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Permeative Separation of Metal Ions Through the Polymer Membrane Containing Gluconate Group

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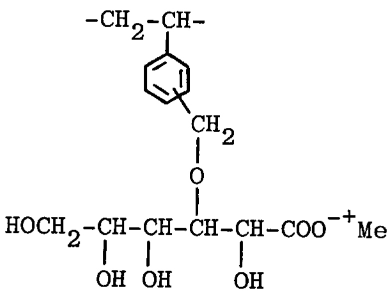
The separation of heavy metals by the use of membrane has become important from the standpoints of the saving of energy and the recovery of resources. Some chelating resins capable of adsorbing metals selectively were used for chromatographic separation of metal ions (GUILBAULT *et al.* 1973; BLASIUS and BROZIO 1967) but few attempts have been made to apply chelating polymers for membranes (SAEGUSA *et al.* 1977). In order to attain high permeation rate as well as selective permeation, the chelating polymer should have appropriate stability constant and hydrophilicity. The oxycarboxylic acids such as gluconic acid, tartaric acid (FUJITA *et al.* 1974), and citric acid are attractive for the purpose.

We have given attention to the polymers having sugar derivatives as side groups (KOBAYASHI and SUMITOMO *et al.* 1977 and 1978). In the present article, the membrane of the copolymer of 3-O-vinylbenzyl gluconate (*1*) and acrylonitrile is used for adsorption and permeation of metal ion mixture and has proved of potential value for metal ion separation.



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RESULTS AND DISCUSSION

The membrane of poly(sodium 3-O-vinylbenzyl gluconate-co-acrylonitrile) of 0.01mm thick were prepared according to the procedure described previously (KOBAYASHI and SUMITOMO 1978). The mole fraction of

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the sugar residue in the copolymer was 0.39 and the estimated content of the carboxylate group was about 2.4 mmole/g of the dry membrane. The combination of Ca:Mg, Cu:Zn, Cd:Ca, and Cu:Cd was arbitrarily adopted as an exploratory work. For the measurement of adsorption, the dry membrane of poly(sodium 3-O-vinylbenzyl gluconate-co-acrylonitrile) was immersed in the aqueous solution of the mixed metal chlorides and the concentration in the supernatant was determined by atomic absorption analysis. Permeation was measured through the membrane which had been pre-equilibrated in the mixed metal chloride solution.

As shown in Figures 1 and 2, the excellently selective adsorption and permeation of Cu and Cd ions were observed. Much larger amount of Cu ion was not only adsorbed but also permeated than Cd ion. The Cu/Cd ratio of the equilibrium adsorption was 3.9 and that of the permeation was 2.0. Selective adsorption was also observed for the combinations of Ca:Mg, Cu:Zn, and Cd:Ca: the ratio of adsorption were 4.2, 4.0, and 1.5, respectively. In spite of the high selectivity in adsorption, the selective permeation of Ca:Mg and Cu:Zn mixtures has not yet been achieved. Interestingly, the selectivity in adsorption and permeation of the Cd:Ca mixture was reversed: the more adsorpted was Cd ion but the more permeated was Ca ion. The Ca/Cd ratio of the permeation was 1.4. There seems a complicated relationship between the adsorption and permeation.

Fig. 1 shows that the total amount of the adsorbed metal cations increased rapidly and approached closely to a constant value within 1 hr. Even after that, however, the amount of the individual metals changed with time. The two metals were indiscriminately adsorbed immediately after mixing, but the less stable ion was gradually replaced by the more stable one until the equilibrium was reached. The marked tendency was true for the other combinations employed. It can be said that the adsorption was controlled kinetically at the beginning and thermodynamically at the end. The total capacity in equilibrium was in the range of 0.7 to 1.0 mmole/g, suggesting that 60 to 80% of the carboxylate group was complexed with the divalent metal cations. It was also found that the adsorbed amount of a metal depended upon the other coexisted metal.

The quantitative analysis of chloride ion by Volhard method indicated that the permeated metal cation was accompanied with the equivalent chloride counter ion. It is not an ion-exchange membrane but a dialysis membrane. Another striking character of the present membrane was that the permeation rate was high and the selectivity in adsorption and permeation was effected even in almost neutral solution. It can be assumed that rather definite ion channel was opened in the membrane

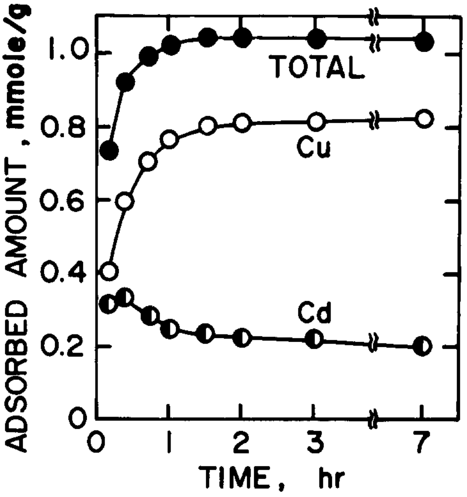

Fig. 1. Selective adsorption of Cu and Cd ions on the poly(sodium 3-O-vinylbenzyl gluconate-co-acrylonitrile) membrane at 25°C. The membrane, 0.105g; the initial concentration of $CuCl_2$ and $CdCl_2$, 0.002M.

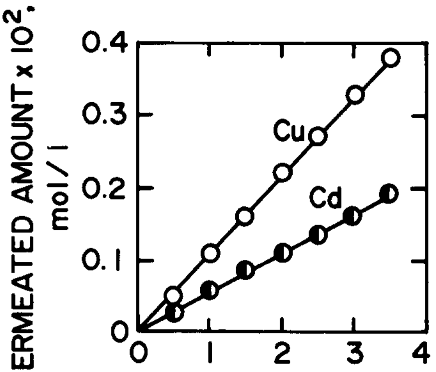

Fig. 2. Selective permeation of Cu and Cd ions through the poly(3-O-vinylbenzyl gluconate-co-acrylonitrile) membrane at 25°C. The thickness, 0.01mm; the effective area, 4.52cm^2; the initial concentration of $CuCl_2$ and $CdCl_2$, 0.01M.

where the isopropylidene protecting group had been removed. The channel would be surrounded by the hydroxy- and carboxy groups, which would lead the chelate formation with metals and make the channel much hydrophilic. We shall assume that the chelation is enough weak to coodinate selectively with metal ions and to desorb readily and the hydrophilic environment favors the diffusion of metal through the membrane. The factors would result in the effective separation of Cu and Cd ions from their mixture by permeation. The membrane containing sugar derivatives is worthy of a further study.

EXPERIMENTAL

Preparation of Poly(sodium 3-O-vinylbenzyl gluconate-co-acrylonitrile) Membrane

The membrane of 0.01mm thick was cast from the DMF solution (5%) of the copolymer between 3-O-vinylbenzyl-1,2;5,6-di-O-isopropylidene-α-D-glucofuranose and acrylonitrile. The mole fraction of the sugar residue was 0.39 and the limiting viscosity number in DMF at 25°C was 3.44. The isopropylidene protection was removed by treating the membrane with trifluoroacetic acid-water (0.2:0.8 v/v) mixture for 30min and then with 12N sulfuric acid for 3hr at room temperature. The subsequent hypoiodite oxidation converted the glucose unit to the sodium gluconate unit.

Selective Adsorption

The dry membrane of 0.1g of poly(sodium 3-O-vinylbenzyl gluconate-co-acrylonitrile) was placed in a 50ml flask, which was maintained in a thermostat at 25°C. The solution (50ml) of a metal chloride mixture was added and stirred magnetically. The initial concentration of each metal was 0.002M. At definite intervals, 0.5ml of the supernatant was pipetted off, diluted into a 10ml volumetric flask, and analyzed using a Hitachi 208 atomic absorption spectrophotometer.

Selective Permeation

The membrane was mounted on the apparatus which was consisted of two 50ml compartments. The effective area of the membrane was 4.52cm^2. Prior to the permeation, the membrane was aged and equilibrated overnight with 0.01M mixed metal chloride solution and washed with water. Into each compartment, 50ml of 0.01M mixed metal chloride solution and 50ml of pure water were added, respectively, and stirred magnetically at 25°C. The metal permeated through the membrane into water was determined by atomic absorption analysis.

SUMMARY

The adsorption and permeation of metal ion mixtures were examined for the membrane of poly(3-O-vinylbenzyl gluconate-co-acrylonitrile). The membrane is found to be effective for permeative separation of metal ions. For the Cu/Cd combination, especially, Cu ion was selectively adsorbed and permeated in a neutral aqueous solution. The high selectivity and the high permeation rate are discussed in connection with the chelate formation and the hydrophilicity of ion channel.

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