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Crosslinking effect on sorption and thermal stability by crosslinked poly(ethyleneimine)

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SUMMARY

The sorption behaviour of copper (II) and uranium (VI) ions on branched poly(ethylenimine) (BPEI) bridged with bifunctional crosslinkers (CR), 1-chloro-2,3-epoxypropane, 1,3-dibromopropane and 1,2-dibromoethane with various degrees of crosslinks has been examined. The effect of crosslinking on the extent of sorption and thermal stability is reported.

INTRODUCTION

Crosslinking sorbents are usually used for the separation of cations and anions from solution (1). The current interest in uranium recovery has revived interest for development and enhancement of new and actual ion exchange materials (2).

During the last few years, we have prepared and studied the sorption properties of many crosslinked sorbents (3-10) derived from branched and linear poly(ethylenimine)s because of their well known ability for metal complexation (11-14). We have reported that these polymers generally have a high sorption capacity for copper (II) and uranium (VI) at pH = 2.0. Uranium (VI) is selectively retained at a lower pH before copper(II) which is indicative of the formation of coordination bonds when sorbents take up copper from weakly acidic solutions.

This paper describes a study of the possible effect of the BPEI/CR feed ratio on the degree of crosslinking and sorption properties of sorbents in order to enhance the uranium (VI) selectivity in preference to copper (II). Also the thermal stability of sorbents were examined to found a correlation with crosslinking degree.

EXPERIMENTAL

Materials

All reagents were purchased commercially and used without further purification.

Crosslinked poly(ethylenimine) was obtained as before (3-10), but with different BPEI/CR feed ratios to yield various degrees of crosslinks. Then, a mixture of the necessary amount of the CR (0.024 up to 0.06 mol), 20 mg SPAN 65 (emulsifier) and 30 ml of petroleum ether (b.p. 100-140°C) were added to 15%

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BPEI aqueous solution (0.12 mol ethylenimine unit) under stirring and heating at 95°C for 8 h. The resin was filtered, washed thoroughly with deionized water and dried in vacuo at 40°C to a constant weight. Finally, the resin particles in free base form were sized by dry screening to 40-60 mesh and used in all the experiments. Elemental analyses of resins were determined.

Analytical grade uranyl acetate and copper (II) sulphate pentahydrate reagents were used.

Sorption and elution of metal ions on the croslinked resins

A batch type equilibration procedure was used to measure the extent of Cu(II) or U(VI) uptake by the crosslinked polymers. In the maximum capacity of load evaluation for Cu(II) and U(VI) 1 g of the resin was used, and three consecutive contacts, for 1 h each, with 0.1 g metal ion in 50 ml aqueous solution at pH 2, were performed by drawing out the supernatants after each contact which were combined. For elution assays, loaded resin samples (0.1 g) were shaken with aqueous sulphuric acid and sodium carbonate solutions (10 ml) at different concentrations for 1 h. The extent of sorption and elution were determined in the supernatants, copper (II) by atomic absorption spectrophotometry and the uranyl ion by colorimetry (3-10).

Thermal stability

A Perkin-Elmer TGS-1 thermobalance was used to examine the thermal stability of the resins. The heating rate was 10°/min in nitrogen atmosphere.

RESULTS AND DISCUSSION

In order to use BPEI as a sorbent for specific metal ions in aqueous solutions, it is necessary to obtain the insoluble BPEI derivative. Thus, the water-soluble BPEI was crosslinked with 1-chloro-2,-epoxypropane, 1,3-dibromopropane and 1,2-dibromoethane with different BPEI/CR feed ratios. The ability of these resins to bind metal ions such as Cu(II), Fe(II) and U(VI) from acidic sulphate solutions have been reported (15), however no attempts to evaluate the crosslinking degree and its effect on sorption properties have been made.

As it is shown in Table 1, generally, crosslinking decreases as the BPEI/CR feed ratio increases. The crosslinking degree (CD) was determined from elemental analyses by considering the halogen content and the C/N mol ratio. It is seen that series A resins have the higher crosslinking degrees (from 31 up to 46%) than series B and C resins. This is most likely due to the high reactivity of the epoxyde ring in the former crosslinker, which crosslinks by nucleophilic addition while the alkyl halides which undergo nucleophilic substitution. Moreover, it is concluded by considering the series B and C resins that the higher the chain length of the alkyl bromides, the lower the crosslinking degree.

Sorption of copper(II) and uranium(VI) was studied, and the results are shown in figure 1. Differences in crosslinking between the water-soluble and -insoluble BPEI may be due to the changes in flexibility, steric hindrance and conformation. As a result of the lack of flexibility of the crosslinking BPEI chains (16), as the crosslinking increases, the copper (II) uptake decreases. On the other

Table 1. Results of crosslinking reaction

Resin	Crosslinking Reagent (CR)	BPEI:CR feed ratio	CR:BPEI[a)] in the resin	X:N[a)] mol ratio	Crosslinking[b)] Degree (CD) %
A-1	1-chloro-2,3-epoxypropane	2:1	0.46	0.00	46
A-2		3:1	0.35	0.00	35
A-3		4:1	0.31	0.01	30
A-4		5:1	0.31	0.00	31
B-1	1,3-dibromopropane	2:1	0.32	0.03	29
B-2		3:1	0.30	0.02	28
B-3		4:1	0.26	0.01	25
B-4		5:1	0.20	0.01	19
C-1	1,2-dibromoethane	2:1	0.36	0.03	33
C-2		3:1	0.35	0.01	34
C-3		4:1	0.29	0.03	26
C-4		5:1	0.27	0.03	24

a) $\frac{CR}{BPEI} = (\frac{C}{N} - 2)\frac{1}{M}$; M = number of carbon atoms of the CR; $\frac{C}{N}$, $\frac{X}{N}$ mol ratios from elemental analyses.

b) $CD = (\frac{CR}{BPEI} - \frac{X}{N}) \times 100$ = percentage of bridged CR per amine group (if all amine groups are crosslinked, CD is 50%)

hand, dependence of the uranium (VI) uptake on crosslinking seems to be negligible. Therefore, a selective sorption of uranium in relation to copper is possible, particularly as it is shown in figure 1A with the higher crosslinked resins from series A. This behaviour can be explained by considering the different mechanisms involved. The results suggest participation of the primary amine moieties of the resins in the formation of the copper(II) complex. Because the increase in crosslinking occurs at the expense of amine residues, the decrease in copper(II) uptake of the more crosslinked matrices might be expected. In contrast, uranium(VI) is sorbed by an adduct formation between ammonium groups and a disulphate dioxouranate(II) complex (2).

Consequently, selectivity for uranium was determined according to the following equation (17):

$$S = \log K_d(U) - \log k_d\ (Cu)$$

where k_d is the distribution coefficient of the respective elements (18). From figure 1 it may be seen that at pH 2 the higher the selectivity for uranium, the higher the crosslinking degree for the three series of resins studied.

The uranium recovery from the resins is higher in a basic medium than an acidic one, after two contacts. It may be due to a more stable tricarbonate dioxouranate (II) complex formed.

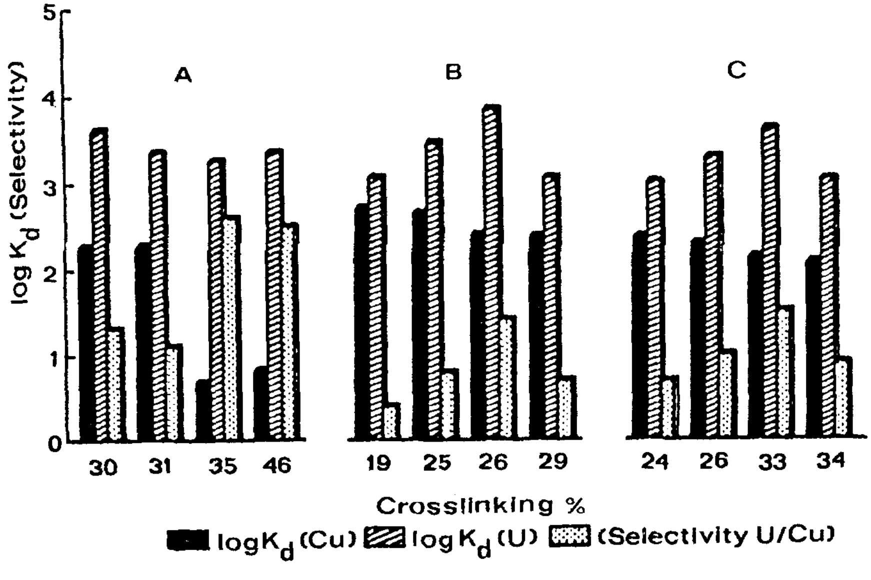

Figure 1. Crosslinking effect on distribution coefficients and selectivity. Diagrams A,B,C correspond to series A,B,C of resins respectively.

Finally, in order to determine the crosslinking effect on thermal stability, thermogravimetric analyses of resins were carried out. From figure 2 it is seen that all the resins are stable over 100°C, but the temperature where 10% loss weight is reached is obviously dependent on crosslinking as well as on halogen content. Presumably, when unreacted alkyl halide moieties are present, hydrogen halide is released under heating in an early stage promoting additional crosslinkage; hence, the thermal stability is decreased.

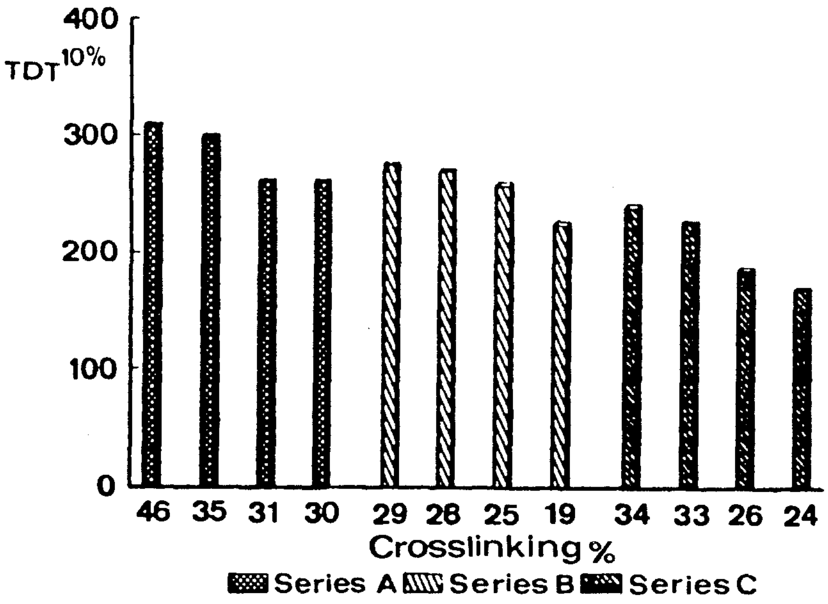

Figure 2. Effect of crosslinking on decomposition temperature at 10% weight loss.

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