Uptake of metal ions from aqueous sulphuric acid by resins

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The uptake capacity towards heavy metal ions in aqueous sulphuric acid of fourteen crosslinked polymer resins has been studied. Some resins contain poly(amido-amine)s or poly(amido-aminoacid)s crosslinked with 1,4-diaminobutane, others contain free NH_2 or oxime groups on a tightly crosslinked structure. All the resins are highly swellable in sulphuric acid solution and, except for the resin containing oxime groups, degrade in a 7–20 days period. All the resins show capacity of retention for Ni^{2+} in 1.53 M sulphuric acid. The resins of the first group also show some selectivity towards several metal ions in this order: $Fe^{3+} \simeq Zn^{2+} > Ni^{2+} > Cu^{2+}$. The resin containing oxime as a donor group does not show such a selectivity, but does exhibit larger retention capacity. N.m.r. spectra indicate the presence of ion pairs in H_2SO_4 solution containing metal ions as $M(HSO_4)_n^{x-n}$, vis. negative species, which are retained from the positively charged resins. For the resin containing oxime groups, the retention seems to occur via a coordination mechanism.

(Keywords: crosslinked polymer resins; aqueous sulphuric acid; adsorbing capacity; metal ions selectivity)

INTRODUCTION

The uptake and concentration of specific metal ions from aqueous solution has been the subject of much research effort. One technique of metal recovery is ion exchange using crosslinked polymer resins. Much of the work on resins is concerned with the uptake of metal ions from aqueous solution in the 1–11 pH range, and in some favourable cases, a complete separation of metal ions may be achieved by varying the pH of the solution.

Up to the present no work has appeared in the literature concerning the uptake of metal ions in strongly acidic solution, probably due to the instability of the majority of resins in this medium. Nevertheless this study is particularly important for the metals industry as the refining of some metals takes place in strong acidic solution, and the presence of other metals as impurities provokes remarkable disadvantages[1].

The problem could be solved if the resins involved present three features:

(i) Stability in strong acidic solution.

(ii) The capability to take up metal ions from this medium.

(iii) Selectivity towards metal ions.

In the present work we have turned out attention to the problem of elimininating metal ion impurities in the refining of copper. Pure copper is generally produced by electrorefining: anodes produced from blister copper are dissolved electrolytically in ~2 M sulphuric acid, and the copper is deposited on pure copper starting sheets to produce cathodes. In virtually all refineries, nickel is the major impurity in the electrolyte (up to 20 grams/litre). The nickel remains in the electrolyte as the copper is stripped out in the purification and is recovered from the resulting acid solution by precipitation as the sulphate in evaporators. In some refineries, dialysers have been utilized to provide a partial separation of the sulphuric acid from the nickel and other impurities. The necessity to maintain closed circuit conditions in the processing plants has increased efforts to recover the by-products from the electrolyte purification and to purify the acid to allow its use for make up in the electrolyte. Therefore, the utilization of resins must be taken into account. The resins must be permeable to Cu^{2+} ions and have good loading capacity towards the other metal ions present in H_2SO_4 as impurities (Fe^{3+}, Ni^{2+}, Zn^{2+} etc.).

The resins studied here belong to two different classes (*Figure 1*):

(i) Class one shows a poly(amido-amine) structure with several different donor groups: –COOH, $-N(CH_3)_2$, $-NH_2$ etc.

(ii) The second class has only oxime groups in its structure.

EXPERIMENTAL

Synthesis of the resins

The structures of all the resins are reported in *Figure 1*.

Resin RN_2C_4. This resin was prepared in H_2O (5 cm^3) by polyaddition of a mixture of *N,N'*-dimethylethylenediamine (0.55 g; 0.0062 mol) and 1,4-diaminobutane, as the crosslinking agent (0.18 g; 0.0020 mol), to 1.4-bisacryloylpiperazine (2.00 g; 0.010 mol) prepared as described previously[2].

The reaction mixture was left at room temperature for 2 days, when it set into a light yellow gel. It was triturated under water and repeatedly extracted with water, methanol and ether. It was then dried at room temperature and 0.1 mm Hg pressure. The potentiomet-

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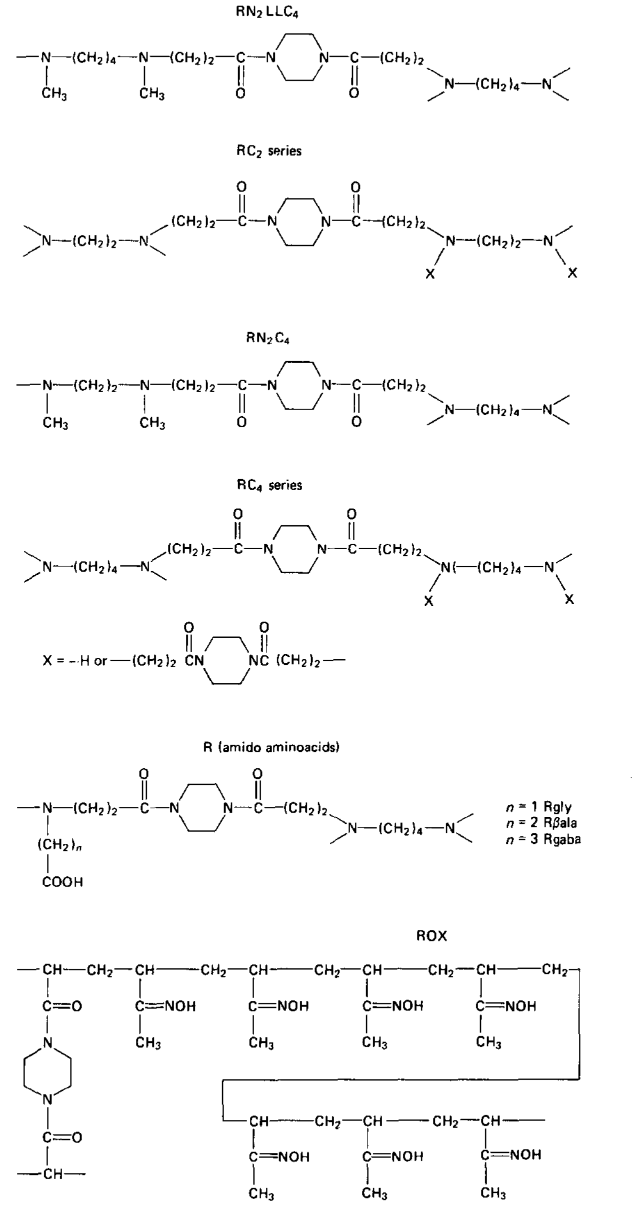

Figure 1 Structures of the resin with: (a) poly(amido-amine) structures with several different donor groups and (b) with oxime groups

ric analysis showed that the ratio between the number of basic nitrogens present in the linear form of the resins and those in the crosslinking agent is 3:1. This ratio agrees with the values expected on the basis of the quantities of reagents used (*Table 1*).

Resin RN_2LLC_4. This resin was synthesized in a similar way to RN_2C_4 by substituting *N*,*N*′-dimethylputrescine for *N*,*N*′-dimethylethyenediamine. The potentiometric analysis confirmed the agreement of the structure with the molar ratio used in the synthesis (*Table 1*). The RN_2LLC_4 resin is white and exhibits a harder mechanical consistency than the RN_2C_4 resin.

RC_2 series resins. These resins were prepared in water (5 cm^3) by polyaddition of ethylenediamine to 1,4-bisacryloylpiperazine in several molar ratios: i.e. 1/1.2; 1/1.4; 1/1.6; 1/2.0 (*Table 1*).

The value of this ratio is correlated with the number of unreacted amino groups which remain free as primary or secondary nitrogens in the structure of the resins. The mechanical consistency depends on this ratio also; the

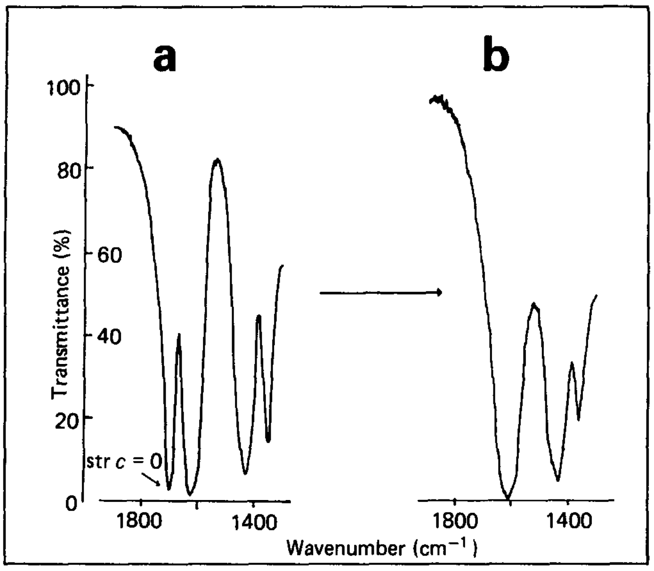

Figure 2 I.r. spectra of the resin in the (A) carbonyl and (B) oxime form

Table 1 Experimental details of resin synthesis

		Resin					
Reagent	Amount	RN_2C_4	RN_2LLC_4	RC_2 (1.2)[e]	RC_2 (1.4)[e]	RC_2 (1.6)[e]	RC_2 (2.0)[e]
1,4-Bisacryloyl piperazine	grams	2.0	2.99	6.0	6.0	6.0	6.0
	moles	0.010	0.0154	0.0309	0.0309	0.0309	0.0309
Ethylenediamine[a]	grams			13.12	11.24	9.84	7.87
	moles			0.0257	0.0221	0.0193	0.0154
N,*N*′-Dimethylethylenediamine[b]	grams	3.28					
	moles	0.0062					
N,*N*′-Dimethylputrescine[c]	grams		5.99				
	moles		0.0092				
1,4-Diaminobutane[d]	grams	1.08	1.57				
	moles	0.0020	0.0031				
Grams of resin obtained		2.70	4.30	7.50	7.30	7.13	6.90
Percentage yield		~100%	~100%	~100%	~100%	~100%	~100%
Initial decomposition temperature (°C)		210	220	215	245	215	230

[a] Ethylenediamine 1.963 mol/kg
[b] *N*,*N*′-Dimethylethylenediamine 1.890 mol/kg
[c] *N*,*N*′-Dimethylputrescine 1.486 mol/kg
[d] 1,4-Diaminobutane 1.855 mol/kg
[e] Figures in parentheses indicate the molar ratio of ethylenediamine to bisacryloylpiperazine

Table 2 Experimental details of resin synthesis

Reagent	Amount	Resin RC$_4$ 1.2	 RC$_4$ 1.4	 RC$_4$ 1.6	 RC$_4$ 2.0
1,4-Bisacryloylpiperazine	grams	7.0	7.0	7.0	7.0
	moles	0.0360	0.0360	0.0360	0.0360
1,4-Diaminobutane[a]	grams	16.17	13.85	12.13	9.70
	moles	0.030	0.0257	0.0225	0.0180
Grams of resin obtained		9.60	9.20	8.95	8.55
Percentage yield		~100%	~100%	~100%	~100%
Initial decomposition temperature (°C		215	225	220	210

[a] 1,4-Diaminobutane 1.855 mol/kg

Table 3 Experimental details of resin synthesis

Reagent	Amount	Resin Rgly	 Rβala	 Rgaba	 ROX
1,4-Bisacryloylpiperazine	grams	5.0	5.0	5.0	5.0
	moles	0.0257	0.0257	0.0257	0.0257
Glycine	grams	1.15			
	moles	0.0154			
β-Alanine	grams		1.37		
	moles		0.0154		
4-Aminobutyric acid	grams			1.58	
	moles			0.0154	
Triethylamine	grams	1.56	1.56	1.56	
	moles	0.0154	0.0154	0.0154	
1,4-Diaminobutane[a]	grams	2.60	2.60	2.60	
	moles	0.0051	0.0051	0.0051	
Methyl vinyl ketone	grams				25.25
	moles				0.3604
Hydroxylamine hydrochloride	grams				27.55
	moles				0.3694
Pyridine	ml				30.0
	moles				0.3884
Grams of resin obtained		6.55	6.78	7.02	35.95
Percentage yield		~100%	~100%	~100%	~100%
Initial decomposition temperature (°C)		240	240	245	265

[a] 1,4-Diaminobutane 1.855 mol/kg

harder resins are those with the larger amounts of crosslinking agent.

RC$_4$ series resins. These resins were synthesized in a similar fashion to those of the previous RC$_2$ series, by substituting 1,4-diaminobutane for ethylenediamine (*Table 2*). Also the mechanical consistency follows a similar trend to that found in the RC$_2$ series.

R-Gly, R-βAla and R-GABA resins. These resins have been prepared, as previously described for RN$_2$C$_4$, by substituting glycine, β-alanine and 4-aminobutyric acid, respectively for *N,N'*-dimethylethylenediamine (*Table 3*).

To the reaction mixture, an equimolar quantity of triethylamine was added to avoid the presence of the amino acid in the zwitterionic form.

ROX resin. This resin was synthesized in two steps:

(i) A mixture of 1.4-bisacryloylpiperazine (5.00 g; 0.0257 mol) and methyl vinyl ketone (25.25 g; 0.3604 mol) in dioxane (15 ml) was left under nitrogen at 60°C for two days with benzoyl peroxide as the initiator. The separated yellow product was washed with water and methanol and dried under reduced pressure.

(ii) In the second step the yellow resin was reacted with hydroxylamine hydrochloride (27.55 g; 0.3694 mol) in ethanol, in presence of pyridine (0.3884 mol), for 24 h (*Table 3*). The brown product was washed with water, C_2H_5OH and finally dried under high vacuum at room temperature.

The i.r. spectra of the carbonyl containing resin show a sharp absorption band at 1705 cm^{-1} which disappears completely after treating with hydroxylamine, to give a C=N–OH containing resin (ROX) (*Figure 2*).

Chemical stability of the resins

None of the resins are degraded or dissolved by water or any other common solvent. However, most of them are partially degraded in 1.53 M H_2SO_4 solution. The degradation occurs after about 10 days for the basic resins (*Table 4*) and is quite obvious because the resins assume a semi-solid jelly-like appearance. After this time the basic resins become impractical as column packing substrates.

Column operations

Each resin was ground with a pestle and mortar to obtain a material which would pass through a 60 mesh sieve. The adsorbing capacities of the resin towards heavy

Table 4 Chemical stability and swelling of the resins in 1.53 M H_2SO_4

Resin	Colour	Stability	Column packing height^a (mm) dry resin	swollen resin	% Swelling
RN_2C_4	light yellow	7 days	14	64	357.1
RN_2LLC_4	white	7 days	12	60	400.0
RC_2 (1.2)	white	7 days	15	65	333.3
RC_2 (1.4)	white	15 days	15	50	233.3
RC_2 (1.6)	white	15 days	13	35	169.2
RC_2 (2.0)	white	20 days	13	35	169.2
RC_4 (1.2)	white	15 days	18	60	233.3
RC_4 (1.4)	white	15 days	15	50	233.3
RC_4 (1.6)	white	15 days	15	45	200.0
RC_4 (2.0)	white	20 days	15	40	166.6
Rgly	white	10 days	17	22	29.4
Rβala	white	10 days	12	25	108.3
Rgaba	white	10 days	12	26	116.6
ROX	brown	>5 months	12	45	275.0

^{a}2.0 cm column filled with 2.00 g resin as 25 mesh particles

metal ions in columns were tested in the following way. A glass tube with an internal diameter of 2.0 cm was filled with resin (2.0 g). The resin was weighed dry and equilibrated with 1.53 M H_2SO_4. The H_2SO_4 solution was then removed and 25.0 ml of a fresh H_2SO_4 solution was used to fill the column and to cover the resin. A solution (1.0 cm^3) containing only 10.40 grams/litre (g/l) of nickel ion, or a solution containing 1.72 g/l of Fe^{3+}, 28.20 g/l of Cu^{2+}, 4.48 g/l of Zn^{2+} and 10.40 g/l of Ni^{2+} in 1.53 M H_2SO_4 was then introduced into the column, and eluted with 25.0 ml of a 1.53 M H_2SO_4 solution. The elution rate was 1.0 $cm^3 min^{-1}$. The eluates were collected and analysed for metal ion concentration by plasma emission spectrophotometry.

Potentiometric measurements

All potentiometric measurements were made at 25°C in 0.1 M NaCl. Potentiometric titrations were performed using a digital PHM-84 Radiometer potentiometer, an Ag–AgCl reference electrode, an Orion 91–01–00 glass electrode, and a salt bridge containing 0.1 M NaCl solution.

Electron microscopy

Electron micrographs were obtained using a I.S.I. 100 B scanning electron microscope with a P.G.T. microprobe. The surface of the resin was coated with gold to obtain a 60 Å thickness using a Polaron SEM coating unit at 0°C. The dot map for nickel was obtained by X-ray fluorescence.

Metal analysis

The analysis on the eluate was carried out by plasma emission spectrophotometry using a Perkin–Elmer ICP/5500 spectrophotometer.

I.r. spectroscopy

I.r. spectra in KBr pellets were obtained by using a Perkin–Elmer 597 spectrophotometer.

N.m.r. spectroscopy

N.m.r. spectra were performed in H_2O/D_2O 1:1 and in D_2O/H_2SO_4 2M 1:1 using a Varian XL 200 spectrophotometer supplied with a UNIVAC 32K computer.

RESULTS AND DISCUSSION

Swelling

The swelling of all the resins in 1.53 M H_2SO_4 is marked and this somewhat limits their practical applications (*Table 4*). In H_2SO_4 all the basic nitrogens obviously are protonated and the greater swelling than in pure water[3] can be related to the presence of charges which repulse one another provoking a stiffening effect.

The RN_2C_4 and RN_2LLC_4 resins show the highest swelling properties while the series obtained by polyaddition with amino acids, which presents only one nitrogen to be protonated in the repeating unit of the linear part of the resin, swell to a minor extent. Of these two series the swelling increases with the lengthening of the aliphatic chain between the basic groups present in the linear part of the resin.

The different lengths of the crosslinking agent determine a negligible effect as we can observe by comparing the swelling of the RC_2 and RC_4 resin series, where, within the same series, the resins with the higher degrees of crosslinking show the lower swelling capacity.

Thus we observe a greater swelling when the resin presents a greater number of protonatable groups in its structure and when the linear part of the resin is more flexible.

The behaviour of the ROX resin and its swelling cannot be related to the other resins owing to the lack of basic groups in its structure.

Stability in H_2SO_4

The ROX resin is stable in H_2SO_4 (1.53 M) at room temperature, for several months (*Table 4*), without any loss of capacity. The other resins present a maximum lifetime of 3 weeks in this medium, and the stability increases with crosslinking. The stability of these resins correlates well with their swelling capacity, both being dependent on the number of charged groups present on the resin in the strong acidic medium.

SEM analysis

The surfaces of all the resins appear smooth when examined by transmission electron microscopy; only the ROX and RC_4 resins show a more indented structure (*Figure 3*).

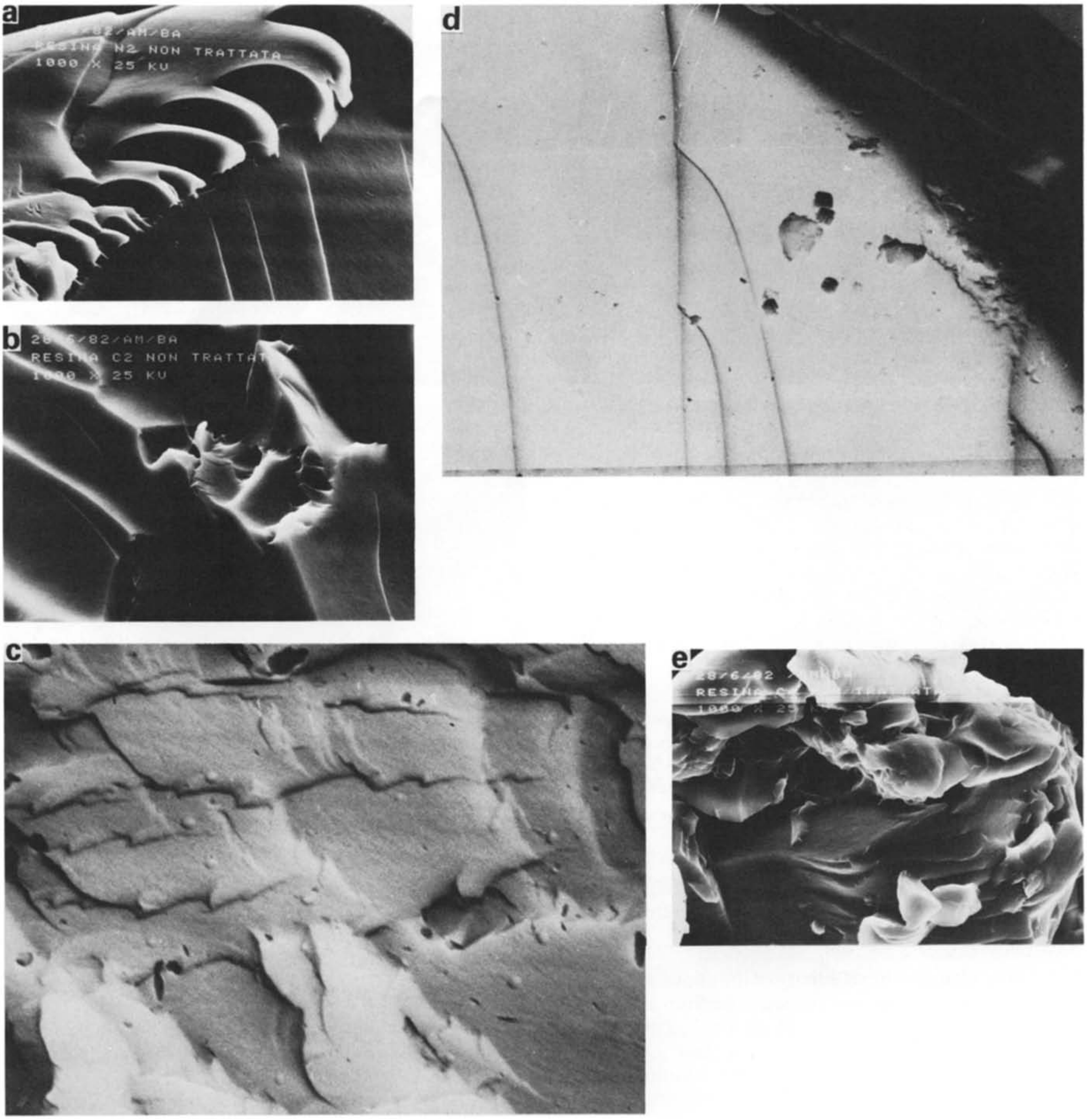

Figure 3 Electron micrographs of the dry resins (× 1000): (a) RN_2C_4; (b) RC_2 (2.0); (c) RC_4 (1.6); (d) RC_4 (2.0); (e) ROX

After contact with the H_2SO_4 solution, extensive damage and incipient cracks could be detected in all the resins, except for the ROX resin, which appeared unchanged (*Figure 4*). The chemical analysis carried out on the surface using the microprobe always revealed the presence of the sulphur together with the metal ions present in the H_2SO_4 solution (*Figure 5*).

Uptake of metal ions in aqueous H_2SO_4

Uptake of nickel^{2+}. All the resins were able to take up nickel ions in 1.53 M H_2SO_4. The milligrams of nickel adsorbed per gram of dry resin are reported in *Table 5*; in the same Table the percentage of metal adsorbed with respect to the amount initially present in the solution (10.4 mg of Ni^{2+}) is also given.

The resins with the same degree of crosslinking belonging to the RC_2 and RC_4 series show a similar capacity. The capacity decreases by increasing the degree of crosslinking, which is not unexpected, since the more crosslinked resins have a more compact structure.

Also RN_2C_4 and RN_2LLC_4 resins are able to take up nickel in 1.53 M H_2SO_4, the capacity of RN_2C_4 being particularly high.

The amphoteric resins R-Gly, R-βAla and R-GABA show lower adsorbing capacity which is probably related to the minor amounts of basic nitrogen in their structures (see below).

Finally, resin ROX shows a capacity roughly equivalent to that of the RC_2 and RC_4 resins. It must be pointed out that the structure of this resin is completely different from

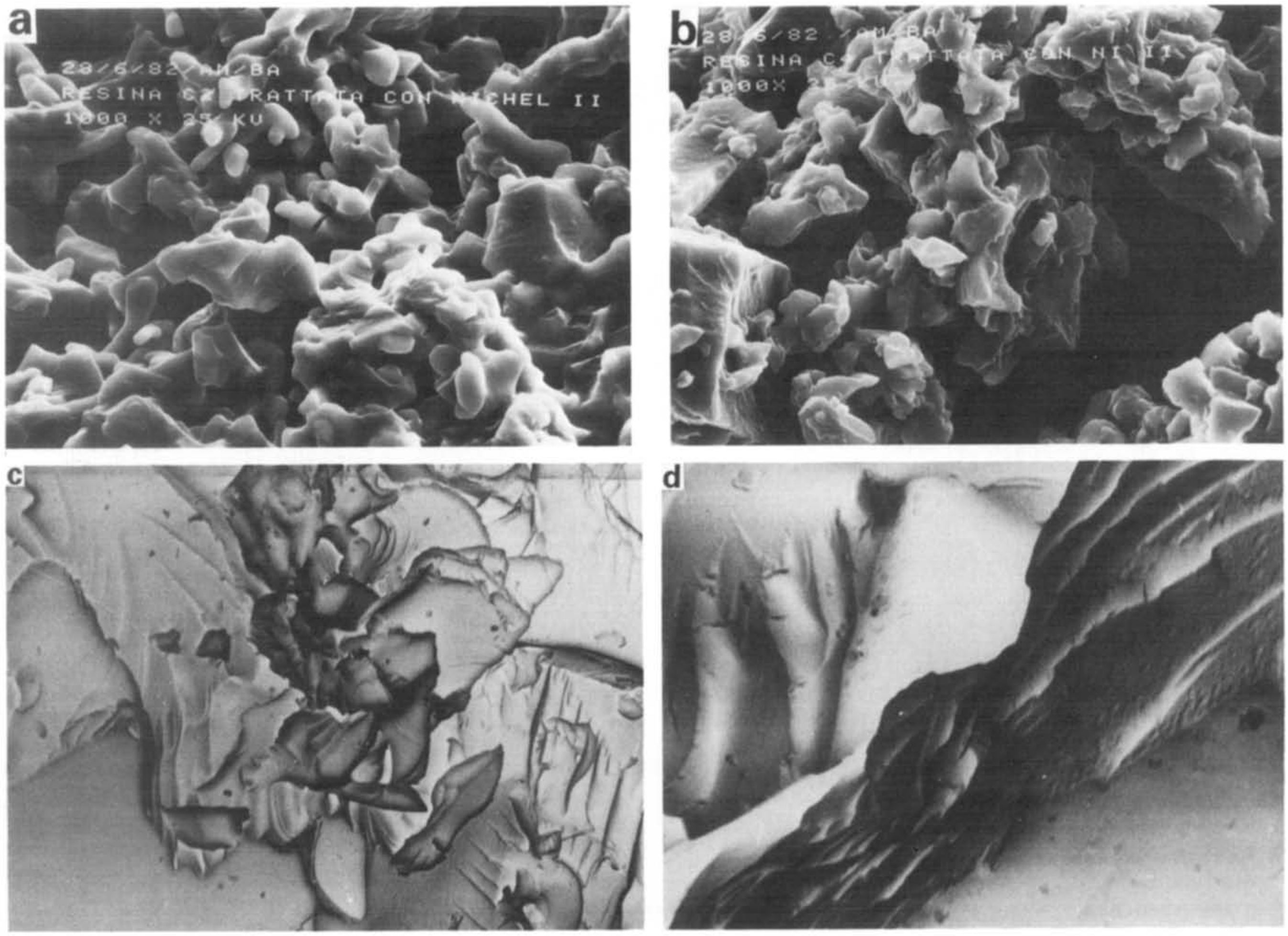

Figure 4 Electron micrographs of the resins after contact with the H_2SO_4 solution (× 1000): (a) RC_2 (2.0); (b) RC_4 (2.0); (c) Rgaba (× 250); (d) ROX

that of the other resins described in this paper, and also the adsorption mechanism is probably different.

Selectivity studies

In order to study the selectivity of the above resins, the same adsorption experiments were performed with a 1.53 M sulphuric acid solution of the Fe^{3+}, Zn^{2+}, Ni^{2+} and Cu^{2+} ions. The concentrations of these ions correspond to those present in the working solution of the electrorefining of copper. The results are shown in *Table 6*. Not all the resins were treated with this solution, but only those with a well defined structure.

As shown in *Table 6* the total capacity is at a maximum for resin ROX, while the capacities of the resins RN_2C_4 and RN_2LLC_4 are almost 1/2 of that for ROX, and three times those of the amphoteric resins derived from amino acids.

The percentage of metal ions adsorbed for all the resins are in the order $Fe^{3+} \simeq Zn^{2+} > Ni^{2+} > Cu^{2+}$ (*Table 6*), with the exception of ROX, which, practically speaking, does not show selectivity. The selectivity of the amphoteric resins is slightly higher than that of RN_2C_4 and RN_2LLC_4 resins (*Table 6*).

It may be observed that our resins do not show a very high selectivity, but on the other hand, their selectivity does follow an order which is different from that usually observed with the same resins in aqueous solution at higher pH[2,3]. This indicates that the adsorption mechanism is not the same, involving, in our opinion, anionic species instead of the free ions (see below). In particular, it must be pointed out that the affinity of the resins, especially the amphoteric ones, for copper is unusually low with respect to the other metals.

Adsorption mechanism

It is known that heavy metal ions in aqueous solution containing large amounts of sulphate ions are inclined to form anionic species like $M(SO_4)_n^{x-2n}$ (refs. 4,5).

In 1.53 M sulphuric acid most sulphate ions are present as HSO_4^-. The reaction taking place in 1.53 M H_2SO_4 solution is

$$M^{x+} + n\,HSO_4^- \rightleftharpoons M(HSO_4)_n^{x-n}$$

Therefore, we may assume that the metal ions are mainly present as $M(HSO_4)_n^{x-n}$. We confirmed the presence of such a species by n.m.r. spectroscopy, by measuring the relaxation time of water protons in a solution of Cu^{2+} (15 g/l) in both H_2O/D_2O (1/1) and H_2SO_4 (2M) in D_2O. The T_1 relaxation time decreases from 5.39 ms to 4.68 ms and the T_2 relaxation time decreases from 4.44 ms to 3.22 ms, by changing from the H_2O/D_2O to the H_2SO_4/D_2O medium. The dependence of the T_1 and T_2 values of the protons on the type of medium can be interpreted in terms of the charge density around the Cu^{2+} ions[6]. An increase in both relaxation times is generally observed when an inner sphere complex is formed in solution; such a complex determines a release of

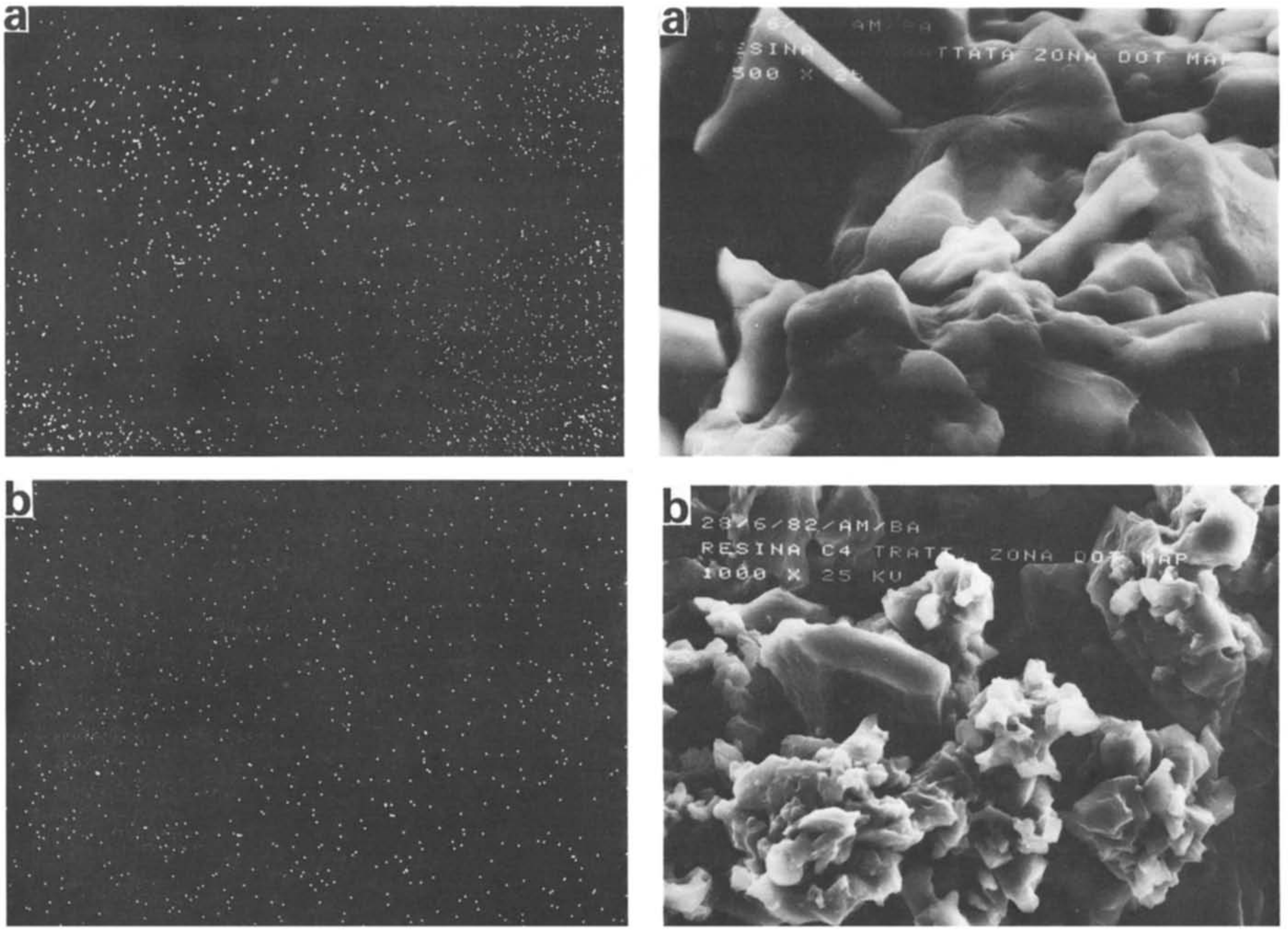

Figure 5 Dot map of Ni^{2+} on the surface of the same resins in *Figure 4*, obtained by X-ray fluorescence: (a) RC_2 (2.0) (× 2500); (b) RC_4 (2.0) (× 1000) with corresponding electron micrograph of the surface

Table 5 Uptake of Ni^{2+} from 1.53 M H_2SO_4

Resin	mg Ni^{2+}/g dry resin	Percentage uptake for Ni^{2+} ion[c]
RN_2C_4[a]	3.6	25.8
RN_2LLC_4[a]	2.1	14.9
RC_2 (1.2)[b]	2.0	23.8
RC_2 (1.4)[b]	1.8	21.9
RC_2 (1.6)[b]	1.5	17.7
RC_2 (2.0)[b]	1.0	11.7
RC_4 (1.2)[b]	1.7	20.2
RC_4 (1.4)[b]	1.1	13.7
RC_4 (1.6)[b]	1.2	14.1
RC_4 (2.0)[b]	1.0	12.2
Rgly[b]	0.5	5.2
Rβala[b]	0.2	2.3
Rgaba[b]	0.7	7.7
ROX[b]	1.5	17.3

[a] 1.50 g resin
[b] 2.50 g resin
[c] Eluted solution: 10.40 g/l Ni^{2+}

water molecules from the coordination sphere of Cu^{2+}. The decrease of both T_1 and T_2 from H_2O to H_2SO_4 instead seems to indicate the formation of ion pairs in the latter medium; the decrease of the relaxation times arises from the change in the rotational correlation time and the electron spin relaxation times. On the other hand, the ratio T_1/T_2 increases from water (1.21) to sulphuric acid (1.45) and this may be only due to a change in the electron spin longitudinal time of Cu^{2+}, τ_s, which emphasizes the change in the environment around the copper(II) ion, due to the formation of ion-pairs with the HSO_4^- species.

Therefore, the metal ions investigated are mainly present in 1.53 M H_2SO_4 as ion-pairs, with negative charges which are responsible for the adsorption of these species on the protonated resins. The adsorption occurs via an ion-exchange mechanism, the general ion exchange reaction being

$$(n-x)RX^- + M(HSO_4)_n^{x-n}$$
$$\rightleftharpoons R_{(n-x)}M(HSO_4)_n^{x-n} + (n-x)X$$

The $M(HSO_4)_n^{x-n}$ species displace the other anionic species for they carry more negative charges.

A similar process has been discussed in a wide investigation by Warshawsky *et al.*[7] who, studying the complexation of polymeric pseudo crown ethers with iron(III) in phosphoric and hydrochloric acid mixtures, found that the complexation depends on the acid concentration, hence on the presence of $[FeCl_4]^-$ species.

The mechanism of adsorption of the resin ROX containing oxime groups is different from that of the other resins, because it does not carry basic acid groups to be protonated in the acid solution. Therefore, we may suppose a coordination mechanism via the C=N–OH groups as suggested for other resins[8].

Table 6 mg metal retained/g dry resin (eluted solution: Ni^{2+} 10.40 g/l; Cu^{2+} 28.20 g/l; Fe^{3+} 1.72 g/l; Zn^{2+} 4.48 g/l)

Resin[a]	Ni^{2+} (% of metal retained)	Cu^{2+} (% of metal retained)	Fe^{3+} (% of metal retained)	Zn^{2+} (% of metal retained)	Total mg Me/g dry resin
RN_2C_4	2.0 (19.0)	4.3 (15.1)	0.5 (28.5)	1.2 (27.5)	8.0
RN_2LLC_4	2.4 (23.0)	4.7 (16.7)	0.5 (28.5)	1.3 (29.7)	8.9
Rgly	1.2 (11.3)	1.7 (6.0)	0.3 (20.9)	0.8 (17.2)	4.1
Rβala	1.2 (11.8)	1.7 (6.1)	0.3 (19.8)	0.8 (17.9)	4.0
Rgaba	1.1 (10.6)	0.7 (2.5)	0.4 (21.5)	0.9 (19.0)	3.1
ROX	4.2 (40.8)	11.3 (39.9)	0.8 (45.3)	2.0 (45.5)	18.3

[a] 2.0 g of dry resin

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REFERENCES

1 (a) Kirk-Othmer, F. 'Encyclopedia of Chemical Technology', 3rd Edn. 1980, Vol. 6; (b) Kenneth, C. J. and Randall, A. P. *J. Met.* 1979, 19; (c) Kenneth, C. J. and Grinstead, R. R. *Chem. Ind.* 1977, 632; (d) Anderson, T. N., Wright, C. N. and Richards, K. J. Second International Symposium on Hydrometallurgy, AIME, New York, NY, 1973, p. 171; (e) Phillips, R. J. and Frita, J. S. *Anal. Chem. Acta* 1980, **121**, 225; (f) Derotani, A. and Sebille, B. *Anal. Chem.* 1981, **53**, 1742

2 Ferruti, P., Riolo, C. B., Soldi, T., Pesavento, M., Barbucci, R., Beni, M. C. and Casolaro, M. *J. Appl. Polym. Sci.* 1982, **27**, 2239

3 Pesavento, M., Soldi, T., Ferruti, P., Barbucci, R. and Benvenuti, M. *J. Appl. Polym. Sci.* 1983, **28**, 3361

4 Mattoo, B. N. *Z.P. Chemie Neue Folge* 1959, **19**, 5156

5 Magini, M. *J. Chem. Phys.* 1979, **70**(1), 317

6 Comparini, I. B., Gaggelli, E. and Valensin, G. *J. Inorg. Biochem.* 1983, **18**, 349

7 (a) Warshawsky, A., Patchornick, A., Kalier, R., Ehrlich, S. and Rogozinski, S. *Hydrometallurgy* 1979, **4**, 93; (b) Warshawsky, A. and Kahana, N. *J. Am. Chem. Soc.* 1982, **104**, 2663

8 (a) Elening, C. A. *Trans. Inst. Min. Metall., Sect. C* 1979, **88**, 253; (b) Goszczynski, S., Szymanowski, J. and Borowiak-Resterna, A. *J. Chem. Technol. Biotechnol.* 1981, **31**, 333