

THE COORDINATION ADSORPTION OF AMINES ON CARBOXYL RESIN IN Cu^{2+} FORM FROM NON-AQUEOUS MEDIUM AND DESORPTION WITH ANHYDROUS ELUANT*

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Abstract The adsorption of aniline, *N*-methylaniline and *N,N*-dimethylaniline onto carboxyl resin in Cu^{2+} form from water, ethanol and *n*-hexane have been studied. The results show that the adsorption affinities from *n*-hexane are higher than that from water, and nearly zero from ethanol. The separation factors for the adsorption of these three amines from mixed solution were also examined. The results of continuous column operations show that the breakthrough capacity of aniline from *n*-hexane reaches 90 mg/g dry resin in Cu^{2+} form, and the amines adsorbed can be stripped with anhydrous ethanol effectively. Adsorption onto carboxyl resin in Cu^{2+} form from non-aqueous medium and desorption with anhydrous eluant can overcome the run-off of Cu^{2+} from the resin, and would show potential advantages in the separation of some water-insoluble natural products.

Keywords Coordination adsorption, Adsorption selectivity, Amine, Ligand

INTRODUCTION

Conventionally, natural products, which have been widely used in the pharmaceutical, beverage and food industries, are mainly separated from raw materials by means of extraction (usually combined with distillation, precipitation and crystallization), which consumes large volume of solvent. With the advance of polymer science and technology, polymeric adsorbents show increasing advantages in the separation of natural products because of their simple processes and easy regeneration^[1–3]. However, the separation of natural products by polymeric adsorbents is mainly achieved from aqueous solution, since hydrophobic interaction between the adsorbate and adsorbent in aqueous systems offers a strong driving force for the adsorption, while common adsorbents are less effective in adsorption from non-aqueous system. In their studies of hydrogen bonding adsorption in series, Payne *et al.*^[4–6] reported that hydrogen bonding adsorption could be carried out in non-polar solvents (*n*-hexane was often used in their studies). But it must be noted that the adsorption capacity or the adsorptive affinity from *n*-hexane is much less than that from water, with respect to the same adsorbent and adsorbate. So it is difficult to separate water insoluble natural products from the raw materials by use of conventional polymeric adsorbents.

Most of the transition metal ions, such as Cu^{2+} and Ni^{2+} and so on, can form coordination compounds with their ligands, while many natural products, such as some of the alkaloids and flavonoids, are naturally potential ligands. This implies that, if the complexing metal ions are loaded on the particular resin, such resin should be able to adsorb some of the natural products, also from non-aqueous system. In this study, we take aniline, *N*-methylaniline and *N,N*-dimethylaniline as the model ligands to investigate the adsorption behavior and desorption conditions of this kind of adsorption resin. The adsorption capacity of carboxyl resin in Cu^{2+} form for the above

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mentioned three aromatic amines from *n*-hexane and elution with anhydrous ethanol are reported. For comparison, the adsorption from water was also presented.

EXPERIMENTAL

Adsorbent

Carboxylic resin (D152) and sulphonic resin (D72), both of which are cross-linked macroporous polymeric acid exchangers, were gifts from the Chemical Plant of Nankai University. Prior to use, the resin was washed with 2 mol/L NaOH solution, distilled water, 2 mol/L HCl and distilled water. The resin was then extracted with acetone for at least 8 h, and packed into a glass column and rinsed slowly with an excess amount of cupric sulfate solution. The resin was washed with distilled water till the effluent was free from Cu^{2+} , then washed with ethanol and *n*-hexane sequentially, and air-dried. By this same method, Na^+ , Ag^+ , Ca^{2+} , Cu^{2+} , Zn^{2+} , Al^{3+} and Fe^{3+} were loaded on the D72 and D152 respectively. The resin was sieved to obtain a 30–40 mesh fraction. The properties of the carboxyl resins in H^+ and Cu^{2+} form are listed in Table 1.

Table 1. Properties of carboxyl resin in H^+ and Cu^{2+} form

	Resin exchange capacity (meq/g dry resin)	Surface area (m^2/g)	Skeletal density (g/cm^3)
H^+	6.8	41.6	1.31
Cu^{2+}	3.1	36.7	1.61

* The Cu^{2+} content of resin (mmol/g dry resin)

Reagents

Aniline, *N*-methylaniline and *N,N*-dimethylaniline were reagent grade, and were purified by distillation before use. Anhydrous ethanol, *n*-hexane and methylamine in ethanol were reagent grade and used without further purification. All the metal ions salts, NaCl, AgNO_3 , CuSO_4 , CaCl_2 , $\text{Zn}(\text{NO}_3)_2$, FeCl_3 and $\text{Al}_2(\text{SO}_4)_3$ were reagent grade.

Analysis

The concentrations of all the individual aromatic amine solutions were determined by measuring their UV absorption with a spectrophotometer. When the solute mixture were studied, gas chromatography was used to measure the liquid concentration. A Shimadzu gas chromatograph (model GC-9A) was used with a SE30 column at 423 K. The exchange capacity of resin was determined by washing with an excess amount of 1 mol/L NaOH solution followed by back titration with standard acid. The Cu^{2+} content of resin was determined by washing with an excess of acid followed by titration with EDTA.

Adsorption Experiments

In all the equilibrium studies for individual solutes, measured amounts of the resin in Cu^{2+} form were vigorously shaken with a certain volume of adsorbate solution for at least 10 h in tightly stoppered flasks at 298 K. A range of concentrations was employed for each amine. The concentrations of initial and residual amines were measured using UV spectrophotometry. The amines adsorbed on the resin were calculated from the following equation (Eq.1):

$$q = (c_0 - c)V/M \quad (1)$$

where q is the equilibrium adsorbed-phase concentration (mg/g of dry adsorbent), c_0 and c are the initial and final solute concentrations (mg/L), V is the volume of adsorbate solution (L), and M is the mass of the dry adsorbent (g). All the equilibrium adsorption studies were confined to low solute concentration regions in order that the adsorbed amounts vary as linearly as possible with the equilibrium solute concentrations. The adsorption affinity of the solute (q/c) was determined as ratio of the adsorbed to dissolved solute concentrations and is identical to the slopes of the adsorption isotherms.

A range of concentrations of three amines in mixed solutions was employed to examine the adsorption selectivity from the mixtures. The separation factors (α) from mixtures containing aniline, *N*-methylaniline and

N,N-dimethylaniline are defined as:

$$\alpha_{1,2} = (q/c)_1/(q/c)_2$$

(2)

where $\alpha_{1,2}$ represents the separation factor for selective adsorption of solute 1 and solute 2 from mixed solution, $(q/c)_1$ and $(q/c)_2$ represent the adsorption affinities of solutes 1 and 2 in the mixed solution. So the separation factor for the selective adsorption of aniline and *N*-methylaniline is: $\alpha_{A,M} = (q/c)_A/(q/c)_M$, and for the selective adsorption of aniline and *N,N*-dimethylaniline is $\alpha_{A,D} = (q/c)_A/(q/c)_D$.

The adsorption was also measured as a function of time under vigorous agitation at the same temperature by taking a small volume of solution sample out of the total adsorbate solution at intervals. A column run was performed to determine the breakthrough capacity and the saturation capacity. The preconditioned resin in Cu²⁺ form was placed in a 1.0 cm-diameter glass column. The resin bed was carefully back washed with *n*-hexane to eliminate the entrained air, then tapped to ensure compact packing of the bed. The breakthrough capacity was defined as the total quantity adsorbed per gram of resin when the concentration of effluent reaches 20 × 10⁻⁶ mmol/L by continuous column method.

Recovery of Adsorbed Amine from Resin in Cu²⁺ Form

Elution of adsorbed amine from the resin was conducted by continuous flow column method with anhydrous ethanol as eluant. The flow rate was 2 bed volumes (BV)/h in a down flow fashion.

RESULTS AND DISCUSSION

Adsorption Percentage of Different Resins Loaded with Different Ions

We first examined the adsorption percentage of aniline on different resins (D72 and D152) loaded with different ions. The results are shown in Table 2.

Table 2. Adsorption percentage of aniline on D72 and D152 loaded with different ions

Matrix	Adsorption							Adsorption						
	From water (%)							From <i>n</i> -hexane (%)						
	Na ⁺	Ag ⁺	Cu ²⁺	Zn ²⁺	Ca ²⁺	Al ³⁺	Fe ³⁺	Na ⁺	Ag ⁺	Cu ²⁺	Zn ²⁺	Ca ²⁺	Al ³⁺	Fe ³⁺
D72	2.4	93.2	89.4	78	23.1	33	86.5	12.5	96	95.7	88.7	31	41	81.8
D152	2.1	88.8	85.6	72	18.7	29	81	8.7	89	88.6	78	27	36	77.9

Resin: 0.1 g; Aniline solution: 10 mL; Initial concentration 2 mmol/L; T = 298 K

As shown in Table 2, when the resin, either D72 or D152, is loaded with Na⁺, Ca²⁺ or Al³⁺, which have weak coordination ability, the adsorption percentages are lower. When the resin is loaded with Ag⁺, Cu²⁺, Zn²⁺ or Fe³⁺, which have strong coordination ability, the adsorption percentages are much higher. These indicate that the adsorption of aniline on the resin loaded with Ag⁺, Cu²⁺, Zn²⁺ or Fe³⁺ is based on the coordination interaction between the ions on the resin and ligand aniline.

Resins loaded with Ag⁺ and Cu²⁺ have the highest adsorption percentages, but CuSO₄ is cheaper than AgNO₃. According to literature^[7] reports, the carboxyl resin holds Cu²⁺ more firmly than the sulphonic resin. So we choice the D152 in Cu²⁺ form to study the coordination behavior and the desorption condition.

Equilibrium Adsorption

The equilibrium data for the adsorption of three aromatic amines from different media were plotted against the equilibrium solution concentrations as shown in Fig. 1. To facilitate the comparison of effects of media on the adsorption affinity, the isotherms were approximated as being linear and passing through the origin. The results show that the affinities for adsorption of three amines from *n*-hexane are higher than that from water. The reason for this fact is that water is a weak ligand, which, to some extent, suppresses the adsorption of amines. It is interesting that the adsorptive affinity from ethanol is nearly zero. The higher adsorptive affinity of carboxyl Cu²⁺ resin for three amines from *n*-hexane demonstrates that the ligand adsorption resin can be employed to adsorb the potential ligand from some of the non-aqueous systems. The close-to-zero adsorptive affinity from ethanol

implies that ethanol could be used as the eluant, which is confirmed in the following section.

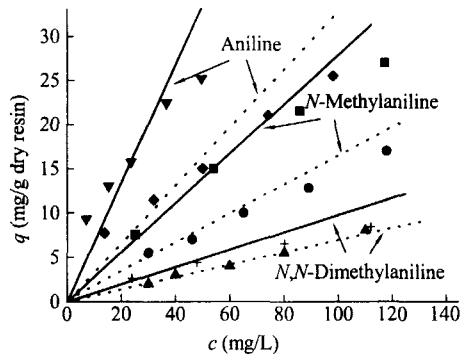


Fig. 1 Selective adsorption of three amines from water (dotted lines) and *n*-hexane (solid line), $T = 298\text{ K}$

Figure 1 also shows the adsorptive selectivity for different aromatic amines from water and *n*-hexane, respectively. The selectivity of ligand adsorption is related to the basicity and the steric hindrance around the electron-donor atom of ligand^[8, 9]. Aniline, *N*-methylaniline and *N,N*-dimethylaniline are similar in their basicity (the values of pK_b of aniline, *N*-methylaniline and *N,N*-dimethylaniline are 8.42, 8.3 and 8.94 respectively), but their steric hindrance varies when they complex the Cu^{2+} on the resin. As it can be seen from Fig. 1, aniline has the highest affinity, and *N,N*-dimethylaniline has the lowest affinity. The sequence of adsorptive selectivity from *n*-hexane is the same as that from water, although the adsorptive affinity from *n*-hexane is higher than from water for each species of three aromatic amines. The adsorptive selectivity from water or *n*-hexane is undoubtedly due to the difference of steric hindrance of various species of amines.

To further investigate the adsorption selectivity, we examined the separation factors for these aromatic amines from the mixture solution of *n*-hexane. The results are shown in Fig. 2. In the lower range of equilibrium concentration, the separation factor for aniline and *N*-methylaniline ($\alpha_{A,M}$) is 3, and for aniline and *N,N*-dimethylaniline, the factor ($\alpha_{A,D}$) is 12.

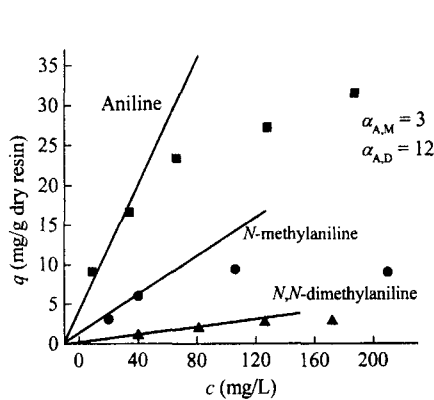


Fig. 2 Separation factors for three amines from mixture solution of *n*-hexane
 $T = 298\text{ K}$

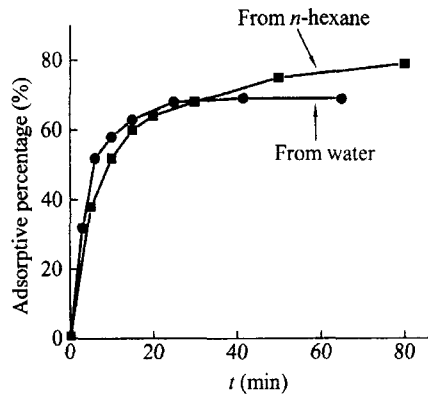


Fig. 3 Rates of aniline adsorption from water and *n*-hexane
0.6 g Dry resin in 60 mL of 200 mg/L aniline solution; $T = 298\text{ K}$

The adsorption rates for aniline from water and *n*-hexane are shown in Fig. 3. The adsorption rate from water is a little higher than that from *n*-hexane, which may be due to the difference of compatibility with Cu^{2+} between water and *n*-hexane. In the process of adsorption, the adsorbate diffuses from the medium to the fixed

metal ion. The diffusion from water is easier than that from *n*-hexane to the fixed Cu^{2+} because water is more compatible with Cu^{2+} than *n*-hexane.

Continuous Column Runs

Figure 4 shows the breakthrough curves for aniline from *n*-hexane and water. The color of resin in Cu^{2+} form was changed to yellow-blue, and the color band extended down the column slowly as the adsorption proceeded. The breakthrough capacity and the saturation capacity of aniline adsorbed from *n*-hexane are 90 and 125 mg/g dry resin while 120 and 166 mg/g dry resin from water. It must be noted that adsorptive affinity of aniline adsorbed from water is lower than from *n*-hexane, although the adsorptive capacity from water is higher than from *n*-hexane. As described above, the lower adsorptive affinity from water is due to the weak coordination of water. But in water, more adsorptive sites on the resin are effective in adsorption because the resin in Cu^{2+} form is about 39% swelled in water and does not swell at all in *n*-hexane, which accounts for the higher breakthrough and saturation capacities from water than from *n*-hexane.

Figure 5 shows the results of elution. To overcome the run-off of preloaded Cu^{2+} from the resin, we use non-aqueous solvent as the eluant. The reason for this run-off is due to the presence of other ions in the aqueous solution, which displace the preloaded metal ions on the resin by ion exchange reaction during the adsorption or the desorption^[10]. But when non-aqueous solution is used as the adsorption medium or as eluant, there are much fewer ions in the solvent such as anhydrous ethanol, and none at all in non-polar solvent such as *n*-hexane. As it can be seen from Fig. 5, aniline was stripped effectively with anhydrous ethanol as eluant, although the curve is a little bit tailed. The stripping percentage is about 88% when the volume of effluent reaches 3BV. To improve the elution effects, a small portion of methylamine was used. When up to 5% methylamine is introduced into ethanol as eluant (ammonia in anhydrous ethanol, of course, would be equally effective, but methylamine in anhydrous ethanol can be easily obtained commercially), the curve is thoroughly non-tailed. When the stripping percentage reaches about 96%, the resin returns to its original blue color as the volume of effluent reaches 3 BV. It is reasonable that the resin is easy to regenerate, because both ethanol and methylamine are more volatile when the resin is air-dried^[11].

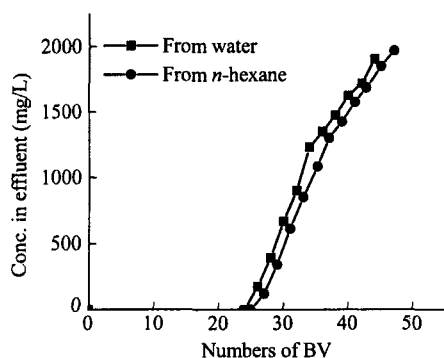


Fig. 4 Breakthrough curves of aniline column
2 g dry resin (BV in water and *n*-hexane is 5.0 and 3.6 mL) in 10 mm I.D. column at room temperature
The flow rate is 2 BV/h and initial conc. is 2×10^{-9}

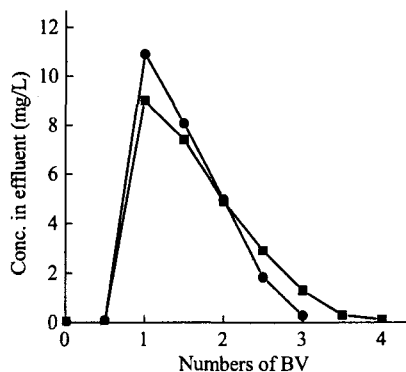


Fig. 5 Stripping of aniline with anhydrous ethanol (■) and 5% methylamine in ethanol (●)
BV = 3.6 mL and flow rate is 2 BV/h

CONCLUSIONS

The ligand adsorbent, polyacrylic acid resin in Cu^{2+} form, can adsorb potential ligands from non-aqueous medium (*i.e.* *n*-hexane in this study) effectively and has good adsorption selectivity for different ligands with different steric hindrance. The adsorbed ligands can be easily stripped with anhydrous ethanol as eluant. The ligand adsorption from non-aqueous medium and desorption with anhydrous solution can overcome the undesirable run-off of metal ions from the resin. This demonstrates that the ligand adsorbent will show special

advantages in the separation of some water-insoluble natural products as potential ligands.

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