absorbed cation, but measurements could be made only up to pH 2·6, because the hydroxide precipitated at higher pH values. Cadmium appears to have a behaviour intermediate between those of the major groups, and is also different in that the degree of extraction is markedly different for the two polymers, a feature also shown by nickel. For cadmium, the greater extraction occurs with polymer (IV), but polymer (III) extracts more of the nickel.

From this examination of the complex formation properties of the polymers, the results indicate that these polymers show considerable promise as specific extractants for certain cations. An example of this specific extractability would be the case of mixed uranyl and ferric ions. At low pH values, around 2·0—2·5, in the range in which uranium leach liquors are usually found, the polymer absorbs Fe^{3+} very specifically and it is suggested that the polymer might find a use for the removal of iron from such liquors before the uranium removal step. At higher pH values, *ca.* 5, the polymer would then be able to extract UO_2^{2+} quite specifically, and initial tests with mixed solutions strongly suggest that the relative extractabilities shown by the ions singly are retained in mixtures.

Although use of the polymers on a commercial basis is attractive since they are relatively inexpensive, the synthesis of 4-aminosalicylic acid is considerably more complex than the 5-isomer, and so the 5-amido-polymer would be preferred on economic grounds. The stability of the polymers means that the materials could be used for many cycles of cation recovery.

The authors thank Professors M. Stacey, C.B.E., F.R.S. and S. G. Ward for their interest in this work and G. Harrison for technical assistance.

[2/1709 *Received*, 19*th July*, 1972]