

Ligand Sorption Kinetics of Aromatic Amines on New Ligand-Exchanger Sporopollenin in Cobalt Ion Form

U. S. VURAL, M. ERSOZ,* and E. PEHLIVAN

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

SYNOPSIS

An approach to study of intraparticle ion-exchange kinetics of aromatic amines such as *p*-chloroaniline, *p*-toluidine, and *p*-nitroaniline as ligands on Co²⁺ loaded-ligand exchanger of sporopollenin (carboxylated epichlorohydrine [CEP]-sporopollenin) is presented and the ligand-exchange reaction in the resin matrix is shown to be rate-determining. Kinetic studies of aromatic amines as ligands on the CEP-sporopollenin have been performed using continuous column runs. The observed rate seems to be related to the rate of ligand sorption with the mobile phase (ion) and pH in the aqueous phase. The rate of attainment of equilibrium sorption and breakthrough curves of aromatic amines is seen to be nearly similar. With the sorption mechanism deduced to be dominantly particle diffusion-controlled, diffusion coefficients determined were found to range from 1.10^{-8} to $1.0 \cdot 10^{-9} \text{ cm}^2 \text{ s}^{-1}$. Coupled with the fact that different concentrations of solution were employed, these results may be interpreted as indicating that particle diffusion is the rate-determining step; on the contrary, film diffusion was not a rate-controlling step in the ligand-sorption process under the conditions employed. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Aromatic amines are of particular concern as atmospheric pollutants, particularly in the workplace, because some are known to cause urethral track cancer (particularly of the bladder) in exposed individuals.¹ Aromatic amines are widely used as chemical intermediates, antioxidants, and curing agents in the manufacture of polymers, drugs, pesticides, dyes, pigments, and inks. In the atmosphere, amines can be attacked by a hydroxyl radical and undergo further reactions. Amines that possess pairs of free electrons are capable of displaying electron-donating properties and of functioning as ligands.

Polymeric sorbents, which can selectively remove target contaminants and be regenerated efficiently, are highly desirable for large-scale commercial applications.² In this regard, sorption of aromatic amines has been investigated by the novel metal ligand exchanger.

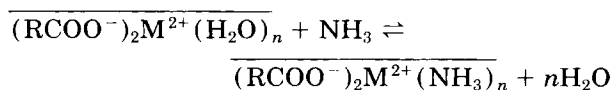
Many kinds of ion exchangers and adsorption resins have been synthesized and are widely used in industrial ion-exchange operations, catalytic reaction, and adsorption.³⁻⁹ However, macroreticular ion-exchange resins and gel ion-exchange resins have been rarely studied on intraparticle diffusion.¹⁰⁻¹³ This article reports the ligand sorption and stripping kinetics of carboxylated epichlorohydrine (CEP)-sporopollenin.

The importance of the sorption of aromatic amines by such metal ligand exchangers has created an increasing need for the understanding of the mechanism and kinetics of the sorption/stripping process to permit prediction and optimization of the performance of the sorption processes. Studies of kinetic aspects of performance can be generally divided into two types according to the mode of operation: (i) stirred tank operation and (ii) packed bed column operation. In the first type, the amine solution is stirred using a magnetic stirrer or a shaking bath and its concentration during sorption is measured by a spectrophotometer using periodical sampling or continuous recording. In packed column operation, the sorption is determined by feeding the

* To whom correspondence should be addressed.

bed with different concentrations of amine and monitoring the UV absorbance at the outlet. In both types of operation, the pH and ionic strength of all solutions and slurries used is preadjusted using buffer and salt solutions.

Ligand exchange was conceptualized and formally introduced by Helfferich.^{14,15} Cu(II)- or Ni(II)-loaded weak acid cation-exchange resins were used by Helfferich to enhance the sorption of various ligands through relatively strong Lewis acid-base interactions. In such ligand-exchange processes, the water molecules (weak ligands) present at the coordination spheres of immobilized Cu(II) and Ni(II) in the cation-exchange resins are replaced by relatively strong ligands, such as ammonia or ethylenediamine. The following provides a typical ligand-exchange reaction with ammonia where "M" represents a divalent metal ion with strong Lewis acid properties:



The overbars denote the exchanger phase and R represents the polymer matrix. During the last 30 years, a great deal of work has been done to apply the concept of ligand exchange in different areas such as separation technology and pollution control processes with a varying amount of success.

Sporopollenin is a natural polymer¹⁶⁻¹⁸ obtained from *Lycopodium clavatum* which is highly resistant to chemicals, has a high capacity, is stable, has a constant chemical structure, and occurs naturally as a component of spore walls and exhibits very good stability after even prolonged exposure to mineral acids and alkalis. Sporopollenin is produced by oxidative polymerization of carotenoids and carotenoid esters, which led to the proposed monomer structures of the macromolecular sporopollenin. At present, sporopollenin is generally considered to be a biopolymer and the chemical structure of sporopollenin is as yet unknown. Its empirical formula has been found to be C₉₀H₁₄₄O₂₇.¹⁹ In the experiments described here on the sorption of aromatic amines of a Co²⁺ loaded-ligand complex, the latter was prepared using the reaction of epichlorohydrine with bromoacetic acid.

The primary objectives of this article were to present a speciality chelating polymer as a metal host for ligand-exchange processes involving aromatic amines; to present convincing experimental results exhibiting high-sorption affinities of some

aromatic amine ligands of interest toward this metal-loaded sorbent and also the preparation of other types new metal-ligand complexes of sporopollenin; and to utilize aromatic amines as sorbent in pollution control and to obtain fundamental information for the application of sporopollenin. The objective also was to investigate through the measurements and analyses of sorption and stripping kinetics of single aromatic amines in a single-component solution on new ligand-exchanger resin.

EXPERIMENTAL

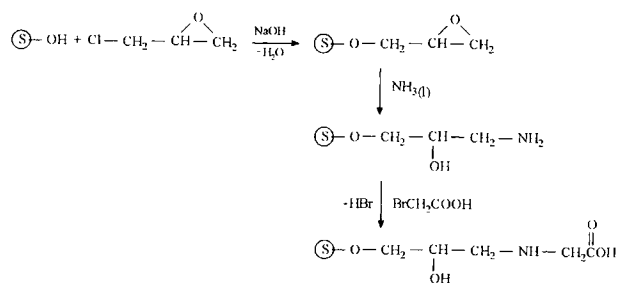
Materials

The resin used was *Lycopodium clavatum* of a 20 μm particle-size mesh from BDH. All chemicals were purchased from Merck and were reagent grade. Deionized water was used in preparing all solutions.

Preparation of Carboxylated Epichlorohydrine-Sporopollenin (CEP-Sporopollenin)

For epoxidation, a suspension of sporopollenin from *L. clavatum* was reacted with epichlorohydrine in 2N NaOH under a N₂ atmosphere according to an established procedure.²⁰ The epoxidation of hydroxyl groups takes place on the polymer. The resulting product was treated with ammonia solution for denoting the groups as —NH and —OH, at room temperature. Then, the mixture was carboxylated with bromoacetic acid as a ligand exchanger (CEP-sporopollenin). This ligand-exchange resin was treated with a Co²⁺ ion which is fixed to the resin matrix.

The modification reactions can be represented as follows:



In the above equation, Ⓢ indicates sporopollenin (*L. clavatum*).

In the IR spectrum, the biopolymer was treated with epichlorohydrine, the characteristic absorption band was observed at 1255 cm⁻¹, and this band

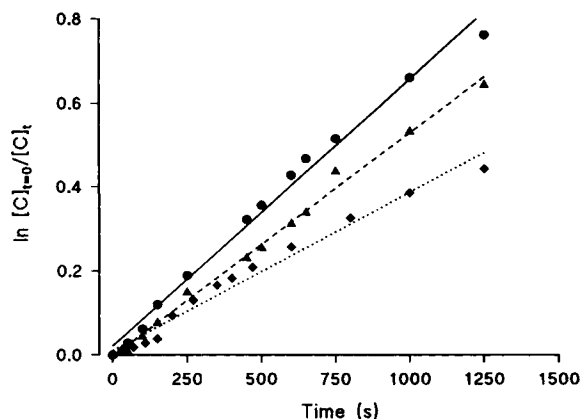


Figure 1 The sorption rate of aromatic amines on CEP-sporopollenin: (▲) *p*-chloroaniline; (●) *p*-toluidine; (◆) *p*-nitroaniline; pH 6.6.

disappeared when treated with ammonia solution. The IR spectrum of the chelating exchanger was different from that of the starting biopolymer and it showed a new band at 1720 cm^{-1} , which is the characteristic stretching vibration of the carbonyl group of the anchored functional group and also a broad absorption owing to the amino group in the range of $3400\text{--}3500\text{ cm}^{-1}$.

Sorption Experiments

The sorbent particles were packed between two layers of glass wool. To avoid air bubbles, the column was carefully packed under water. The aromatic amines were eluted through the column packed with CEP-sporopollenin, using buffers (between pH ranges 4.0–6.6) as the eluant. The flow rate was 1 mL/min. The ligand concentration of amines was chosen to be approximately 2.3–5.5 mmol/L. The experiment was conducted at room temperature. The flow of the solution was started at time $t = 0$ and samples of the effluent were recorded by a spectrophotometer (UV-160 A Shimadzu) at wavelength 290 nm. The amount of sorbed ligand was calculated from the change in the ligand concentration in the effluent solution. The column was stripped after equilibrium with acetate or phosphate buffers and the amount of ligand retained in the sorbent was also determined by a spectrophotometer. Fresh sorbent was used for the determining of breakthrough curves. The reported V_R values were calculated by means of the independent runs. The control of pH was made with an Orion SA-720 pH meter by using a combined electrode.

RESULTS AND DISCUSSION

The rate of ion exchange was found to be rather small compared with that of ordinary commercial resins. This has led us to undertake the kinetic studies described below.

Assuming that the ion-exchange reaction is first-order with respect to ligand concentration, the following equation can be written:

$$-\frac{d[C]}{dt} = k[C] \quad (1)$$

where $[C]$ and k represent the concentration of a ligand in the solution phase and rate constant, respectively. Integration of the equation gives

$$\ln \frac{[C]_{t_1}}{[C]_{t_2}} = k(t_2 - t_1) \quad (2)$$

where $[C]_{t_1}$ and $[C]_{t_2}$ are the concentrations at times t_1 and t_2 , respectively. According to eq. (2), a plot of $\ln [C]_{t_1}/[C]_{t_2}$ against $(t_2 - t_1)$ should be a straight line having a slope of k . In fact, each plot of our results is a straight line, as can be seen in Figure 1. The ion-exchange reactions were therefore first-order in respect to the ligand concentrations. As seen in Figure 2, the effect of pH on the ligand-exchange reaction rate is negligible in the studied pH ranges.

Preliminary experiments were conducted in order to compare the sorption and stripping behavior of resins with respect to all aromatic ligands chosen for the study. The results are presented in Table I.

The sorption of aromatic amines from aqueous solutions at a 5.5 mmol/L initial concentration in

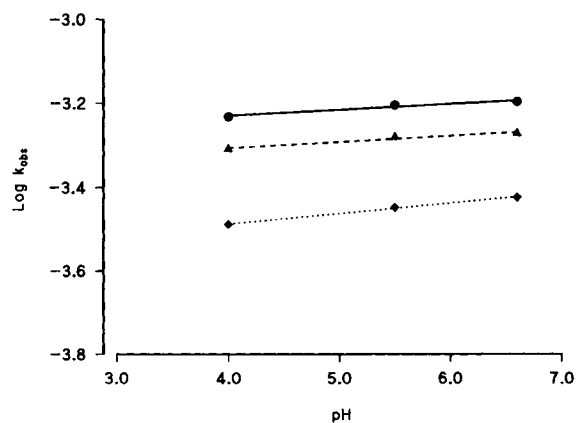


Figure 2 Effect of pH on the sorption rate of aromatic amines: (▲) *p*-chloroaniline; (●) *p*-toluidine; (◆) *p*-nitroaniline.

buffers (pH 4.0–6.6) onto CEP-sporopollenin was measured as a function of time on continuous column runs. Such data are plotted in Figure 3 as the fractional attainment of equilibrium sorption as a function of time. It is seen that *p*-toluidine has a very high rate of initial sorption, being attained in 100 s, and full equilibrium sorption, within 200 s, whereas *p*-chloroaniline and *p*-nitroaniline were about 300 s. The rate of attainment of equilibrium sorption of aromatic amines is seen to be nearly similar.

A very fast initial sorption resulting in an almost instantaneous attainment of the bulk of the equilibrium sorption was followed immediately by a very slow rate of sorption. This suggests that the bulk of the sorption possibly takes place in a shallow outer layer of the resin bead with high diffusivity while inner layers contribute very little to the sorption.

Depending on the concentration of the ligand, there are three alternative rate-determining steps when ligands bind to the ion-exchange resin. Early kinetic studies of ion exchange were summarized by Helfferich, who identified three separate stages: film diffusion, particle diffusion, and chemical reaction at the fixed ionic groups.¹⁴ The differences in the conclusions concerning the rate-determining step in the literature show that kinetic studies of the ion-exchange process are difficult. Provided that the rate of exchange can be proved to be governed predominantly by the "particle diffusion" step, such measurements lead to values of the diffusion coefficient of the exchanging species.

The establishment of ligand-exchange equilibrium between the resin and the external solution depends on two basic processes: first, diffusion of mobile ligands, metal ions, and their complexes in solution, in the resin granules, and through the phase boundary, and, second, the exchange of ligands in the coordination sphere of the sorbed metal. A few publications devoted to the study of the diffusion

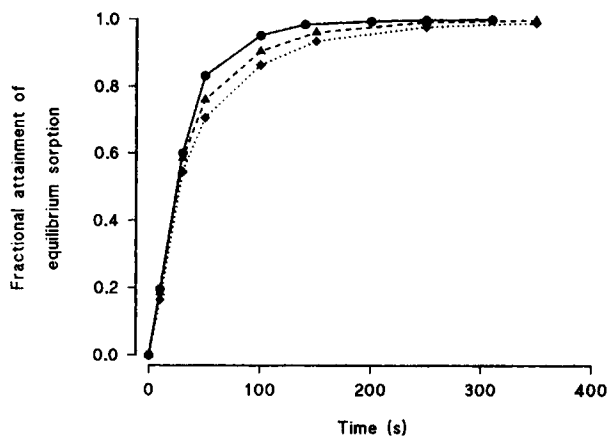


Figure 3 Rate of sorption of (▲) *p*-chloroaniline, (●) *p*-toluidine, and (◆) *p*-nitroaniline on CEP-sporopollenin. Initial concentration of amines in feed 5.5 mmol/L.

processes and the kinetics of ligand exchange in stationary and sorption complexes have appeared in the literature.²¹

For particle diffusion-controlled ion-exchange processes, equilibrium sorption is a function of Dt/R^2 , where D is the diffusion coefficient of counterions in the resin; t , the time; and R , the particle radius. Therefore, the time required to attain any given conversion should be inversely proportional to the square of the radius, and it should be independent of other variables, such as concentration. From the result presented in Figure 5, it is seen that the rate of attainment of equilibrium sorption is practically independent of sorbate concentration in the external solution. The experimental data obtained from the present work were examined by the use of diffusion equations.² This may be interpreted as indicating that particle diffusion is the rate-controlling step and film diffusion was not rate-controlling in the sorption processes under the conditions employed.

Table I The Sorption, Stripping Behavior, and Particle Diffusion Coefficients of Aromatic Amines on CEP-Sporopollenin

Ligand	pH	% Sorption	% Stripping	\bar{D}_e ($10^{-8} \text{ cm}^2 \text{ s}^{-1}$)
<i>p</i> -Chloroaniline	6.60	51.09	67.3	1.17
	4.05	47.45	56.05	0.574
<i>p</i> -Toluidine	6.60	54.7	70.83	1.68
	4.05	49.09	60.37	0.797
<i>p</i> -Nitroaniline	6.60	41.18	53.56	0.729
	4.05	36.60	49.25	0.234

A film diffusion-controlled ion-exchange experiment can be described with the following equation²:

$$U(t) = 1 - \exp\left(\frac{3k(\bar{V}C + VC)}{RCV}t\right) \quad (3)$$

where $U(t)$ is the fractional attainment of equilibrium sorption at time t ; k , the mass transfer coefficient; \bar{V} , the volume of the resin; V , the volume of the solution; \bar{C} , the ligand concentration in the resin; C , the ligand concentration in the solution; and R , the radius of resin bead. If the sorption of ligand onto the resin were under film control, a graph of $-\ln[1 - U(t)]$ vs. t would be a straight line. Since this relation was not found to be the case, the ligand sorption may be considered to be not under film-diffusion control. On the other hand, particle diffusion gave a good fit to the data, indicating that particle diffusion is the rate-controlling step in the ligand-sorption process.

The performance of the ligand exchanger in a continuous operation was studied by conducting column runs. Typical breakthrough curves obtained for aromatic amine sorption on the column packed with the resin are shown in Figure 4. Figures 4 and 5 show typical breakthrough curves for aromatic amines obtained with the resin column and influent containing 5.5 mmol/L amines.

The corresponding experimental kinetic investigations were performed for aromatic amines as ligands. Amines form complexes with a fairly high stability constant.²¹ It may be assumed that they are strongly held at the ligand-sorption sites to render them immobile in the particle phase. It may also be postulated that when a solution containing sorbate

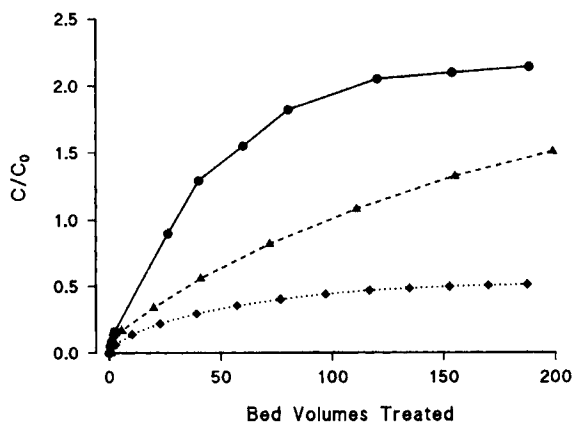


Figure 4 Breakthrough curves for (\blacktriangle) *p*-chloroaniline, (\bullet) *p*-toluidine, and (\blacklozenge) *p*-nitroaniline sorption during a column run on CEP-sporopollenin, pH 6.6.

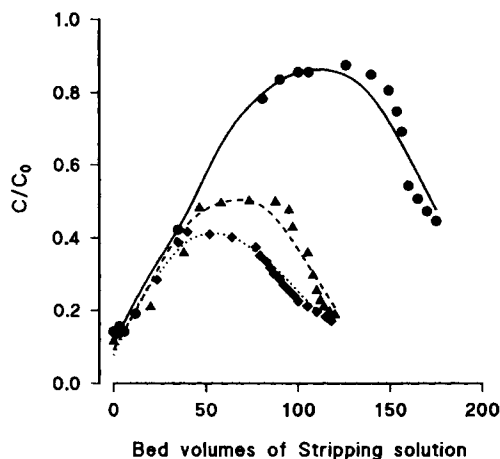


Figure 5 Stripping of CEP-sporopollenin resin column loaded, respectively, with (\blacktriangle) *p*-chloroaniline, (\bullet) *p*-toluidine, and (\blacklozenge) *p*-nitroaniline. Flow rate of stripping solution 1 mL/min.

species is brought into contact with the ligand-sorption resin the reaction of ligand sorption occurs at the outer skin of the particle, the zone of reaction then moving into the solid, leaving behind a spent or saturated region.²¹ The sorbate molecules diffuse through the spent zone toward the inner core where further sorption takes place, but sorption takes place mostly at the ligand-sorption sites.²¹ Moreover, since the saturation sorption capacity of the resin is rather small, the resin particle size may be assumed to remain unchanged with sorption.

In conclusion, a minicolumn apparatus was used to study the kinetics of ligand sorption of aromatic amines onto a metal-ligand exchanger of sporopollenin resin. It is shown that the kinetic parameters measured on single-component experiments provide good prediction behavior.

The authors wish to thank Selcuk University for research facilities.

REFERENCES

1. S. E. Manahan, *Environmental Chemistry*, Lewis, Chelsea, MI, 1991.
2. 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.
3. M. Chanda, K. F. O'driscoll, and G. L. Rempel, *React. Polym.*, **7**, 251 (1988).
4. B. Feibush and B. L. Cohen, *J. Chromatogr.*, **282**, 3, (1983).

5. Y. Zhu, A. K. Sengupta, and A. Ramana, in *Ion Exchange Advances, Proceedings of IEX '92*, M. J. Slater, Ed., Elsevier, London, New York, 1992, p. 287.
6. E. Hemmasi, *J. Chromatogr.*, **109**, 43 (1975).
7. Y. Inoue, Y. Liu, L. H. Tong, and T. Ouchi, *J. Chem. Soc. Perkin Trans. 2*, 1947 (1993).
8. 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).
9. A. E. Rodrigues, *Ion Exchange: Science and Technology*, Martinus Nijhoff, Dordrecht, 1986.
10. M. Q. Ferreira and A. E. Rodrigues, *Chem. Eng. Sci.*, **48**, 2927 (1993).
11. S. K. Ihm, S. S. Suh, and I. H. Oh, *J. Chem. Eng. Jpn.*, **15**, 206 (1982).
12. N. L. Smith and N. R. Amundson, *Ind. Eng. Chem. Eng. Proc. Dev.*, **43**, 2156 (1951).
13. F. Helfferich, *J. Phys. Chem.*, **66**, 39 (1962).
14. F. Helfferich, *Ion Exchange*, McGraw-Hill, New York, 1962.
15. F. Helfferich, *Nature*, **189**, 1001 (1961).
16. G. Shaw, in *Phyto Chemical Phylogeny*, J. B. Harborne, Ed. Academic Press, London, New York, 1970, Chap. 3.
17. J. Brook and G. Shaw, *Nature*, **220**, 678 (1968).
18. G. Mackenzie and G. Shaw, *Int. J. Pep. Prot. Res.*, **15**, 298 (1980).
19. G. Shaw, in *Sporopollenin*, J. Brooks, P. R. Grant, M. Muir, P. Van Gijzel, and G. Shaw, Eds., Academic Press, London, New York, 1971, pp. 305-348.
20. L. Andersson, *J. Chromatogr.*, **315**, 167 (1984).
21. M. Chanda, K. F. O'Driscoll, and G. L. Rempel, *React. Polym.*, **2**, 279 (1984).

Received October 31, 1994

Accepted June 5, 1995