Novel Chelating Resins with Remarkably High Selectivities for Copper(II) over Zinc(II) Ions

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Poly(styrene-co-divinylbenzene) and poly(glycidyl methacrylate-co-ethylene glycol dimethacrylate) resins carrying 2-aminomethyl pyridine and 2-pyridyl-2-imidazole ligands show remarkably high selectivity for the extraction of copper(II) ions in the presence of a large excess of zinc(II) ions.

The concept of attaching a chelating ligand to a porous polymer resin for use in the selective extraction of a particular metal ion (or metal ions) from a solution of mixed ions remains a technologically important one. In principle a ligand structure known to form a strong complex with the metal ions of interest (i.e. a complex with a high stability constant) should be adequate to achieve this objective.[1] In practice, this argument based on thermodynamics is a useful guide, but does not alone provide a practical solution. Additional factors such as metal ion exchange kinetics and resin–feed solution compatibility, intervene to complicate the situation. As a result, while many chelating resins designed to show selectivity for a particular metal ion do so in practice,[2–4] the level of selectivity achieved usually falls far below the original

expectation and, in particular, below the performance of analogous low molecular weight liquid–liquid ion extractants.[5] Another important factor is that functionalisation of resins is not straightforward. There is now growing evidence that much of the published literature is of limited value because of the low structural purity of chelating resins produced by long synthetic sequences performed on resins.[6]

We have described[7] recently the syntheses of a large number of chelating resins based on styrene and glycidyl methacrylate, carrying nitrogen containing ligands, in which the number of chemical steps performed on the resin matrix has been kept deliberately to a minimum. This communication describes some of the remarkably high Cu[II] ion extraction selectivities which have been achieved,[8] and will be followed

Table 1. Structural and physical parameters of resins.

Resin	Particle diameter/μm	Nominal crosslink ratio (%)	% Wt. N.	Ligand loading (%)	Surface area[a]/ ($m^2 g^{-1}$)	Pore volume[a]/ ($cm^3 g^{-1}$)	Water imbibition/ ($g g^{-1}$)
Ps/AMPy[b]	300—1000	20[f]	4.4	23	137	0.43	0.41
Ps/PyIm[c]	300—1000	20[f]	2.8	10	—	—	0.83
GMA/AMPy[d]	300—800	40[g]	4.6	33	119	0.38	0.85
GMA/PyIm[e]	300—800	40[g]	5.9	29	—	—	0.81
XFS/43084	300—1100	—[h]	8.2	—[h]	34	0.14	0.41

[a] In the dry state. [b] Corresponds to IbM in Table 4, ref. 7. [c] Corresponds to IaM in Table 4, ref. 7. [d] Corresponds to IIIbM in Table 6, ref. 7. [e] Corresponds to IIIaM in Table 6, ref. 7. [f] Divinylbenzene crosslinker, macroporous via 2-ethylhexanol as porogen. [g] Ethylene glycol dimethyacrylate crosslinker, macroporous via cyclohexanol–dodecanol (9:1) as porogen. [h] Full structural detail unknown (see refs. 11—13).

Table 2. Extraction capacities and kinetics of resins for Cu^{II} and Zn^{II} ions from single metal ion solutions at pH 5 and 25 °C.
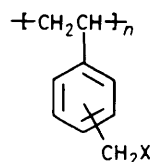
Resin	Cu^{II} capacity/ (g Cu l^{-1} resin)		Zn^{II} capacity/ (g Zn l^{-1} resin) by loading	$t_{\frac{1}{2}}$/min for Cu^{II}
	By loading	By elution		
Ps/AMPy	15	11	1	27
Ps/PyIm	12	5	3	20
GMA/AMPy	16	14	5	8
GMA/PyIm	14	16	7	16
XFS/43084	40	38	12	84

in due course by a full description of all the batch[9] and column[10] extraction studies which have now been performed. In the present context, the most important resins contain 2-aminomethyl pyridyl (AMPy) and 2-pyridyl-2-imidazole (PyIm) ligands attached as shown in the displayed structures. Ps/AMPy, Ps/PyIm, GMA/AMPy, and GMA/PyIm were synthesised in our laboratory,[7] while XFS/43084 was a commercial sample kindly supplied by the Dow Chemical Company.[11-13] Structural and physical parameters of these are summarised in Table 1. Aminomethyl-pyridine[11-13] and pyridyl-imidazole[14-16] ligands have been described before as the basis of potentially selective chelating resins. Previously the support has been based only upon styrene-divinylbenzene resins, with their inherently hydrophobic character.
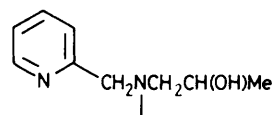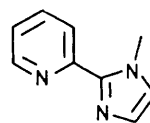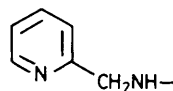
Each resin was contacted for 1 h with an excess of ammonium hydroxide (10 vol%) before being washed to pH 7 with distilled water. A known 'wet-settled' volume (5 ml) of each was then contacted in a batch process with a solution (500 ml) containing Cu^{II} ions (1000 mg l^{-1}) as its sulphate at pH 5 and 25 °C. The metal ion content of the supernatant was monitored by atomic absorption spectroscopy over a period of 24 h. The extraction of Zn^{II} ions was measured similarly. Resins thus loaded with Cu^{II} ions were then eluted in a batch process with H_2SO_4 (2 M; 500 ml) at 25 °C, and the appearance of free Cu^{II} ions monitored during 24 h. From the loading profiles for Cu^{II} ions the time to achieve loading to half the final capacity (24 h), $t_{\frac{1}{2}}$, was calculated. Since resin particle diameters were of similar magnitudes $t_{\frac{1}{2}}$ values represent a reasonable basis for a comparison of kinetic performance. The results are summarised in Table 2. These indicate: (i) all the resins show a selectivity for Cu^{II} over Zn^{II} ions as predicted for most nitrogen containing ligands;[17,18] (ii) the capacity (24 h) for Cu^{II} ions is much larger for XFS/43084 than for the other resins, possibly reflecting the higher overall ligand content;[12,13] (iii) resins GMA/AMPy, GMA/PyIm, and XFS/43084 load and elute Cu^{II} reversibly, whereas Ps/AMPy and Ps/PyIm show some evidence for retention of Cu^{II} ions even after 24 h elution; and (iv) resin GMA/AMPy, and to a lesser extent resin GMA/PyIm, shows rapid loading characteristics ($t_{\frac{1}{2}}$ values) for Cu^{II} ions while in particular XFS/43084 is slow.

In order to examine the selectivity behaviour under competitive conditions, resins were contacted in a batch process, with aqueous solutions containing 250 mg l^{-1} each of Cu^{II}, Ni^{II}, Co^{II} and Zn^{II} ions at pH 5 and 25 °C. The loading capacities at 24 h for Cu^{II} ions on Ps/AMPy, Ps/PyIm, GMA/AMPy, and GMA/PyIm were 8, 5, 16, and 16 g Cu l^{-1} resin respectively. *For Ni^{II}, Co^{II}, and Zn^{II} no extraction was detectable under these conditions.* In order to evaluate the separation of Cu^{II} and Zn^{II} ions under more stringent conditions Ps/AMPy and GMA/AMPy were each contacted in batch processes with an aqueous solution containing 1 g l^{-1} Cu^{II} and 150 g l^{-1} Zn^{II} ions as their sulphates at pH 5 and
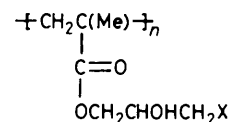
Polystyrene (Ps) resins

$\text{--CH}_2\text{CH--}_n$

CH_2X

Poly(glycidyl methacrylate) (GMA) resins

$\text{--CH}_2\text{C(Me)--}_n$
$C{=}O$
$OCH_2CHOHCH_2X$

X	Ps resins	GMA resins
(pyridyl)CH_2NH-	Ps/AMPy	GMA/AMPy
(pyridyl-imidazole)	Ps/PyIm	GMA/PyIm
(pyridyl)$CH_2NCH_2CH(OH)Me$	XFS/43084	

Resin structures

25 °C. The loading capacities (24 h) for Cu^{II} ions were 7 and 11 g Cu l^{-1} resin, respectively. In this instance, all Cu^{II} was subsequently eluted with 2 M H_2SO_4. The concentration of Zn^{II} ions was too high in the supernatant to detect any depletion on loading, but on elution only 0.25 and 1.0 g Zn l^{-1} resin respectively were detected. For comparison, resin XFS/43084 was examined similarly and this displayed a loading capacity (24 h) for Cu^{II} ions of 26 g Cu l^{-1} resin, but on elution Cu^{II} ions were accompanied by 16 g Zn l^{-1} resin. The former separations are remarkable and correspond to separation factors of 4200:1 for Ps/AMPy and 1650:1 for GMA/AMPy (*i.e.* at least equivalent to the factors achievable for certain metal ion separations by liquid–liquid extractions). Bearing in mind the overall higher capacity of GMA/AMPy and its superior kinetic behaviour, this resin appears to be the best candidate for further technological development. The results obtained using this resin in column extraction tests have already borne out the promise of the batch testing results and will be reported in full shortly.[10]

Quite clearly, the use of glycidyl methacrylate based resins not only presents a very convenient and efficient one-step route for the immobilisation of amino ligands,[7] but also, as macroporous species, they provide the potential for much higher metal ion selectivities and faster exchange characteristics. However, it is not clear in a molecular–structural sense why these advantages should arise. Undoubtedly, the structural homogeneity is an important factor, along with the intrinsically higher polarity of these resins compared with styrene-divinylbenzene based systems. The glycidyl methacrylate based resins may provide a more favourable micro-environment for aqueous metal ion solutions, and a more suitable pore structure. The results suggest that further

changes in the design of resins, rather than in the specific ligands, could provide yet further improved performance.

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