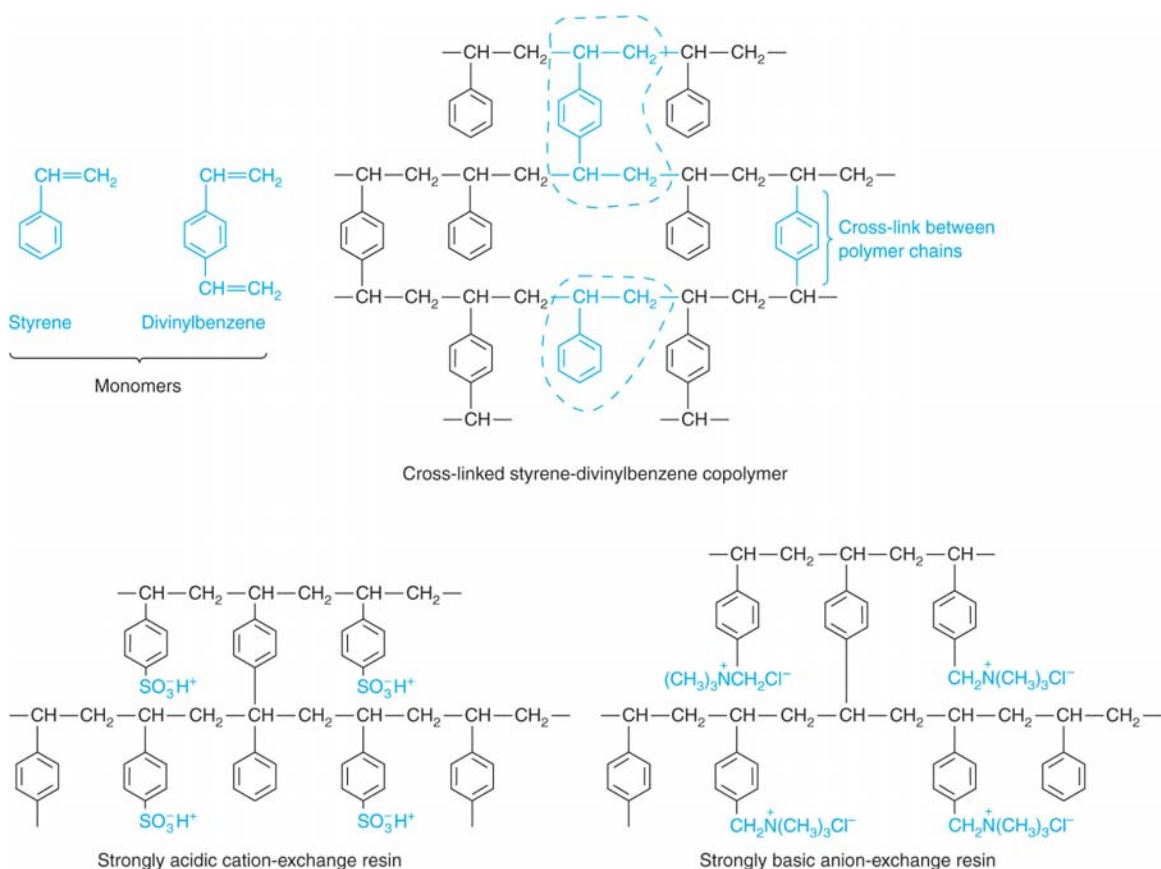


Chem 321 Lecture 24 - Ion-Exchange Chromatography

11/26/13

Student Learning Objectives

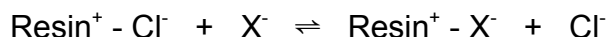
Your cobalt unknown is an aqueous solution containing Co^{2+} and Fe^{3+} . In order to analyze the unknown quantitatively for cobalt by a complexometric titration, the Co^{2+} must be separated from the Fe^{3+} . This is achieved by **ion-exchange chromatography**. Ion-exchange chromatography is a form of liquid chromatography in which the stationary phase is an inert polymer that is derivatized with charged groups that can bind (exchange) ions of opposite charge. The most common cation and anion exchange resins consist of a styrene-divinylbenzene crosslinked copolymer (Fig. 17.1). The cation-exchange form is derivatized with a sulfonate ($-\text{SO}_3^-$) group while the anion-exchange form has a quaternary ammonium ($-\text{CH}_2\text{N}(\text{CH}_3)_3^+$) group covalently bonded to the styrene (Fig. 17.1). This copolymer support is very stable and can be used with both very acidic and very basic solutions.



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Figure 17.1 Structures of styrene-divinylbenzene cross-linked ion-exchange resins

As an example, consider a mixture of anions placed on an anion-exchange column. The resin is associated with a counter ion such as Cl^- . As the anion mixture moves through the column, the anions (X^-) can displace Cl^- and bind to the positive charge group on the resin.



The extent to which a given ion exchanges with the column counter ion depends on factors such as the charge density of the ion and the mobile phase composition. If the ions in the mixture have sufficiently different affinities for the stationary phase, the ions will migrate through the column at different rates and a separation of the mixture components will occur. The affinity that a generic ion (M^+) has for the stationary phase is often expressed as a distribution coefficient (D_v) where

$$D_v = \frac{[\text{M}^+]_{\text{resin}}}{[\text{M}^+]_{\text{soln}}}$$

A large value of D_v means that a particular ion has a large affinity for the resin and will move through the column slowly for the specified elution conditions.

A very large number of studies have been done to determine the behavior of various ions on ion-exchange columns under a variety of conditions. Figure 17.2 summarizes the behavior of ions on an anion-exchange resin as a function of the HCl mobile phase concentration. This is the ion-exchange system that you use to separate the Co(II) and Fe(III) in your unknown. Notice that Fe(III) has some affinity for the column at all concentrations of HCl while Co(II) has maximum binding (largest D_v) to the resin at an HCl concentration of about 10 M. At HCl concentrations less than 5 M, Co(II) does not bind to the resin.

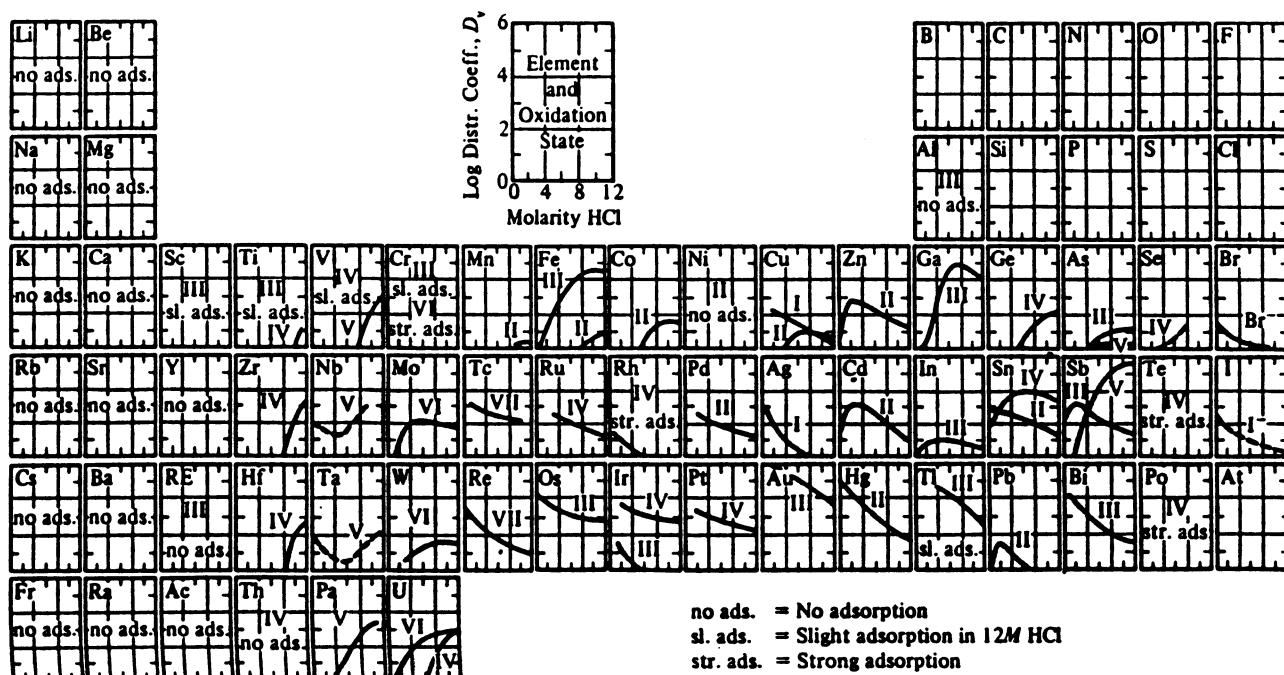


Figure 17.2 Adsorption properties of various ions on an anion-exchange column at varying HCl concentrations

Check for Understanding 17.1

Solutions

- At what HCl molarity does Fe(III) bind the strongest to an anion-exchange resin? Below what HCl molarity does Fe(II) not bind to an anion-exchange resin?
- How might deionized water be prepared from tap water using a combination of an anion-exchange resin and a cation-exchange resin?

At first it may seem surprising that these metal ions have any affinity for a positively-charged resin. The reason for this is that metal ions, like Co^{2+} , in aqueous solution exist as complexes in which the metal ion is bound to some number of **ligands** (Fig. 17.3). A ligand is an ion or molecule with at least one nonbonding electron pair that it can donate to a metal cation to create a bond. In dilute aqueous solution, $\text{Co}(\text{H}_2\text{O})_6^{2+}$ is the principal form of $\text{Co}(\text{II})$. Here the Co^{2+} ion is surrounded by six water molecules in an octahedral geometry. A nonbonding pair of electrons on each oxygen atom is donated to the metal ion. Recall that it is the loss of H^+ from a water molecule in these complexes that accounts for the acidity of highly charged metal ions in aqueous solution. Similarly, $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ is the predominant form of $\text{Fe}(\text{III})$ in very acidic aqueous solution.

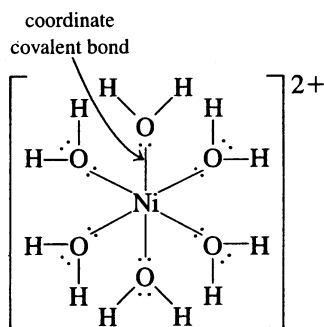
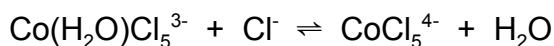
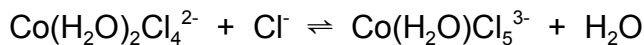
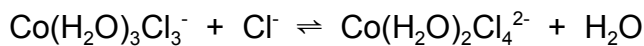
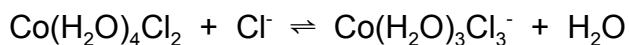
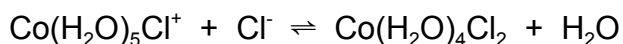
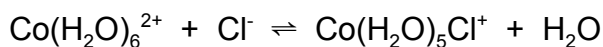


Figure 17.3 Structure of the complex formed by $\text{Ni}(\text{II})$ in aqueous solution

If HCl is added to a dilute aqueous solution of $\text{Co}(\text{II})$, Cl^- can displace H_2O as the ligand bound to the metal ion. As the HCl concentration increases, the equilibria below are shifted to the right, favoring Cl^- as the ligand.



Replacing neutral water molecules with chloride anions also changes the charge on the complex. After 3 H_2O have been replaced by 3 Cl^- , the cobalt complex in solution is anionic. At this point it will have some affinity for an anion-exchange resin.

The predominant forms for the Co^{2+} and Fe^{3+} complexes in the 4 M HCl and 0.5 M HCl mobile phases used in your separation are listed below.

metal ion	4 M HCl	0.5 M HCl
Co^{2+}	$\text{Co}(\text{H}_2\text{O})_5\text{Cl}^+$, $\text{Co}(\text{H}_2\text{O})_4\text{Cl}_2$	
Fe^{3+}	$\text{Fe}(\text{H}_2\text{O})_3\text{Cl}_3$, $\text{Fe}(\text{H}_2\text{O})_4\text{Cl}_2^+$, $\text{Fe}(\text{Cl})_4^-$	$\text{Fe}(\text{H}_2\text{O})_4\text{Cl}_2^+$

Even in 4 M HCl, $\text{Co}(\text{II})$ forms a cationic or neutral complex so it will not have any affinity for the column and it elutes as fast as the mobile phase. The iron complex binds strongly in 4 M HCl. As the HCl concentration is lowered and the equilibria shift in favor of water as a ligand, the complex becomes neutral or cationic and no longer binds to the anion-exchange resin. Thus, you can efficiently elute the iron with the 0.5 M HCl. Note that even in 4 M HCl the anionic iron complex does not irreversibly bind to the column and can be eluted with sufficient mobile phase.

One of the most striking features of this ion-exchange separation is the series of color changes that the cobalt ion in solution undergoes. Initially the band containing cobalt on the column is blue-green and as it elutes from the column with 4 M HCl it is pink. As the solution containing the eluted cobalt ion is heated and the solution volume is reduced it turns blue, then pink again when water is added.

Recall that in order for a solution to appear colored, it must have some significant absorption in the visible region. The connection between observed color and absorbed color is given in the table below. Also remember that absorption in the visible is generally associated with electronic excitation of the valence electrons. For transition metal ions like Co^{2+} , the valence electrons are in the 3d orbitals. Excitation of these electrons to higher energy orbitals requires more energetic photons than are found in the visible region. However, it is believed that the 3d orbitals, normally degenerate in the gas-phase ion, are split when complex ions like $\text{Co}(\text{H}_2\text{O})_6^{2+}$ form in solution. This allows for a lower energy excitation between the split d orbitals, that can be caused by photons in the visible region, to occur.

TABLE 17-1 Colors of visible light

Wavelength of maximum absorption (nm)	Color absorbed	Color observed
380–420	Violet	Green-yellow
420–440	Violet-blue	Yellow
440–470	Blue	Orange
470–500	Blue-green	Red
500–520	Green	Purple
520–550	Yellow-green	Violet
550–580	Yellow	Violet-blue
580–620	Orange	Blue
620–680	Red	Blue-green
680–780	Red	Green

Harris, *Quantitative Chemical Analysis*, 8e
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Figure 17.4 shows how the five d orbitals are oriented with respect to the x , y and z axes along which the metal ion interacts with ligands in an octahedral geometry.

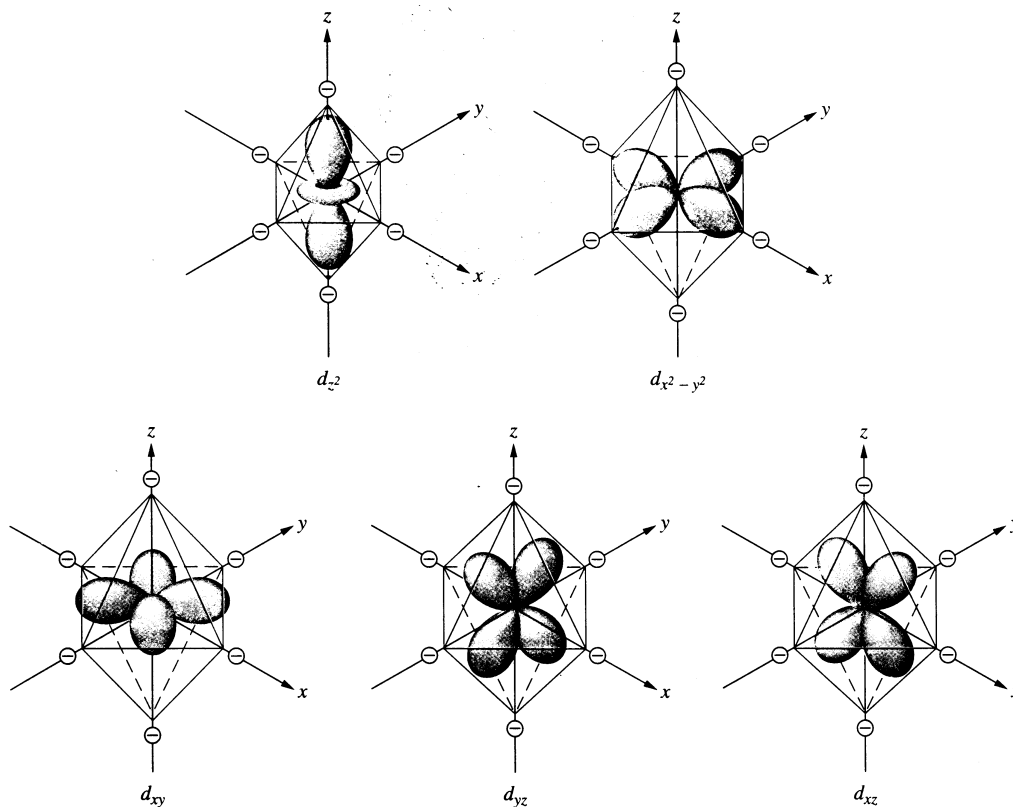


Figure 17.4 Interaction of d orbitals with ligands in an octahedral geometry

Because the lobes of the d_{z^2} and $d_{x^2-y^2}$ orbitals point along the axes, these will interact more strongly (with more repulsion) with electron-donating ligands. The result is to raise their energy with respect to that of the other d orbitals. This leads to the splitting pattern shown in Figure 17.5.

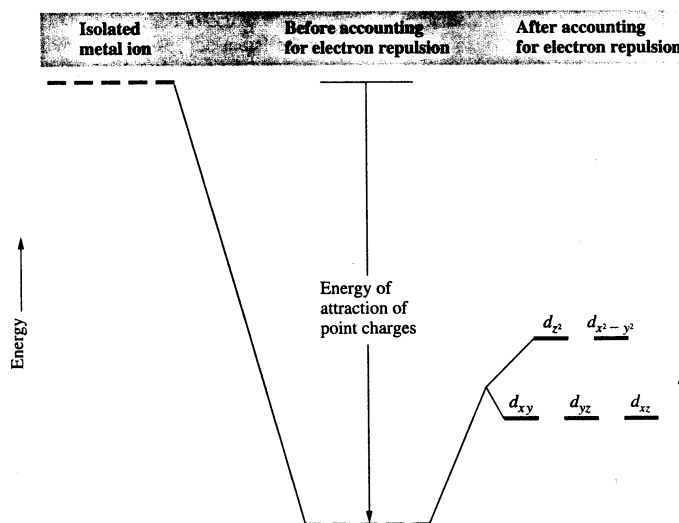
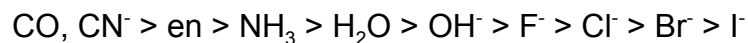


Figure 17.5 Splitting of d orbitals energy in an octahedral ligand field

The difference in the split d orbital energies (Δ) depends on the metal ion and the ligands involved. For a given metal ion, Δ generally varies with ligand according to the spectrochemical series



where en stands for ethylenediamine ($\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}_2$). Thus, when H_2O is the predominant ligand complexed with Co^{2+} , the splitting is larger than when Cl^- is the predominant ligand. The larger Δ means that a shorter wavelength is needed to excite electrons from the lower d orbital to the upper d orbitals. Consequently, the blue cobalt complex (absorption around 675 nm) is associated with chloride as the predominant ligand and the pink complex (absorption around 500 nm) correlates with water as the predominant ligand. The transition point between these complexes occurs as the concentration of HCl reaches about 5 M.

Check for Understanding 17.2

Solution

1. What must be happening to the HCl concentration in the eluted cobalt ion solution as it is heated and its volume is reduced? Explain.

Exercises for Ion-Exchange Chromatography