A Novel, Highly Copper(II)-selective Chelating Hydrophilic Ion Exchanger based on Imidazole modified Poly(glycidyl methacrylate)

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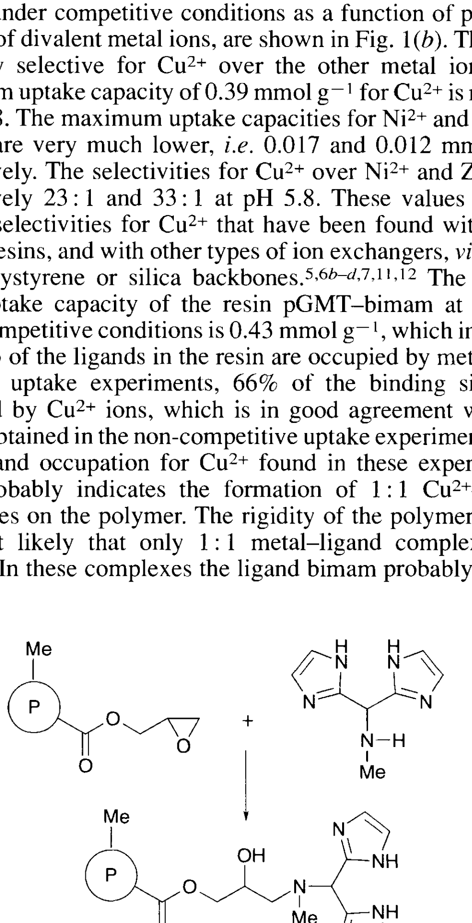
Anchoring the imidazole ligand bis(imidazo-2-yl)methylaminomethane (bimam) onto poly(glycidyl methacrylate-*co*-trimethylpropane trimethacrylate) (pGMT) by a ring-opening reaction of the pendant epoxy group with the secondary amine group of the ligand, results in a novel hydrophilic resin, which contains 0.59 mmol of the ligand per gram of resin; the ligand binding and the resin structure have been characterized by ^{13}C solid-state CP-MAS NMR spectroscopy and elemental analyses; batch extraction experiments show a very high selectivity in the pH range 1.1–6.0 for Cu^{2+} over Ni^{2+}, Co^{2+}, Zn^{2+} and Cd^{2+}, as chloride salts in buffered solutions under competitive conditions.

The need for more highly specific, metal recovery processes in both hydrometallurgical and environmental applications has led to an increasing interest in selective ion exchange. In particular the search for 'ion-specific' resins which, under proper operating conditions, are selective for only one ionic species[1–4] has intensified. Important properties of such ion exchangers should include high capacity, high selectivity and fast kinetics.[2] Most of the commercial resins,[1] when tested in waste-water treatment show a high capacity, but a very poor selectivity towards different metal ions. In some cases the kinetics are slow, due to the hydrophobic character of the polymer backbone. Therefore, studies towards the development of resins with improved selectivity and better kinetic performance have been initiated in our laboratory. Sahni *et al.* immobilized the ligand *N,N'*-bis(benzimidazolylmethyl)amine onto polystyrene and obtained a Cu^{II}-selective chelating ion exchanger. An important drawback of this resin, however, was again the slow exchange kinetics.[5] Subsequently, poly(glycidyl methacrylate-*co*-ethylene glycol dimethacrylate) (pGMA) and poly(glycidyl methacrylate-*co*-trimethylol propane) (pGMT) have been found to be convenient and versatile starting materials for the synthesis of more hydrophilic chelating ion exchangers.[6] Amines react by ring-opening of the epoxy groups of glycidyl methacrylate yielding resins with very favourable uptake kinetics for transition metal ions, due to the hydrophilic character of the resulting resins.[7]

This communication describes the synthesis and metal-ion uptake experiments of a novel, highly Cu^{II}-selective hydrophilic ion-exchange resin based on pGMT with bis(imidazo-2-yl)methylaminomethane (bimam) as the chelating ligand. This ion exchanger, pGMT–bimam, combines a high selectivity for Cu^{II} ions with fast exchange kinetics.

The polymer pGMT was prepared by suspension polymerization using a mixture of glycidyl methacrylate (GMA) and trimethylol propane (TRIM) (1 : 1 *v*/*v*) with *n*-butyl acetate as a porogen (monomer : porogen 1 : 2 *v*/*v*) as described by Verweij *et al.*[8]† The synthesis of the ligand bimam has been published elsewhere.[9] The resin pGMT–bimam was prepared according to Scheme 1. A mixture of pGMT and bimam in ethanol was heated at 80 °C under N_2 for 74 h. The resin was filtered and purified by extraction in a Soxhlet apparatus with ethanol, followed by conditioning with 0.5 mol dm^{-3} H_2SO_4 and 0.5 mol dm^{-3} NaOH. The resin was washed with water until neutral pH and dried *in vacuo* at 50 °C for 48 h. The resulting pGMT–bimam resin was characterized by elemental analysis (C,H,N,O)‡ and solid-state ^{13}C CP-MAS NMR spectroscopy.§ The degree of conversion of the epoxy groups after reaction with bimam was calculated to be 0.20, corresponding to a ligand concentration of 0.59 mmol g^{-1} of resin.

Batch metal-uptake experiments under competitive and non-competitive conditions with pGMT–bimam were performed with the metal chlorides of Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+} and Cd^{2+} in buffered solutions. The metal-ion capacities were determined as a function of pH.¶ Fig. 1(*a*) shows the metal uptake of the resin pGMT–bimam under non-competitive conditions. The behaviour of pGMT–bimam shows that the uptake for all divalent metal ions increases with increasing pH. The uptake of Cu^{2+} is highest over the whole pH range. At pH > 3 the metal-uptake capacities decrease in the order $Cu^{2+} \gg Ni^{2+} > Zn^{2+} > Cd^{2+} > Co^{2+}$, which is in accordance with the Irving–Williams stability series.[10] The maximum uptake capacity for Cu^{2+} is 0.38 mmol g^{-1} at pH 5.7, which indicates that 64% of the ligands are chelating. The metal-ion capacities of pGMT–bimam under competitive conditions as a function of pH for a number of divalent metal ions, are shown in Fig. 1(*b*). The resin is highly selective for Cu^{2+} over the other metal ions. The maximum uptake capacity of 0.39 mmol g^{-1} for Cu^{2+} is reached at pH 5.8. The maximum uptake capacities for Ni^{2+} and Zn^{2+} at pH 5.8 are very much lower, *i.e.* 0.017 and 0.012 mmol g^{-1} respectively. The selectivities for Cu^{2+} over Ni^{2+} and Zn^{2+} are respectively 23 : 1 and 33 : 1 at pH 5.8. These values are the highest selectivities for Cu^{2+} that have been found with these type of resins, and with other types of ion exchangers, *viz.* those with polystyrene or silica backbones.[5,6b–d,7,11,12] The overall metal-uptake capacity of the resin pGMT–bimam at pH 5.8 under competitive conditions is 0.43 mmol g^{-1}, which indicates that 73% of the ligands in the resin are occupied by metal ions. In these uptake experiments, 66% of the binding sites are occupied by Cu^{2+} ions, which is in good agreement with the results obtained in the non-competitive uptake experiments. The high ligand occupation for Cu^{2+} found in these experiments, most probably indicates the formation of 1 : 1 Cu^{2+}–ligand complexes on the polymer. The rigidity of the polymer matrix makes it likely that only 1 : 1 metal–ligand complexes are formed. In these complexes the ligand bimam probably acts as



Scheme 1 Immobilization of the ligand bimam onto the polymer pGMT

a didentate *N*-donor ligand, even though three *N*-donor atoms are present in the molecule. The tertiary amine nitrogen is likely to be too sterically hindered to be involved in a tridentate coordination bite as was shown by modelling studies.[13b] At low pH the tertiary amine group is protonated which makes coordination to a metal ion virtually impossible. At higher pH values a different coordination mode may be possible, *viz.* a combination of the tertiary amine nitrogen together with only one of the imidazole nitrogens,[13a,b] in which case the bimam ligand is still a didentate ligand.

Distribution coefficient measurements according to Roozemond *et al.*[14] were performed with the Cu^{2+} ions as a function of pH. These experiments show that the stability of the complexes formed decreases from a log D value of 4.1 at pH 5.8 to a log D value of 2.6 at pH 1.3. This is consistent with the lower uptake capacity for Cu^{2+} at low pH. The log D values obtained for the resin pGMT–bimam are remarkably higher than log D values obtained for other ion-exchange resins,[4] which indicates that the high selectivity for Cu^{2+} of pGMT–bimam is, at least partly, due to a favourable thermodynamic stability of the complexes on the polymer. Thus the formation of Cu^{2+} complexes is favoured for thermodynamic reasons.

Kinetic experiments performed with the ion exchanger pGMT–bimam and the $CuCl_2$ stock solution (0.16 mol dm^{-3}) at pH 4.5, resulted in a $t_{1/2}$ (time for loading to half maximum capacity) for the loading of Cu^{2+} of 9 min. Compared to other GMA-based ion exchangers[3–5] this is relatively fast, implying that the formation of Cu^{2+} complexes on the polymer is also favoured for kinetic reasons.

The loading capacity of the ion-exchange resin pGMT–bimam for Cu^{2+} remains the same after several cycles of consecutive loading with the 0.16 mol dm^{-3} $CuCl_2$ stock solution at pH 4.5 and stripping with 1.0 mol dm^{-3} H_2SO_4, indicating that the resin structure, backbone with ligand, is chemically and mechanically stable when treated with strong acid.

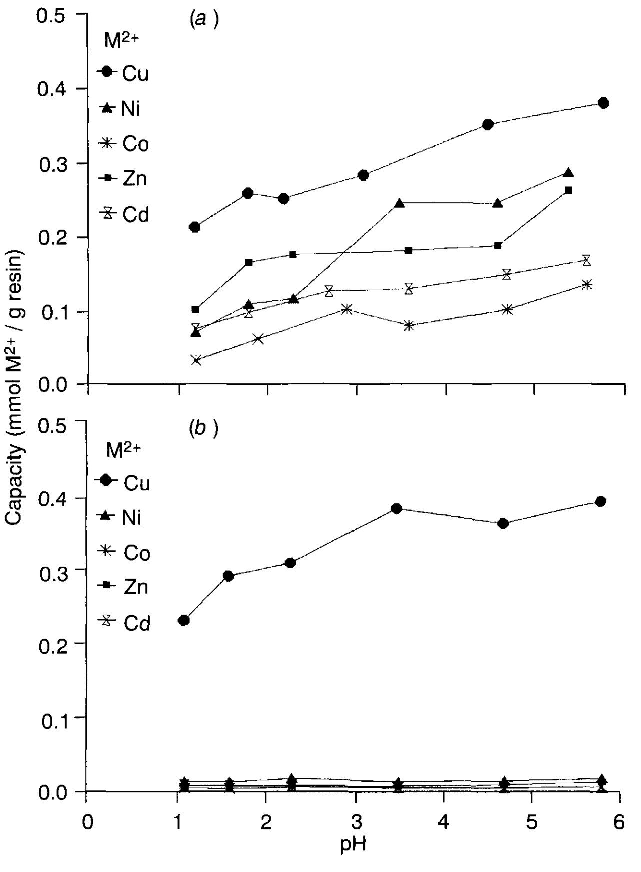


Fig. 1 Capacities of pGMT–bimam for divalent metal ions under (*a*) non-competitive conditions and (*b*) under competitive conditions as a function of pH

In summary, we have demonstrated that the novel chelating hydrophilic ion-exchange resin, pGMT–bimam, has a very high selectivity towards Cu^{2+} ions in the presence of other divalent transition metal ions in the pH-range 1.1–6.0. Subsequent work will deal with the study of the coordination geometry around the metal ion in the polymer phase, using ligand field, EPR and IR spectroscopy. The new ion exchanger pGMT–bimam will be tested under competitive conditions, *i.e.* the resin will also be tested in the presence of competing chelating ligands in solution.

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Footnotes

† The BET surface area of the starting pGMT polymer in the dry state is 170 m^2 g^{-1} and the pore volume is 1.27 cm^3 g^{-1}. The average particle diameter of the polymer beads is 375–500 μm.

‡ The elemental analysis of pGMT–bimam yields (calculated values in parentheses): C 58.1 (58.1), H 7.6 (7.5), N 4.1 (4.1), O 30.1 (30.2)%.

§ Solid-state CP-MAS ^{13}C-NMR data for pGMT–bimam: δ 7.3 (Me crowded), 24.3 (Me), 41.4 (>CH–N ligand); 46.0 (–C– polymer backbone), 56.1 (–CH_2– polymer backbone), 67.5 (O–CH_2–epoxy), 127.5 (C^2/C^3 imidazole), 145.6 (C^1 imidazole), 176.3 (C=O).

¶ Batch metal-uptake experiments were performed using standard 0.16 mol dm^{-3} MCl_2 solutions and buffer solutions (I = 0.6 mol dm^{-3}) NaOAc–HOAc (pH 2.5–6.0) and NaCl–HCl (pH 1.1–2.3) at room temp. with a shaking time of 48 h. For the competitive experiments, batches of 0.2 g of the resin were used, together with a mixture of 25 ml of buffer and 25 ml of standard MCl_2 solution. For the non-competitive tests, batches of 0.2 g of resin were contacted with an aqueous solution containing 5 ml of each of the standard MCl_2 solutions and 25 ml of buffer. Samples for metal analysis were prepared by destructing 0.1 g of the loaded resins. The metal contents of the resulting solutions were determined by AAS spectroscopy using a non-linear calibration method.

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