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Sorption of Aromatic Amines on a New Ligand Exchanger of Sporopollenin-Bound Co^{2+} Ion

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ABSTRACT

The mechanism of ligand-exchange sorption of aromatic amines such as *p*-chloroaniline, *p*-toluidine, and *p*-nitroaniline as ligands on a Co^{2+}-loaded ligand exchanger has been studied. The observed rate seems to be related to the rate of ligand sorption with the mobile phase and pH in the aqueous phase. The saturation capacity and binding constant of ligand sorption on the resin increase with increasing basicity of amines. The rate of attainment of equilibrium sorption of aromatic amines is seen to be nearly similar. Coupled with the fact that different concentrations of solution were employed, these results may be interpreted as indicating that particle diffusion is the rate-controlling step. On the contrary, film diffusion was not rate-controlling step in the ligand sorption process under the conditions employed. It is shown that the kinetic parameters measured in single component experiments provide good prediction behavior. The pH dependencies and sorption isotherms of aromatic amines on the resins were also studied.

INTRODUCTION

The ligand-exchange technique is a process, first described by Helfferich (1–4), in which a cation-exchange resin is loaded with transition metal

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ions that are capable of forming complexes (5). It is employed for the separation of compounds according to their ability to enter into the coordination sphere of a complex-forming ion. The principle upon which ligand exchange is based is that a transition metal is fixed on a solid support and this solid sorbent can be used for the exchange of bound ligands of the metal. An exchange of ligands takes place between the external solution and the coordination shells of the metal ions in the resin. The resin holds the metal firmly by complexing with the fixed ionic groups, and the ligand can be displaced with the pH gradient of the buffer solution.

Early kinetic studies of ion exchange identified three separate stages: film diffusion, particle diffusion, and chemical reaction at the fixed ionic groups (1). The differences in the conclusions concerning the rate-determining step in the literature show that kinetic studies of the ion-exchange process are difficult. It has been established that the rate of exchange of counterions between ion-exchange resins and electrolyte solutions is controlled by diffusion of counterions in the resin, particle diffusion, film diffusion, and chemical exchange. But work on diffusion has received less attention. 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.

There are several reason for choosing aromatic amines as the test of ligand sorption. 1) The —NH_2 group in aromatic amines is about 10^6 less basic than in aliphatic amines. Consequently, these solutes do not deplete Co^{2+} from the column and ligand exchanger. 2) Ring substitutions have large effects on the properties of the aromatic amines. Therefore, the elution order of these compounds can give better insight into the sorption mechanisms. 3) Ligand sorption of aromatic amines has been studied (6), so comparisons can be made. 4) Aromatic amines are of practical value and are often used as intermediates in various industrial products such as dyestuffs, drugs, and perfumes.

Sporopollenin is a natural polymer (7–9) obtained from *Lycopodium clavatum*. The structure and properties of sporopollenin has been reported (10, 11). The experiments described here are on the sorption of aromatic amines of a Co^{2+} loaded-ligand complex which was prepared using the reaction of epichlorohydrine with bromoacetic acid.

While the information presently available on kinetic studies and the rate-determining step with commercial ion exchangers is abundant (12–21), only a few kinetic studies with ligand exchangers are available (6, 12, 13). Therefore, in these studies the ligand sorption capacity and the sorption kinetics of a new modified metal–ligand exchanger toward aromatic amines were studied.

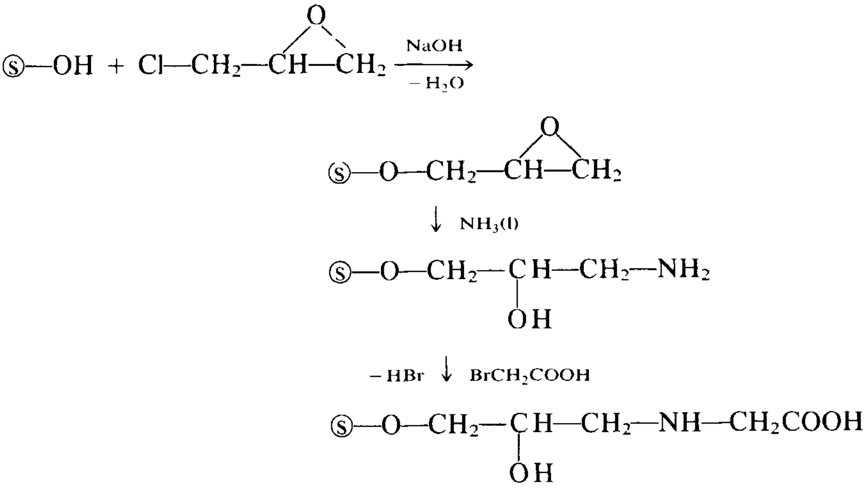
EXPERIMENTAL

Materials

The resin used was *Lycopodium clavatum*, 20 μm particle size mesh from B.D.H. All chemicals were purchased from Merck and were reagent grade. Deionized water was used in the preparation of all solutions.

Preparation of Carboxylated Epichlorohydrine-Sporopollenin (CEP-Sporopollenin)

For epoxidation, a suspension of sporopollenin from *Lycopodium clavatum* was reacted with epichlorohydrine in 2 N NaOH under N_2 atmosphere. The epoxidation takes place with hydroxyl groups on the polymer. The resulting product was treated with ammonia solution at room temperature to denote the groups as —NH and —OH. Then the mixture was carboxylated with bromoacetic acid as a ligand exchanger (carboxylated epichlorohydrine-sporopollenin). This ligand-exchange resin was treated with Co^{2+} ion which is fixed to the resin matrix. The modification reactions can be represented as follows:



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

Sorption Experiments

The sorbent particles were packed between two layers of glass wool. The column was carefully packed under water to avoid air bubbles. The inside diameter of the column was 4 mm and the packing height was approximately 7.0 cm in all cases.

For the single component minicolumn sorption experiments, the ligand concentrations of the amines were chosen to be approximately 2.3–5.5 mmol/L. The sorption of aromatic amines has been carried out at various pH gradients (4–6.6) of eluant. The feed solution flows (1 mL/min) from a constant head reservoir through to small column by a peristaltic pump (Pharmacia Fine Chemicals). The experiment were conducted at room temperature. 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 and the weight of the dry resin used. The column was stripped after equilibrium with acetate or phosphate buffers (in the pH range of 4.0 to 6.6), and the amount of ligand retained in the sorbent was also determined by spectrophotometer. The mass balance was confirmed in all cases. The pH was controlled with an Orion SA-720 pH meter by using a combined electrode.

RESULTS AND DISCUSSION

The Ligand-exchange method involves the formation of labile complexes between cations and solutes that can act as ligands. Amines that possess pairs of free electrons are capable of displaying electron-donating properties and of functioning as ligands.

The equilibrium sorption of aromatic amines on the sorbent was determined, and the sorption data are plotted against the equilibrium concentration in Fig. 1 which shows typical sorption isotherms of aromatic amines on CEP-sporopollenin. The concentration of ligands in the resin phase was calculated as

$$q = (C_0 - C)V/W \tag{1}$$

where C_0 and C denote the initial and equilibrium concentrations of the ligands in the aqueous phase, respectively, V is the volume of the aqueous phase, and W is the dry weight of the resin. Sorption isotherms were obtained by plotting ligand adsorbed (mmol) per gram of resin versus concentration of ligand remaining in solution at equilibrium.

Figure 1 shows that the uptake of aromatic amines was very similar. The sorption isotherms of the uptake of ligands could be expressed as either Langmuir or Freundlich isotherms. Ligand sorption constants and correlation coefficients for the *p*-chloroaniline, *p*-toluidine, and *p*-nitroaniline on the resin were calculated from Freundlich as well as Langmuir

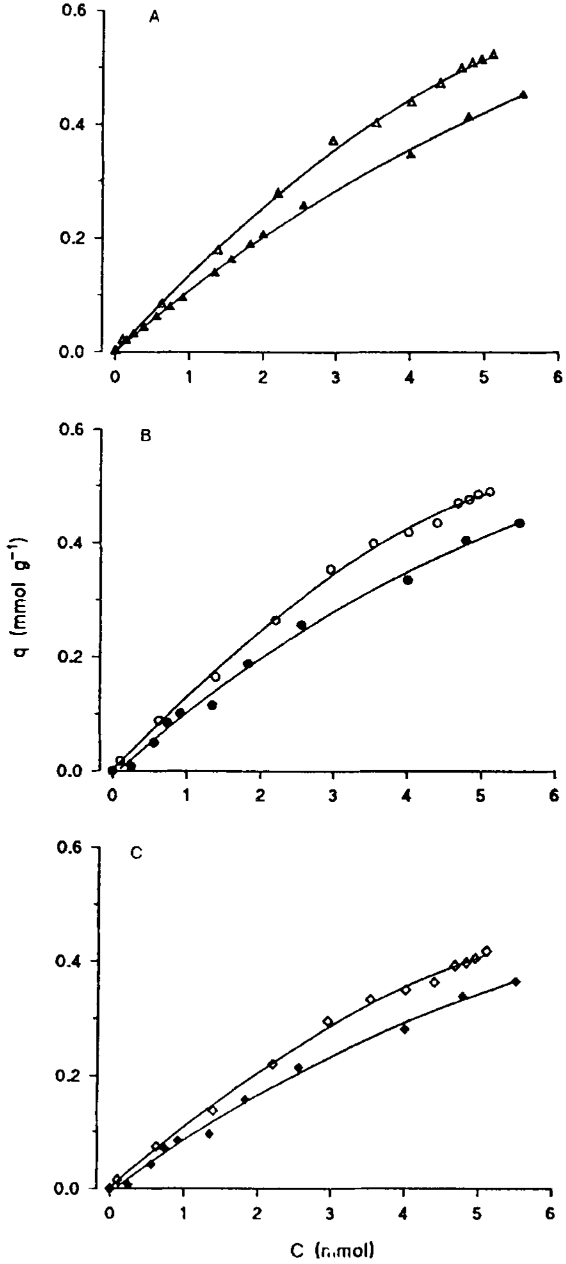


FIG. 1 Sorption isotherms of (A) *p*-chloroaniline, (B) *p*-toluidine, and (C) *p*-nitroaniline on the CEP-sporopollenin (solid symbols, pH 4.0; open symbols, pH 6.6).

plots and are given in Table 1. The sorption data in respect to aromatic amines provide an excellent fit to the Freundlich isotherm, and give correlation coefficients in the 0.964 to 0.995 range for the Freundlich isotherms and 0.758 to 0.924 for the Langmuir isotherm on the resin. To test fit the data, the Freundlich isotherm equation is written as

$$q = kC^{1/n} \tag{2}$$

where k and n are empirical parameters. The Langmuir isotherm is written as

$$C/q = 1/K_bA_s + C/A_s \tag{3}$$

where the parameters K_b and A_s are the sorption binding constant (mmol^{-1}) and the saturation capacity (mmol ligand/g dry weight resin), respectively. The Langmuir and Freundlich isotherms parameters were determined by least-squares fit of the sorption data in Fig. 1.

In the experiments reported here, the total amount of aromatic amines was held in the higher pH. This is appropriate for testing models for the pH dependence of sorption. The increase in the stability of the chelating metal–ligand complexes can be attributed to a combination of such factors as the polymer entropy effect and a lower dielectric constant of the resin matrix.

Preliminary experiments were conducted in order to compare the sorption and stripping behavior of a resin with respect to all ligands chosen for the study. The results are presented in Table 2.

The stability constant of ligand sorption on the Co^{+2}-form resin increases with increasing basicity of the amines. The level of pH of the aqueous medium has a large influence on sorption capacity, sorption kinetics, and binding constant. While both the sorption capacity and sorption

TABLE 1
Parameters of Langmuir and Freundlich Isotherms for Sorption of Aromatic Amines on CEP-Sporopollenin

	Langmuir isotherm, Eq. (3)			Freundlich isotherm, Eq. (2)		
Ligand	A_s (mmol/g dry resin)	K_b (mmol^{-1})	Correlation coefficient	k (mmol/g dry resin)	n	Correlation coefficient
p-Chloroaniline	1.329	0.107	0.758	0.117	1.132	0.995
p-Toluidine	1.946	0.083	0.824	0.132	1.109	0.987
p-Nitroaniline	1.058	0.117	0.924	0.088	1.184	0.964

TABLE 2
The Sorption, Stripping Behavior, and Particle Diffusion Coefficients of Aromatic Amines on CEP-Sporopollenin

Ligand	pH	% Sorption	% Stripping	$\overline{D}_e$ (10^{-8} $cm^2 \cdot s^{-1}$)
p-Chloroaniline	6.60	51.09	67.30	1.17
	4.05	47.45	56.05	0.574
p-Toluidine	6.60	54.70	70.83	1.68
	4.05	49.09	60.37	0.797
p-Nitroaniline	6.60	41.18	53.56	0.729
	4.05	36.60	49.25	0.234

rate on the resin increase at higher pH, the binding constant decreases.

The values of A_s and K_b are presented in Table 1. These values refer to sorption for *p*-chloroaniline, *p*-toluidine, and *p*-nitroaniline. Since, as shown, the sorption is influenced by pK_a, the values of A_s and K_b also would be expected to depend on pK_a. It is evident that the saturation sorption capacity increases at increasing pH (Fig. 2) while the binding constant, as would be expected due to protonation of the —NH_2 ligand group, decreases relative to that at higher pK_a, the effect being more pronounced for the more basic amines. Since a more basic amine would coordinate more strongly, the binding constant K_b would be expected to increase with the basicity of the amine. This is corroborated by Fig. 2.

Kinetic data for the sorption of amines on Co-loaded resin at pH 4.05 and pH 6.6, where the sorption of aromatic amines occurs, are presented in Fig. 3. The rate of attainment of equilibrium sorption of aromatic amines is seen to be nearly similar, and the ligand exchange reaction in the resin matrix is shown to be rate-determining. The rate of sorption is seen to be increased markedly at high pH, which may be attributed to greater accessibility of the ligand sorption sites due to a lower degree of hydrolysis.

Protonation of amines at lower pH would reduce their ligand sorption on the resin. The ligand sorption capacity of Co^{2+}-loaded resin for amines would therefore be expected to increase as the pH of the aqueous medium is increased. This is corroborated by the results shown graphically in Fig. 3. The fact that the optimum ligand sorption of the amines occurs at a relatively neutral pH is advantageous with regard to the use of the Co^{2+}-loaded resin, since it is known that pH (6–8) contributes to higher stability of the Co state (11).

Amines removed by ligand sorption on Co-loaded resin are easily stripped (Fig. 4). Since the aforesaid amines form complexes with fairly

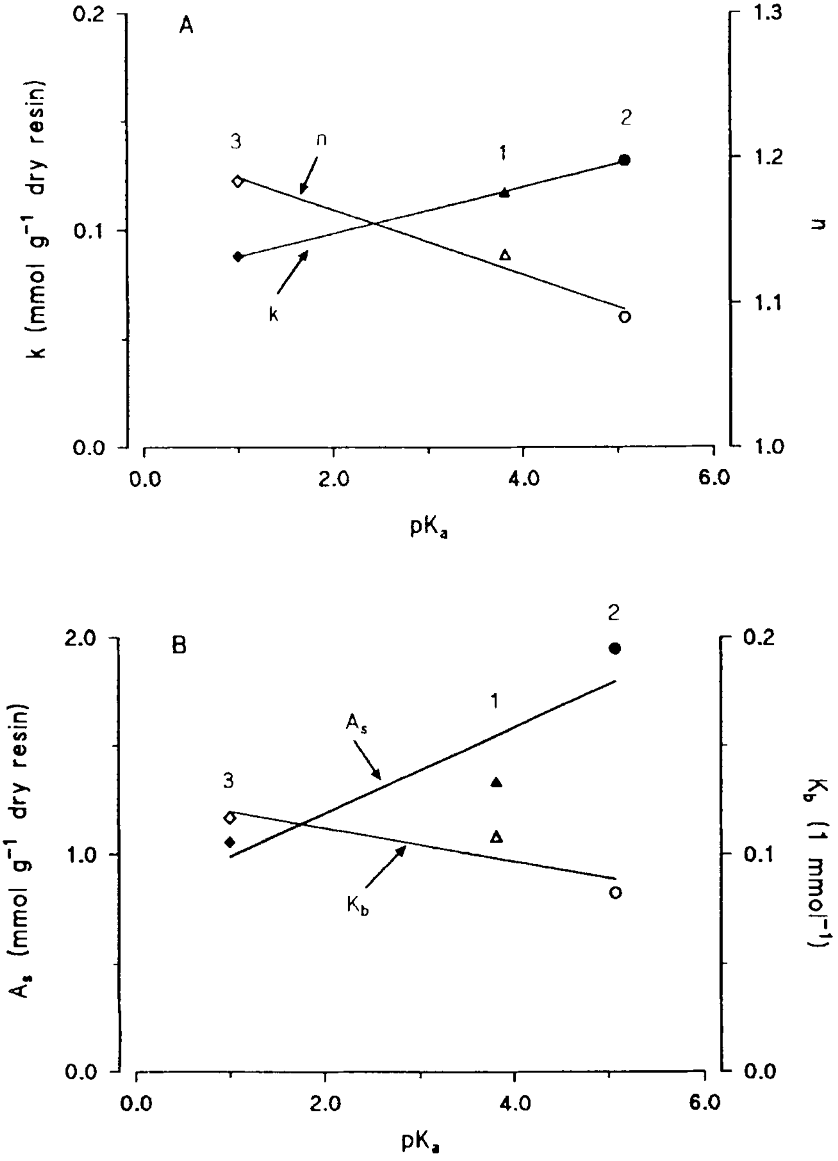


FIG. 2 Variation of (A) Freundlich and (B) Langmuir isotherm parameters for sorption of (1) *p*-chloroaniline, (2) *p*-toluidine, and (3) *p*-nitroaniline on CEP-sporopollenin.

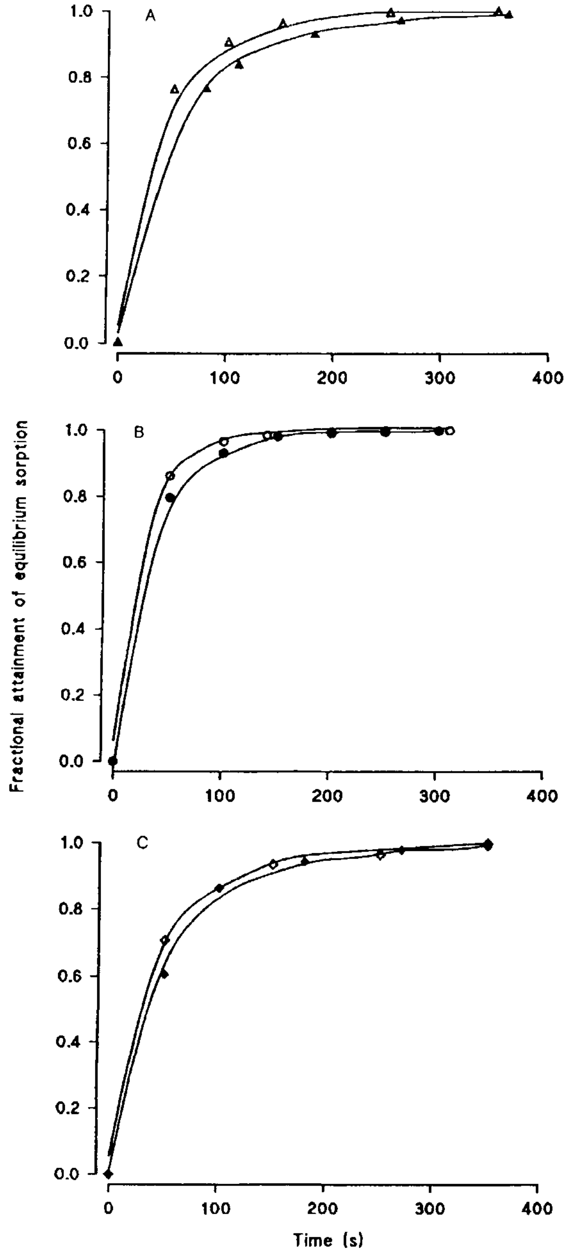


FIG. 3 Rate of sorption of (A) *p*-chloroaniline, (B) *p*-toluidine, and (C) *p*-nitroaniline on CEP-sporopollenin. Initial concentration of amines in feed, 5.5 mmol/L (solid symbols, pH 4.0; open symbols, pH 6.6).

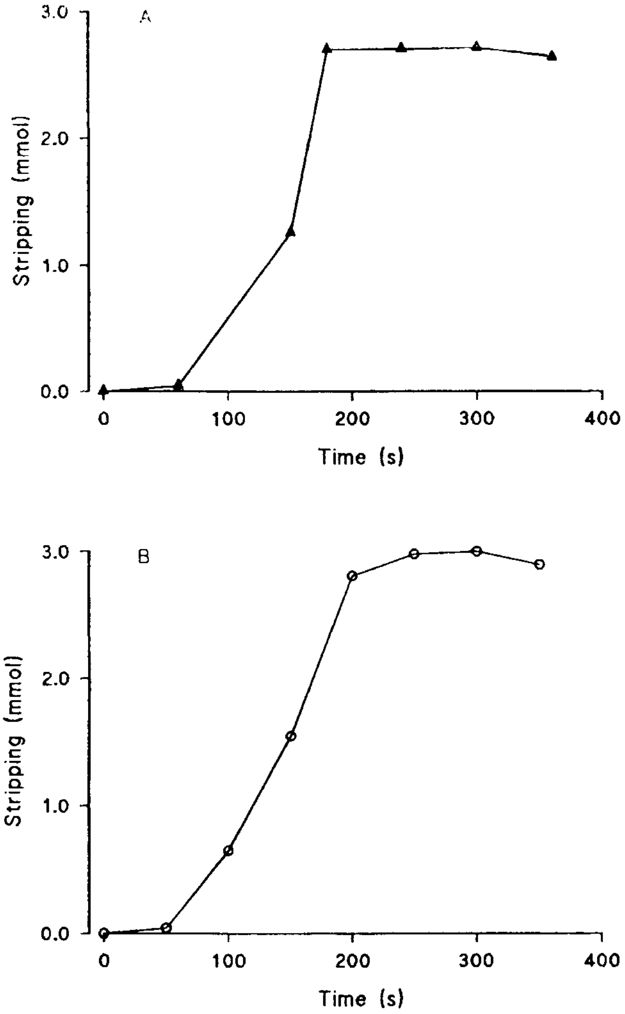


FIG. 4 Rate of stripping of (A) *p*-chloroaniline and (B) *p*-toluidine sorbed on CEP-sporopollenin.

high stability constants (6), it may be assumed that they are strongly held at the ligand sorption sites which renders them immobile in the particle phase. It may also be postulated that when a solution containing sorbate species is brought into contact with the ligand's 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 (6). The sorbate molecules diffuse through the spent zone toward the inner core where further sorption take place, since sorption takes place mostly at the ligand sorption sites (6). Moreover, since the saturation sorption capacity of the resin is rather small, the resin particle size may be assumed to remain unchanged with sorption.

Diffusion equations for both particle diffusion control and film diffusion control (1, 12) were tested with sorption and stripping experimental rate data, which show that film diffusion was not rate controlling. 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. There is good agreement with Chanda et al. (6).

Reactivation of the stripped resin was performed in one step by washing with acetate and phosphate buffer solutions which reconverts the resin to the chelated form. The regenerated ligand exchangers exhibit a higher sorption capacity due to additional ion-exchange sorption by the carboxyl groups.

The results presented here and analysis indicate that the metal–ligand complexes of sporopollenin show an ability to sorb ligands from aqueous solution with increasing pH. It is noteworthy that the sorption of ligands increases with increasing pH. This high sorption ability of the resin may be due to the formation of a metal chelate in the carboxyl groups. It was mentioned above that the metal–ligand complex resins contain carboxyl and phenolic groups. Ligand sorption is unfavorable at a lower pH value because the dissociation constant p*K* value of the carboxylic and phenolic functional groups is low. However, sorption with this resin takes place at higher pH for all amines, which may be attributed to the large difference between the acid dissociation constant of the alcoholic hydroxyl group of the carotenoid ester unit of sporopollenin and that of the carboxyl group.

The metal cations are taken up by coordination to nitrogen and oxygen donor atoms of the functional groups of the carboxylated resin, thus creating very strong coordination compounds in the resin phase. Electrostatic attractive forces between metal and carboxyl or hydroxyl groups prevail in complex formation.

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. The performance of the ligand exchanger in continuous operation was studied by conducting column runs. It was shown that the kinetic parameters measured in single component experiments provide good predictive behavior. The level of pH of the aqueous medium also has an influence on sorption kinetics.

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