Sorption of Target Anions by Ligand Exchange

Y. ÇENGELOĞLU, B. MERCIMEK, H. KARA, M. ERSÖZ

Department of Chemistry, Faculty of Arts and Sciences, Selcuk University, Campus, 42079 Konya, Turkey

ABSTRACT: The sorption of anionic ligands such as I^-, Br^-, and SCN^- onto diaminoethyl−sporopollenin (DAE−sporopollenin) was investigated in both column and batch experiments at room temperature. The isotherm binding constants suggest that the resin is most efficient at the binding of I^- compared with Br^- or SCN^-. The general ligand sorption affinity series observed was $I^- > Br^- > SCN^-$. This ligand sorption could be described by considering the hydration of ions in the exchanger. The sorption behavior of the ligand exchanger and the possibilities of selectively removing and recovering ligands are discussed on the basis of their chemical and complexing properties. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 771−774, 1998

Key words: ligand exchange; sorption; anionic ligands; chelating polymers

INTRODUCTION

The ligand-exchange technique, which displays a high selectivity for organic molecules and ions in an aqueous solution, has found extensive laboratory and industrial application for removing target contaminants.[1−5] Knowledge of the speciation behavior of toxic and contaminated pollutants in the environment is important for the determination of their bioavailability. Complexation of the organic or inorganic ions in the solution phase is relatively well understood and a number of general chemical speciation models are available. There is no universally accepted model for the sorption of target contaminants in waste water. The analysis of single-ligand exchange is important to determine the interdependence between equilibrium and mass-transfer phenomena and also to give information about ligand exchange in chromatography. Single-ligand retention by chelating resins has been investigated by many researchers.[2−8]

Chelating exchangers, which can selectively remove target contaminants and be regenerated efficiently, are highly desirable for industrial applications.[8−10] In particular, the sorption of contaminating inorganic ions such as thiocyanates and cyanide is a major removal problem from the point of view of environmental pollution. Ligand-exchange resins differ from those of cation and anion exchange in a number of important aspects. It therefore seems convenient to begin with the investigation of ligand sorption of iodide, bromide, sulfate, nitrate, and thiocyanate using a chelating metal−ligand exchanger. Using metal-loaded special chelating polymers, we tried to develop an industrial application of the natural polymer. The primary objectives of this work were to present a special chelating polymers as a metal−host for ligand-exchange processes involving anions and to evaluate the modified ligand exchanger for its high-sorption affinities of contaminated ligands for pollution control.

EXPERIMENTAL

Materials

The resin used was *Lycopodium clavatum,* 20-μm mesh size, from BDH Chemicals (Poole, England). All chemicals used were of analytical grade. KCl,

KBr, KI, CoCl$_2$, H$_2$SO$_4$, K$_2$SO$_4$, KNO$_3$, KSCN, ethylenediamine, and citric acid monohydrate were obtained from Merck (Darmstadt, Germany); H$_3$BO$_4$, from Riedel-de Haën ag Seelze (Hannover, Germany); and Na$_3$PO$_4 \cdot$ 12H$_2$O, from Panreac Co. (Barcelona, Spain). The bromide, chloride, sulfate, nitrate, and thiocyanate were dissolved in deionized water (0.1 mol/L) adjusted to a desired concentration and pH. The ligand-exchanger (DAE–sporopollenin) resin was prepared in this laboratory.[11] Then, the resin was treated with Co^{2+} ion (1M CoCl$_2$) which is fixed to the resin matrix.

Sorption Experiments

For the batch experiment, 0.1 g of the exchanger and 10 mL of the aqueous solution containing ligands were shaken at the room temperature for 24 h to achieve equilibration. The released Cl concentration (resin initially in chloride form) was determined by an ionmeter (Orion EA 940), using a Cl ion-specific electrode (Orion 9417-B). The amount of sorption of the bromide or iodide concentration in the resin was also controlled by use of a bromide (Orion 94-35) or iodide (Orion 9453) ion-selective electrode.

Column experiments were performed according to the method described previously.[12] The inside diameter of the column was 3 mm and the packing height was approximately 2.0 cm in all cases. The sorption of anionic ligands was carried out at pH 6.5 of the eluant. The flow rate was 0.49 mL/min. The amount of sorbed ligand was calculated from the change in the ligand concentration in the effluent solution and the weight of the dry resin used. The column was stripped after equilibrium with 2.0M H$_2$SO$_4$ and the amount of ligand retained in the sorbent was also determined by the ionmeter. In each case, the resin was used after washing thoroughly with deionized water; then, the resin was converted into the Cl$^-$ form by treatment with 1M CoCl$_2$ for 24 h. The control of pH was made with an Orion SA-720 pH meter by using the combined electrode.

RESULTS AND DISCUSSION

For the determination of the ligand sorption of I$^-$, Br$^-$, SCN$^-$, NO$_3^-$, and SO$_4^{2-}$ (the resin is initially in the Cl$^-$ form), the loading solution has I$^-$, Br$^-$, or SCN$^-$ as its only ligand. Sorption isotherms were obtained by plotting the ligand
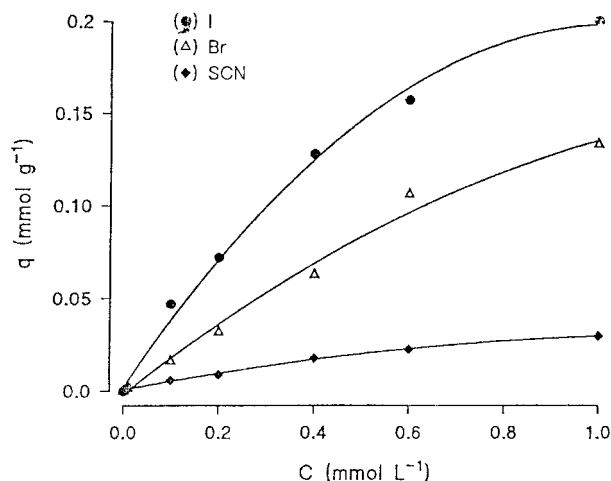

Figure 1 Sorption isotherms of anionic ligands on DAE–sporopollenin.

sorbed (mmol) per gram of resin versus the concentration of the ligand remaining in solution at equilibrium, as shown in Figure 1.

Ion-exchange processes (ligand-exchange processes) are stoichiometric and reversible. To describe the exchange process quantitatively, well-known physical–chemical formulations can be applied. Although the Langmuir or Freundlich isotherms are treated for justifying the exchange process under operational aspects, this seems to be strange for ionic or metal–ligand interactions concerning the exchanger. Therefore, the relevant experimental data were fitted into a basic form of the Langmuir- and Freundlich-type isotherm equations.

Ligand-sorption constants for the anions on the chelating resin were calculated from Freundlich as well as Langmuir plots and are given in Table I. As shown in Table I, by comparison of the correlation coefficients for both the isotherm equations, the degree of fit observed with the type of Freundlich isotherm is better than that obtained with the Langmuir isotherm. Overall, it can be concluded that the Freundlich isotherm equation gives reasonable descriptions of the ligand binding to the chelating exchanger. The values of A_s and K_b refer to the sorption of ligands and also would be expected to depend on the hydrated number. It is evident that the hydration of ions in aqueous solutions is frequently represented as strong binding of nearby molecules.

The amount of sorbed ligand increases in the order I$^-$ > Br$^-$ > SCN$^-$ for the chelating exchanger as shown in Figure 1. Ions are hydrated in aqueous solution and the hydration volume of

Table I Parameters of Langmuir and Freundlich Isotherms for Sorption of Ligands on DAE–Sporopollenin

| Ligand | Langmuir Isotherm Model | | | Freundlich Isotherm Model | | |
	A_s (mmol/g dry resin)	K_b (1 mmol^{-1})	Correlation Coefficient	k (mmol/g dry resin)	n	Correlation Coefficient
I$^-$	1.471	0.109	0.315	0.487	0.697	0.975
Br$^-$	0.901	0.333	0.410	0.238	0.740	0.980
SCN$^-$	0.427	0.917	0.887	0.200	1.541	0.994

I$^-$, Br$^-$, and SCN$^-$ are 37.1, 61.9, and 41.3 cm^3 mol^{-1}, respectively.[13] It is interesting that the sorption of Br$^-$ into the DAE–sporopollenin is slower than that of I$^-$; this is a consequence of the nature of hydration volume of I$^-$ compared with the Br$^-$. The larger hydration shell usually diffuses more slowly in the resin frameworks. In the case of thiocyanate, the hydration number of SCN$^-$ is close to I$^-$, but the SCN$^-$ sorption is found to be lower than Br$^-$ and I$^-$. It was expected that SCN$^-$ should have taken place between I$^-$ and Br$^-$ when the hydration number or hydrated volumes was compared. This result is assumed in that the electron delocalization between thiocyanate atoms is an effective factor for the ligand-sorption process.

Another interesting result observed was that the NO$_3^-$ and SO$_4^{2-}$ ligands were not exchanged with the Cl$^-$ ligand in the exchanger under the conditions employed (concentration of ligands was lower than 1 mmol). The position of the ligand will influence the steric effect and the steric hindrance can be considerable for NO$_3^-$ and SO$_4^{2-}$ ligands as well. It is obvious that there is also electron delocalization between the nitrogen and oxygen or sulfur atoms. In other words, the free electrons are not capable of displaying electron-donating properties due to the electronegativity between atoms. In essence, the ligand-exchange reactions in such cases involve ion exchange accompanied by metal–ligand or Lewis acid–base interactions. The DAE–sporopollenin has functional amine groups and it forms optimum metal–ligand complexes at pH (6–8) ranges.[11,14–15]

Breakthrough curves were measured for I$^-$, Br$^-$, and SCN$^-$ in their single aqueous solution systems using a fixed bed of DAE–sporopollenin particles as given in Figure 2. It is clearly seen from Figure 2 that the breakthrough curves for I$^-$ and Br$^-$ ligands showed particular profiles depending on the hydrated volume of the ligands. Anionic ligands are sometimes present as trace contaminants under reducing conditions of ground water and their removal by traditional strong-base anion exchangers is hindered by the presence of competing ions. Figure 2 shows effluent histories of anionic ligands during the fixed-bed column runs, where I$^-$, Br$^-$, and SCN$^-$ were present in higher concentrations (1 mmol L^{-1}).

Among the separation and sorption techniques, the chelating exchangers are popular due to their complexing ability to ligands and their high degree of specificity. Conventionally, sorption and separations of ligands are carried out in columns packed with porous beads to which the ligand is complexed. The desired ligand sorption to the chelating exchanger via a specific complexing and binding recognition are performed; then, it is replaced by the latter in the mobile phase. In general, the sorption rate in columns is limited by either intraparticle diffusion for large beads or low axial velocities and high pressure drops for small beads.[16,17]

For the determination of the stripping of sorbed ligands on Co-loaded resin, H$_2$SO$_4$ works as the
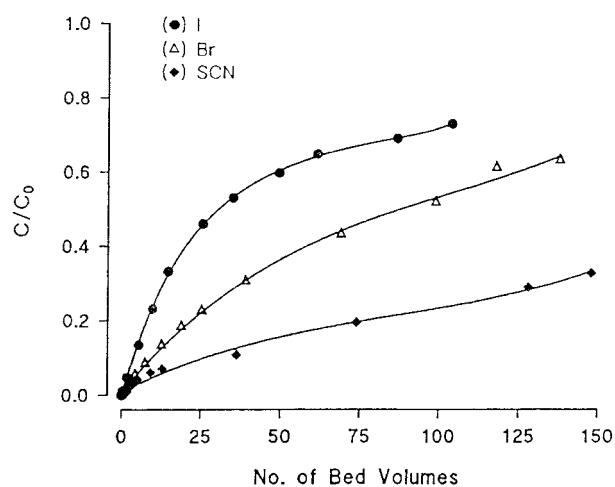
Figure 2 Breakthrough curves for ligand sorption during a column run on DAE–sporopollenin, pH 6.5.
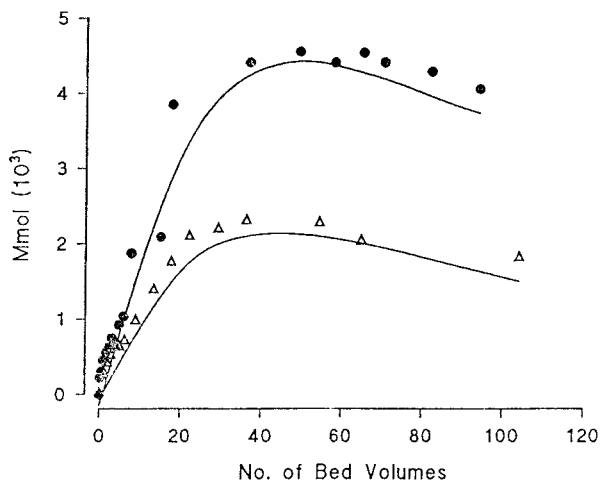
Figure 3 Elution profiles of (●) iodine and (△) bromide concentration during stripping with $2.0M$ H_2SO_4.

feed. Typical stripping results are shown in Figure 3, which shows that a single strip with H_2SO_4 is sufficient to strip the ligands for the given set of conditions. The Co ion is also stripped with H_2SO_4. It is considered that the anionic ligands are strongly held at the ligand-sorption sites to provide the ligands in the particle phase. The reaction mechanism of ligand sorption and ligand stripping has been described in detail.[18,19]

In conclusion, Co^{2+}-loaded DAE−sporopollenin is effective to sorb anionic ligands. This is demonstrated by the fact that the ligand sorption can be correctly predicted from the steric effect, hydration number or hydration volume, complexation constant, and electronegativity between atoms. From an application viewpoint, the process might be promising in areas where the sorption of trace concentrations of target anionic ligands are desirable for the improvement of environmental quality.

REFERENCES

1. L. K. Jang, G. G. Geesey, S. L. Lopez, S. L. Eastman, and P. L. Wichlaez, *Water Res.,* **24,** 889 (1990).
2. Y. Zhu, A. K. Sengupta, and A. Ramana, in *Ion Exchange Advances, Proceedings of IEX '92,* M. J. Slater, Ed., 1992, p. 287.
3. M. Chanda, K. F. O'Driscoll, and G. L. Rempel, *React. Polym.,* **2,** 279 (1984).
4. M. Chanda, K. F. O'Driscoll, and G. L. Rempel, *React. Polym.,* **7,** 251 (1988).
5. M. Chanda, K. F. O'Driscoll, and G. L. Rempel, *React. Polym.,* **8,** 85 (1988).
6. Y. J. Park, K. H. Jung, and T. Y. Park, *J. Colloid Int. Sci.,* **160,** 324 (1993).
7. Y. J. Park and K. K. Jung, *J. Colloid Int. Sci.,* **172,** 447 (1995).
8. U. A. Th. Brinkman and H. Irth, in *Recent Developments in Ion Exchange 2,* P. A. Williams and M. J. Hudson, Eds., Elsevier, London, New York, 1990, p. 195.
9. Y. Inoue, Y. Liu, L. H. Tong, and T. Ouchi, *J. Chem. Soc. Perkin Trans.,* **2,** 1947 (1993).
10. K. Zhang, A. A. Gonzales, S. L. Mukerjee, S. J. Chou, C. D. Hoff, K. A. Kubat-Martin, and G. J. Barnhart, *J. Am. Chem. Soc.,* **113,** 9170 (1991).
11. E. Pehlivan, M. Ersoz, S. Yildiz, and H. J. Duncan, *Sep. Sci. Technol.,* **29,** 1757 (1994).
12. M. Ersoz, U. S. Vural, and S. Yildiz, *Sep. Sci. Technol.,* **30,** 3553 (1995).
13. Y. Marcus, *Ion Solvation,* Wiley, Chichester, New York, Brisbane, Toronto, Singapore, 1985, p. 100.
14. E. Pehlivan, M. Ersoz, M. Pehlivan, S. Yildiz, and H. J. Duncan, *J. Colloid. Int. Sci.,* **170,** 320 (1995).
15. M. Ersoz, E. Pehlivan, H. J. Duncan, S. Yildiz, and M. Pehlivan, *React. Polym.,* **24,** 195 (1995).
16. F. H. Arnold, H. W. Blanch, and C. R. Wilke, *Chem. Eng. B,* **30,** 9 (1985).
17. S. Brandt, R. A. Goffe, S. B. Kessler, J. L. O'Connor, and S. E. Zale, *Bio / Technology,* **6,** 779 (1988).
18. M. Ersoz, U. S. Vural, and S. Yildiz, *Sep. Sci. Technol.,* **30,** 3555 (1995).
19. U. S. Vural, M. Ersoz, and S. Yildiz, *J. Appl. Polym. Sci.,* **58,** 2423 (1995).