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Metal ion uptake by ion-exchange/chelating resins modified with cyclohexene oxide and cyclohexene sulphide

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Abstract

A ring opening reaction with either cyclohexene oxide or cyclohexene sulphide has been used in the modification of two types of polymeric resins. Both resins contained amino groups, one being obtained by reacting the vinylbenzyl chloride/divinylbenzene (VBC/DVB) copolymer with ethylenediamine, the second by reacting the VBC/DVB copolymer with diethyl malonate followed by aminolysis with ethylenediamine. Modification resulted in a set of novel chelating resins, which has been characterised and used in metal ion uptake experiments. These resins are highly selective towards copper(II) in acetate buffered solutions. The selectivity of the modified resins decreases in the order, Cu(II) > Cd(II) > Zn(II) > Ni(II), which is different from the Irving–Williams series. The highest affinity towards Cu(II) ions has been found for the resin modified with cyclohexene oxide, for which log K_d was 4.91 at pH 5.6.

Keywords: Metal ion uptake; Chemical modification; Selectivity

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1. Introduction

In many applications such as waste water treatment, recovery of either toxic or valuable metals from hydrometallurgical liquids, there is a constant demand for more selective chelating resins. In this respect, the chelating polymers containing sulphur donor atoms are receiving a great deal of attention since they display high selectivity towards heavy and noble metal cations. It is well known that this "soft" type donor prefers large and more easily polarisable acceptors such as for example mercury, silver and gold cations. One of the possible ways to introduce sulphur atoms into the ligand structure is to react amino groups with thiocyanate and isothiocyanate and thus obtaining thiourea and alkylthiourea derivatives. For example in Ref. [1], the thiourea based resins were synthesised and used in the removal of noble metals from aqueous solutions. Kinetics of the metal removal was slower than in the case of low molecular analogues, but the resins displayed good capacity and selectivity. Methylthiourea resin was presented in Ref. [2]. The resin was obtained by modification of vinylamine polymer and the reported degree of modification was low. In Ref. [3], linear poly(ethylene glycols), having terminal amino groups, were modified with methylisothiocyanate. Another way of introducing sulphur into the ligand structure is to react amines with carbon disulphide. Such a reaction gives dithiocarbamate functional groups and was presented in Refs. [2,3]. Other reactions leading to the chelating resins with the soft donor atoms include modification of chloromethyl groups with allyl amine followed by the addition of thiol groups to double bonds [4], anchoring an analogue of Cyanex 471 onto vinylbenzyl chloride copolymer [5] and modification of copolymer bearing amino groups with thiophosphonochloridate [6].

A different approach to the synthesis of resins, which are selective towards heavy metal cations, is presented in

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the papers in which sulphur is introduced already at the polymerisation step. Most frequently used monomer is thioglycidyl methacrylate and upon crosslinking with suitable crosslinker (typically ethylene glycol dimethacrylate or divinylbenzene), the resins can be used without chemical modification as for example in Ref. [7], where the macroporous type polymer was used in the sorption of phenols and in Ref. [8], where resins were used in the sorption of common and platinum metals. The chemical modification of such polymers is based on opening of the sulphur-containing ring with amines. Examples of such a reaction include those in Refs. [9,10] in which pyrazole, imidazole, triazole and 1,3-bis(benzamidazol-2-yl)propylamine were used to open the ring in thioglycidyl methacrylate and in glycidyl methacrylate mers. It is also possible to introduce the soft donor atoms through an opening of ring in ethylenesulphide using amino groups present in the structure of polymers. In Ref. [11] *N*-mercaptoethylated derivatives of diethylenetriamine and pyridylamines immobilised on the macroporous polystyrene resins were obtained in such reactions and tested in removal of Ag(I) and Hg(II).

Recently, the resins containing *N*,*N′*-substituted amides of malonic acid have been presented and proved to be more effective in the removal of some metal cations than amides of monocarboxylic acid [12]. One of the synthesised resins contained 2-(aminoethyl) groups, which can serve as a reagent in opening of rings in cyclohexene sulphide. This reaction seems to be a simple, one step way, to obtain ion-exchange/chelating resins, which may show an altered selectivity compared to the resins with amino groups only. It has been also decided to run an analogous reaction with cyclohexene oxide as the reagent. The products of such a reaction will be compared to resins modified with cyclohexene sulphide.

The aim of this work is to obtain chelating resins through both of the above reactions and to investigate their ability to remove metal cations from aqueous solutions.

2. Experimental

2.1. Materials

The copolymer of vinylbenzyl chloride (VBC) and technical divinylbenzene (DVB), having 63.8% of *m*- and *p*-DVB is prepared using suspension polymerisation method. The detailed description of polymerisation and purification procedure has been published previously [12]. Such copolymer is reacted with the sodium derivative of diethyl malonate. Thus, 0.188 mol (30.0 g) of diethyl malonate is dissolved in 200 ml of dry tetrahydrofuran and to this solution 0.170 mol of sodium hydride as 60% suspension in mineral oil is added in portions and the temperature is kept below 25°C. After the reaction is completed and evolution of hydrogen ceased, 12 g of VBC/DVB copolymer (expanded gel type, Cl content 5.60 mmol/g) is added and the entire mixture is refluxed for 24 h. Then, the beads are washed with THF, acetone, water, acetone and dried.

Such a polymer is reacted with ethylenediamine using reaction conditions given in the previous paper [12]. In the last step, the above resin, having already 2-aminoethyl substituted amides of malonic acid as ligands, is subjected to reaction with cyclohexene oxide and cyclohexene sulphide, giving resins 1 and 2, respectively. In both cases, 3.0 g of polymer having 3.25 mmol of primary amino groups per gram is placed in 40 ml of ethanol and 5 g of cyclohexene oxide (or 5.5 g cyclohexene sulphide) mixture and refluxed for 20 h. After that time, the beads are placed in a fritted-disk column and washed with ethanol, ethanol/water, and finally with excess of water.

Resins with $-C_6H_4CH_2NHCH_2CH_2NH_2$ ligands are prepared by aminolysis of the VBC/DVB copolymer with ethylenediamine. Reactions with cyclohexene oxide and cyclohexene sulphide (to obtain resins 3 and 4) are performed under conditions described above for modification of resins with *N*,*N′*-2-(aminoethyl) malonamide ligands.

2.2. Methods

Water regain is defined as the amount of water absorbed by 1 g of polymer. It is measured using centrifugation method in which approximately 1 g of water swollen polymer is placed in a short column with sintered glass bottom and centrifuged at 3000 rpm for 5 min, weighed and dried at 100°C overnight. After cooling in a desiccator, the column is weighed again with and without the polymer. The water regain is calculated as $(m_w - m_d)/m_d$, where m_w is the weight of swollen (wet) polymer after centrifugation, m_d is dry polymer weight.

Nitrogen content is measured using Kjeldahl method, sulphur content is measured according to Bennewitz method.

Affinity of the resins towards Cu(II), Cd(II), Ni(II) and Zn(II) is determined by contacting 1×10^{-4} N Me(II) solutions in 0.2 M acetate buffer pH 3.7 and 5.6 with resins samples. Thus, the amount of the resin equivalent to 0.05 mmol of ligand is shaken with 10 ml of the given metal ion solution for 48 h, which was found to be sufficiently long to reach the equilibrium. Next, polymer is separated by filtration and metal concentration in the solution is measured using AAS method on a Perkin–Elmer AAnalyst 100 spectrophotometer with wavelength set at 324.8, 228.8, 232.0 and 213.9 nm for Cu(II), Cd(II), Ni(II) and Zn(II), respectively.

Table 1
Characteristics of chelating resins

Resin	S content (mmol/g)	N content (mmol/g)	Percentage of solid (%)	Water regain (g/g)
1	0.00	5.54	75.05	0.33
2	1.56	5.82	62.45	0.60
References 1,2[a]	0.00	6.45	50.76	0.97[b]
3	0.00	5.01	45.82	1.18
4	3.39	4.58	56.10	0.78
References 3,4[a]	0.00	6.22	55.56	0.80

[a] Reference resins – resins from which investigated resins 1,2 and 3,4 were obtained by chemical modification.

[b] Data taken from Ref. [12].

Sorption capacity of the resins towards each metal cation is determined by contacting 25 ml of 0.01 N Me(II) solution in appropriate 0.2 M acetate buffer with amount of the resin equivalent to 0.05 meq. of ligand. In the case of experiment under a competitive condition, solution was formulated with 2.5×10^{-3} eq. of each metal ion, so the total concentration of Me(II) in solution was 0.01 N.

3. Results and discussion

Two types of ion-exchange/chelating resins have been prepared in the course of this work. Resins 1 and 2 have been obtained from malonamide containing resin. Characteristics of the starting resin, containing *N*,*N*′-2(aminoethyl)amide of malonic acid, is given in Table 1 (reference resins 1 and 2). It has been subjected to the modification with either cyclohexene oxide (giving resin 1) or cyclohexene sulphide (giving resin 2). Reaction conditions are provided in Section 2 and the procedure described in Ref. [13] are followed. As can be seen, chemical modification in both cases results in lowering of nitrogen content due to the net weight gain during reactions. The decrease of nitrogen content is used to calculate yield of the reactions which is almost the same in both cases. It equals to 63% for resin 1 (modified with cyclohexene oxide) and to 60% for resin 2 (modified with cyclohexene sulphide). In the latter case, 1.56 mmol/g of the sulphur has been found in elemental analysis and this amount is in reasonable agreement with the yield calculated on the basis of the nitrogen content decrease. Water regain of both resins, particularly of resin 1, is markedly below water regain of the starting material and thus indicating their low hydrophilicity.

Resins 3 and 4 have been prepared by the chemical modification of the ethylenediamine modified VBC/DVB copolymer, having 2 wt.% of crosslinker (reference resins 3 and 4 in Table 1). This polymer contains primary and secondary amino groups. Here again, modification results in drop of the nitrogen content, which corresponds to the reaction yield of 49% (resin 3) and 50% (resin 4). Both types of the amino groups, primary and secondary, were taken into account during yield calculations since each one can react [13]. However, in the polymeric matrix, where secondary amino groups are located on bulky benzyl substituent, reaction involving these groups is less likely. In the case of resin 4, 3.39 mmol of S per gram has been found, which would indicate higher degree of modification.

Scheme of the resins syntheses is presented in Fig. 1. The proposed structures are supported by IR spectra.

The distribution coefficient measurements were performed with Me(II) ions under non-competitive and competitive conditions at two pH values. pH was stabilised by using 0.2 M acetate buffer. 50-fold excess of ligands over available metal ions was kept, so the ionic state of resins could be assumed constant during the experiments. In the case of Cu(II), these experiments give $\log K_d$ values from ≈1.50 to 3.20 at pH 3.7. It can be seen that the reference resins display higher affinity for copper ions than resins obtained from them by modification with either cyclohexene oxide or cyclohexene sulphide. Also, the resin obtained from VBC/DVB copolymer by reaction with ethylenediamine and resins 3 and 4 display higher affinity for copper (II) than the polymers derived from malonamide resin (Table 2). The stability of the Cu(II)–ligands on the resins complexes increases with the increase of pH from 3.7 to 5.6. This can be explained by the complete deprotonation of the amino groups and their involvement in the complex formation. Other metal cations studied in this work are having less affinity towards the investigated polymers as evidenced by lower K_d values. For example, at pH 3.7, $\log K_d$ for Cd(II) ranges from ≈0.65 to 1.91, Zn(II) and Ni(II) are in the range of 0.60–1.50. It should be noted here that the reference materials display at pH 3.7, the following affinity order: Cu(II) > Ni(II) > Zn(II) ≅ Cd (II), which agrees with the Irving–Williams series [14]. Resins obtained by their modification, resins 1–4, display enhanced affinity towards cadmium ions, and therefore, affinity order is changed to Cu(II) > Cd(II) > Zn(II) > Ni(II). The only exception here is resin 1, which does not recognise Zn(II) at pH 3.7. Cd(II), Zn(II) and Ni(II) are displaying higher distribution coefficients at pH 5.6 similarly, as has been observed in the case of copper (II).

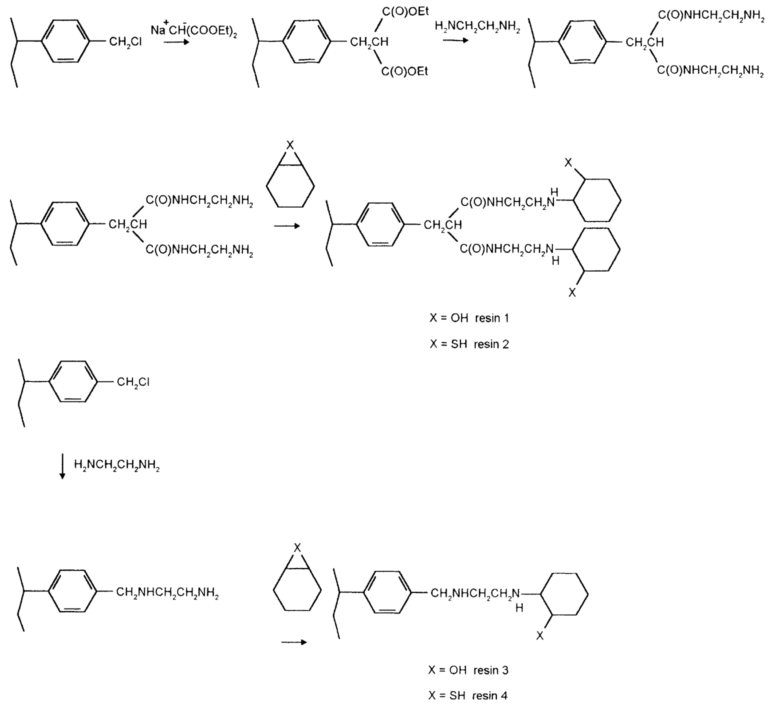

Fig. 1. Schematic diagram of the investigated resins syntheses.

Table 2
Affinity of chelating resins towards metal cations

Resin	Log of distribution coefficient							
	Cu(II)		Cd(II)		Zn(II)		Ni(II)	
	pH 3.7	pH 5.6	pH 3.7	pH 5.6	pH 3.7	pH 5.6	pH 3.7	pH 5.6
1	1.52	2.35	1.37	1.50	–	1.25	0.72	1.28
2	1.93	2.90	1.55	1.58	1.29	1.50	0.79	1.62
References 1,2	2.02	3.81	0.66	1.29	0.59	0.60	1.51	1.40[a]
3	2.89	4.91	1.72	3.13	1.04	2.75	–	3.14
4	2.69	3.98	1.91	1.89	0.92	1.80	–	2.23
References 3,4	3.22	4.90	0.65	2.24	1.00	2.08	1.41	3.19

[a] Data taken from Ref. [12].

Taking high preference of the resins towards Cu(II), their affinity for metals has been checked under competitive conditions, where pairs of Cu(II)/Me(II) have been contacted with polymers. The results are presented in Table 3. It can be seen that in majority of cases, the presence of two metal cations at low concentration does not significantly change their distribution coefficients. This can be rationalised by taking into account 50-fold excess of available ligands over metal cations. With this excess, it is most probable that within polymeric matrix, an array of active sites exists and can accommodate both types of metal ions. An exception is Cu(II)/Cd(II) pair, which seems to be competing for the same ligands on the resin. This results in lowering the $\log K_d$ values for at least one of the above metal cations. One effect, which could have been anticipated, that is, higher preference of the resins with sulphur atom donors towards cadmium ions is not observed. Even if $\log K_d$ presented for Cd(II) in Tables 2 and 3 are higher for resins 1–4 than for the reference ones, there is no significant difference between resins modified with cyclohexene oxide and those modified with cyclohexene sulphide. At pH 3.7, in all cases, $\log K_d$ for resins 1–4 is 2- to 3-fold higher than in the case of the reference ones (Table 2). Difference between resin 1 and resin 2 (i.e. modified with cyclohexene oxide and cyclohexene sulphide) is small, log of distribution coefficient is 1.37 and 1.55, respectively. Same situation can be seen for resins 3 and 4. However, at pH 5.6, the

Table 3
Affinity of chelating resins towards metal cations under competitive conditions

Resin	Log of distribution coefficient					
	Cu(II)/Cd(II)		Cu(II)/Zn(II)		Cu(II)/Ni(II)	
	pH 3.7	pH 5.6	pH 3.7	pH 5.6	pH 3.7	pH 5.6
1	1.58/1.46	2.41/1.54	1.32/–	2.41/–	0.98/0.94	2.34/1.69
2	1.22/1.12	3.09/1.47	2.05/1.21	3.12/1.21	1.68/–	3.02/1.67
References 1,2	1.98/0.57	3.75/1.31	1.96/0.58	3.72/0.52	1.99/1.56	3.80/1.21
3	2.83/0.86	4.60/2.08	3.34/0.96	4.43/1.99	2.93/–	4.39/3.01
4	2.53/2.00	3.99/2.62	2.71/1.40	3.79/2.22	2.64/–	3.75/2.13
References 3,4	2.96/–	4.61/2.19	3.24/1.11	4.60/2.09	3.30/1.23	4.61/2.85

Table 4
Sorption of Me(II) by the investigated resins under non-competitive conditions

Resin	Sorption (mmol/g)							
	Cu(II)		Cd(II)		Zn(II)		Ni(II)	
	pH 3.7	pH 5.6	pH 3.7	pH 5.6	pH 3.7	pH 5.6	pH 3.7	pH 5.6
1	0.016	0.071	0.047	0.041	0.000	0.007	0.030	0.023
2	0.075	0.220	0.056	0.051	0.010	0.036	0.029	0.023
References 1,2	0.082	0.408	0.021	0.047	0.011	0.038	0.087	0.102
3	0.557	1.277	0.010	0.145	0.008	0.283	0.002	0.463
4	0.156	0.400	0.114	0.117	0.009	0.189	0.013	0.099
References 3,4	0.486	1.312	0.014	0.190	0.000	0.156	0.026	0.431

positive influence of modification is less pronounced, which can suggest that mainly deprotonated amino groups are involved in chelation.

Table 4 presents the results of experiments aimed at obtaining the loading capacities of resins towards investigated metal cations. As can be seen, the order of metal uptake is much the same as the affinity order obtained by determination of distribution coefficients. As in the case of ion uptake from diluted solutions, sorption of metals at pH 3.7 is small and again lower for the malonate resins. For Cu(II) at the above pH, these resins display sorption of 0.016–0.082 mmol of metal per gram, which corresponds to 0.6–2.6% of their ligands being involved in chelation. This can be ascribed to inaccessibility of ligands due to the rigidity of polymeric network, which is the result of the chemical crosslinking as well as additional crosslinking occurring in the course of malonate ligand immobilisation on VBC/DVB matrix [12]. Another factor, resulting in low metal ion uptake by these resins, is the presence of weakly basic primary amino groups (resin references 1 and 2), which at low pH are strongly protonated. Increase of pH to 5.6 results in higher uptake of metal ions, but even then only ≈12.6% of ligands are effectively involved in chelation. Better results are obtained for the resins derived from VBC/DVB modified with ethylenediamine for they contain stronger, secondary amino groups in addition to primary ones. Here, ≈7–22% and 17–51% of ligands are effective in the chelating process at pH 3.7 and 5.6, respectively. Other metal ions, having less affinity towards resins, as has been proved by lower distribution coefficients, are at the same time sorbed to a lesser extend than copper.

Since all investigated resins displayed high preference towards copper a sorption experiment under competitive conditions has been performed. The resins have been contacted with buffered solution containing 2.5×10^{-3} eq. of each metal ion, so the total concentration was 0.01 eq. of Me(II) per litre, as it was in the sorption experiment under non-competitive conditions. The following sorption, in mmol Cu(II) per gram has been obtained at pH 3.7: 0.003, 0.003, 0.182, 0.060, 0.013 and 0.204 for resins 1,2,3,4, reference resins 1, 2 and reference resins 3, 4, respectively. Comparison of these values with those reported in Table 4 for sorption of Cu(II) shows that under competitive conditions uptake of copper ions is much lower. It seems that the main reason for this is just lower concentration of copper(II) (i.e., 2.5×10^{-3} eq.) in solution contacted with the resins. The same effect was observed in another work concerning metal uptake by nitrogen containing resins [15]. Moreover, the sorption of other metals under competitive conditions is negligible. At pH 5.6, sorption of Cu(II) gets higher as a result of the deprotonation of amino groups and is 0.013, 0.068, 0.513, 0.160, 0.155 and 0.534 mmol/g for resins listed in Table 4, respectively. The sorption of metal ions under competitive conditions proved high selectivity towards copper.

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