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Publication details, including instructions for authors and subscription information:
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To cite this Article Trochimczuk, Andrzej W. , Kolarz, Bożena N. , Jermakowicz-Bartkowiak, Dorota and Apostoluk, Wiesław(1999) 'Sorption of Dicyanoaurate Anions by Novel Resins Containing *N,N'* substituted Diamides of Malonic Acid', Separation Science and Technology, 34: 11, 2243 — 2250

To link to this Article: DOI: 10.1081/SS-100100769

URL: http://dx.doi.org/10.1081/SS-100100769

SEPARATION SCIENCE AND TECHNOLOGY, **34**(11), pp. 2243–2250, 1999

Sorption of Dicyanoaurate Anions by Novel Resins Containing *N,N′*-Substituted Diamides of Malonic Acid

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ABSTRACT

Two novel ion-exchange/coordinating resins have been synthesized and used in the sorption of dicyanoaurate anions, $Au(CN)_2^-$, from aqueous solution from their mixtures with Fe(III) cyano complexes, Ag(I) cyano complexes, Zn(II) cyano complexes, Fe(II) cyano complexes, Cu(II) cyano complexes, and from solutions containing all of the above species. It has been found that Resin 1 containing the *N,N′*-substituted amide of malonic acid with terminal guanidyl groups is able to remove ca. 10 mg Au/g, and Resin 2 containing the *N,N′*-substituted amide of malonic acid with terminal imidazole groups removes ca. 13 mg Au/g from the above solutions when there is an initial concentration of 5.08 mg Au/dm^3. Resin 1 is selective toward gold over all metals but Fe(II). Resin 2 is more selective, and when sorption is carried out from the solution formulated with all the metals displays the following selectivity coefficients: of gold over Fe(II) + Fe(III), $+\infty$; of gold over Ag(I), $+\infty$; of gold over Zn(II), 3.79; and of gold over Cu(II), 2.81.

INTRODUCTION

Ion-exchange and coordinating resins are widely used in various applications for the removal of metal ions from dilute solutions. By careful choice of the resin matrix and type of ligands attached to the polymer, it is possible to

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make a resin for the specific conditions of a particular process. One of the processes studied recently was removal of gold from its dilute cyanide solutions. Although activated carbon is still used for this purpose, there are numerous papers concerning the synthesis and applications of polymeric resins for gold removal (1–6). Since sorption is carried out from solutions of high pH, where gold is present as anionic cyano complexes, attention has been focused on resins with various amino functionalities. Examples include macroporous styrene with 2,4-diamine-2-methylpentane ligands (3). This resin displayed good selectivity and sorption, which could be further increased by increasing the ionic strength of the solution. A selective resin, MINIX, containing strongly basic groups was synthesized in South Africa and its properties were compared to the commercial Rohm and Haas resin Amberlite IRA 400 (4). MINIX resin was able to remove 26 mg Au/g compared with 11 mg Au/g for IRA 400. Other commercial resins were used for gold sorption by Riveros (6), who tested the weakly basic Dowex MWA-1 and the strongly basic IMAC HP-555s, and found that the weakly basic one was more selective although it displayed smaller sorption (3.9 mg/g compared to 4.8 mg/g for the IMAC). Some authors have reported the syntheses of new polymeric resins. For example, in Ref. 7 a resin containing guanidyl groups was obtained by modification of styrene/divinylbenzene copolymer, and its capacity for gold was determined to be 27 mg/g at pH 10.5. It displayed good selectivity toward gold over Zn, Ni, Fe, Cu, and Ag. The same authors, Schwellnus and Green, described the sorption of dicyanoaurates by a resin with imidazole groups (8). In another paper Green presented a comparison of various imidazole-containing resins obtained either by modification of styrene/divinylbenzene or acrylonitrile/divinylbenzene copolymers. It was found that the more hydrophobic styrene-based resins had higher affinities toward dicyanoaurate despite the fact that they contained a smaller amount of ligands (9). Also, in Refs. 10 hydrophobic resins with vinylbenzylchloride/divinylbenzene containing guanidyl and aminoguanidyl ligands were found to be selective toward gold.

It can be concluded from the above studies that sorption of dicyanoaurates is better on more hydrophobic resins, and that factors like ligand structure and concentration influence resin selectivity. It is also known that when active sites present in a resin's structure can not cooperate with each other, e.g., their concentration is small and thus they are far apart (active site isolation), or when the resin is rigid owing to a high crosslinking level, metal uptake is smaller. One possible way to improve resin performance is to place active sites in the resin in a way which assures their close proximity. In this study we followed procedure used previously (11) to obtain resins with *N*,*N*′-substituted diamides of malonic acid. Such resins have higher uptake of metal ions than resins with analogously substituted amides of monocarboxylic acids.

The aim of this work was to synthesize resins with *N*,*N*′-substituted diamides of malonic acid which contain two types of medium strength amines as terminal groups, guanidine and imidazole, and to determine their performance in sorption of dicyanoaurate from its dilute solutions.

EXPERIMENTAL

Materials

The starting copolymer, vinylbenzylchloride/divinylbenzene, with 2 wt% crosslinker was obtained by using the suspension polymerization method. Polymerization was carried out in the presence of toluene (50 wt% in respect to the mixture of monomers) in order to obtain a material with an expanded gel structure. The resulting polymer was washed with hot water and with acetone from which the resin was dried. After extraction with toluene (in a Soxhlet extractor for 12 hours) and drying the polymer was sieved, and the 0.10–0.18 mm fraction was used after modification. Subsequent modification steps leading to the resin with diethyl malonate and to the resin with *N*,*N*′-substituted amides of malonic acid having terminal imidazole groups are presented in detail in Ref. 11. Modification of diethyl malonate resin leading to the *N*,*N*′-substituted diamides with terminal guanidyl groups was carried out using two steps. First, diethyl malonate resin was subjected to aminolysis with ethylenediamine. The reaction was carried out at 125°C for 18 hours and resulted in a resin having primary amino groups. These groups were subsequently reacted with 1*H*-pyrazole-1-carboxamidine using procedures described in Ref. 12. Both obtained resins were conditioned using distilled water, 1 M NaOH, distilled water, and 1 M HCl. The process was repeated three times. The resins were stored in protonated form and used in swollen form.

All chemicals were purchased from Aldrich and used as obtained.

Methods

Nitrogen analysis was done by digesting a sample of the dry resin in concentrated sulfuric acid using the Kjeldahl method.

Primary amino groups were analyzed using Hecker's method (13). Approximately 1 g of swollen polymer was placed in a column with a fritted disc and washed with 500 mL of 1 M HCl, 200 mL of 0.001 M HCl, and then with 500 mL of 4% sodium sulfate in 0.05 M NH_4OH. The latter eluate was collected in a 500 mL volumetric flask and analyzed for its chloride ion concentration.

Water regain was measured using the centrifugation method. Thus, ca. 1 g of swollen resin was placed in a small column with a fritted-glass bottom and was centrifuged at 3000 rpm for 5 minutes. The column was weighted and placed in dryer at 100°C for 16 hours, cooled in a dessicator, and weighted again. Water regain was calculated as

$$W = (m_\mathrm{w} - m_\mathrm{d})/m_\mathrm{d}$$

where m_w is the weight of swollen polymer (after centrifugation) and m_d is the weight of dry resin.

The appropriate amount of each resin (85.75 mg of Resin 1 and 46.70 mg of Resin 2) in swollen form was contacted for 48 hours with 500 cm^3 of the respective dicyanoaurate solution, the pH of which had been adjusted to 9.6 using 0.1 M NH_4OH + 0.1 M NH_4NO_3 buffer. Three types of solutions were used in the experiments: neat dicyanoaurate (5.08 mg $\mathrm{Au/dm}^3$), solutions containing dicyanoaurate (5.08 $\mathrm{mg/dm}^3$) and one another metal cyano complex like Fe(III) (7.62 $\mathrm{mg/dm}^3$), Ag(I) (5.08 $\mathrm{mg/dm}^3$), Zn(II) (12.70 $\mathrm{mg/dm}^3$), Fe(II) (7.62 $\mathrm{mg/dm}^3$), and Cu(II) (50.80 $\mathrm{mg/dm}^3$); solutions containing dicyanoaurate and all of the above metals. In all cases the solutions had a 100 $\mathrm{mg/dm}^3$ excess of KCN. After 48 hours the polymers were separated by filtration and the metal concentrations in the solutions were analyzed using the AAS method.

Distribution coefficients were calculated as the ratio of the amount of metal adsorbed by 1 g of resin and the amount of metal remaining in 1 cm^3 of solution after sorption.

The selectivity coefficient was calculated as the ratio of the respective distribution coefficients.

RESULTS AND DISCUSSION

Synthesis of the Resins

The general scheme for the synthesis of the resins is presented in Fig. 1. As can be seen, Resin 2 is obtained in a one-step aminolysis reaction using 1-(3-aminopropyl)imidazole. The yield of this reaction is 80%. The resultant resin is characterized by a high nitrogen and ligand content. It is rather hydrophobic, as manifested by its low water uptake (see Table 1).

Synthesis of Resin 1 requires two steps. In the first one the starting polymer with the diethyl ester of malonic acid is converted with ethylenediamine to a diamide with terminal primary amino groups. This intermediate has a nitrogen content of 6.32 mmol/g as determined by elemental analysis. The number of amino groups analyzed using Hecker's method is 3.06 mmol/g (13). These two values are reasonable matchs and show that there is little or no crosslinking during the aminolysis with ethylenediamine. The second step was carried out according to the procedure described in Ref. 12. In that paper the authors presented five different methods of guanylation applicable to different classes

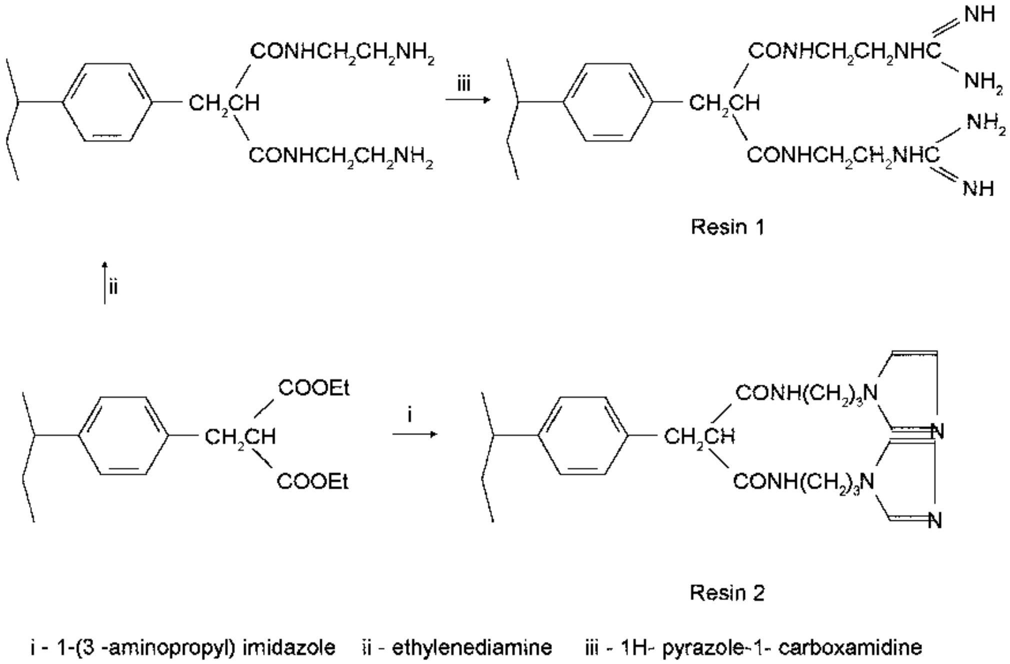

FIG. 1 Scheme for the synthesis of the investigated resins.

of amines (unhindered primary, DMF soluble, aromatic, etc.). Since our guanylation reaction was carried out in a heterogeneous system where amino groups are attached to the polymeric backbone, it was necessary to try more than one reaction condition in order to find one suitable for polymer modification. Three methods were applied: for primary, unhindered amines which are DMF soluble, for amines soluble in an aqueous base, and modification of a method applicable for aromatic amines. They gave 0, 62, and 16% yields of guanylation, respectively. The reaction yield in the second case was only slightly lower than that reported in Ref. 12 for the guanylation of glycine—77%. The Resin 1 obtained has a high nitrogen content, but due to the high percentage of nitrogen per ligand molecule, the number of ligands is lower

TABLE 1
Characteristics of Investigated Resins

Resin	Terminal group	Nitrogen (mmol/g)	Ligand (mmol/g)	Percentage of solid	Water regain (g/g)
1	Guanidyl	9.20	1.72	65.22	0.53
2	Imidazole	8.35	2.78	74.15	0.35

than in the case of Resin 2. The water uptake is higher—0.53 g/g—as shown in Table 1.

The resins were kept in protonated form in distilled water and were centrifuged just before being placed in polyethylene bottles in which they were contacted with various gold solutions.

Contact Studies

Two resins were contacted with solutions in which the gold concentration was 5.08 mg/dm^3. Three sets of solutions were used: a neat one in which only dicyanoaurate anions were present, pairs of dicyanoaurate and one other metal cyano complex, and finally dicyanoaurate and a mixture of all the metal cyano complexes investigated. The results of these experiments are summarized in Table 2. As can be seen, the affinity of both resins toward dicyanoaurate from its neat solution is reasonably high—the distribution coefficients are 2131 and 2861 for Resins 1 and 2, respectively. This corresponds to sorption of 8.94 and 12.13 mg Au/g of dry polymer. The sorption values are slightly lower than those presented for some copolymers in our earlier paper for resins with guanidyl groups (10), but they exceed the results obtained for commercial anion exchangers in Ref. 6. It should be noted that the distribution coefficients are almost constant regardless of the composition of the aqueous solutions. This is an indication of the strong affinity of both resins toward dicyanoaurates and can be additionally caused by the increased ionic strength of the solutions formulated with other metal cyano complexes and in particular the solution containing all the studied metals cyanides. For the latter solution the starting gold concentration is 0.026 mmol/dm^3 whereas the total concentration of other metals is 1.312 mmol/dm^3. It is possible that under such conditions the dicyanoaurate anion, which is quite hydrophobic since it carries one charge on

TABLE 2
Affinity of Investigated Resins toward Cyano Complexes

	Distribution coefficients and final pH											
	Resin 1 (guanidyl)						Resin 2 (imidazole)					
Solution	Au	Fe	Ag	Zn	Cu	pH	Au	Fe	Ag	Zn	Cu	pH
Au only	2131					9.64	2861					9.67
Au + Fe(III)	2412	1004				9.65	3236	0				9.67
Au + Ag(I)	2528		243			9.66	3278		232			9.67
Au + Zn(II)	2557			4418		9.65	3041			5935		9.69
Au + Fe(II)	2645	1.3×10^7				9.55	3108	0				9.67
Au + Cu(II)	2675				0	9.67	3151				1335	9.68
Au + all	2675	7818	0	722	0	9.64	3192	0	0	842	1335	9.71

five atoms, is being “pushed out” from the aqueous into the resin phase. The low charge density of dicyanoaurate anions means it has low hydration needs (6), and hence a smaller anionic radius and hydration sphere. This would also explain why the affinity of both resins toward other cyanometal complexes with a higher charge density, displayed when contact studies were performed using solutions with two components, decreases in experiments with the solution containing all the studied metals. For example, Resin 1 shows $K_{\mathrm{d\ Ag}} =$ 243 from a two-component solution. When sorption is carried out from the multicomponent solution, Resin 1 does not attract silver complexes at all. The affinity of this resin toward both forms of iron and also for zinc decreases as well. Unfortunately, even in the multicomponent solution the uptake of iron, presumably Fe(II), is still very high and exceeds the affinity for gold. Since Resin 1 shows the following order of affinity toward cyano complexes, Fe $>$ Au $>$ Zn $\gg$ Ag, Cu, which does not agree with the well-known order of mono- $>$ di- $>$ trivalent anions in ion exchange, it can be concluded that ion exchange is not the predominant process of anions removal. A probable explanation for high iron sorption may be the presence of amide groups which can be deprotonated and active in complexation at high pH as proposed in another paper concerning the uptake of metals by resins with *N*,*N*′-substituted amides of malonic acid (14). Such deprotonation is shifted toward lower pH, even as low as 7.5, when some metal cations are present in solution. The low molecular analogue of our resins—*N*,*N*″-bis(2-aminoethyl) malonamide—displayed deprotonation at one amide site at pH 7.0 and was deprotonated at both amide functionalities at pH 7.5 (15). Other resins with guanidyl groups, studied earlier (10), did not recognize either form of Fe under exactly the same conditions as those used in the present work, but their guanidine ligands were attached directly to the polymer backbone and hence amides were not present in their structures.

Resin 2 displays better selectivity when sorption is carried out from the multicomponent solution. In this case complex formation also has to be one of the processes of metal sorption since $\mathrm{Cu(CN)_4^{3-}}$ is recognized by the resin to a higher extent than the less charged $\mathrm{Zn(CN)_4^{2-}}$. Gold sorption remains almost unchanged, whereas the small sorption of silver disappears and zinc is complexed to a much smaller extent when sorption is carried out from the multicomponent solution. K_{d} for copper is exactly the same as in the case of sorption from solution Au + Cu(II), which may reflect the high affinity of imidazole complexones toward copper. The following selectivity coefficients can be calculated from distribution coefficients for metal uptake from solutions containing all the studied metals: gold over Fe(II) + Fe(III), $+\infty$; gold over Ag(I), $+\infty$; gold over Zn(II), 3.79; and gold over Cu(II), 2.81.

These results show that Resin 2, which contains imidazole groups, is suitable for the removal of dicyanoaurate anions from alkaline solutions. The presence of other metal cyano complexes does not affect the uptake of gold. Experiments on the regeneration of the resin with thiourea solutions are in progress and will be the subject of another report.

ACKNOWLEDGMENT

Partial support of this work from the State Committee for Scientific Research through Grant 3T09B 093 11 is gratefully acknowledged.

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Received by editor August 30, 1998
Revision received November 1998

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