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Preparation of Palladium(II) and Copper(II) Selective Chelating Resin Bearing 2-Acetylphenol Ligand

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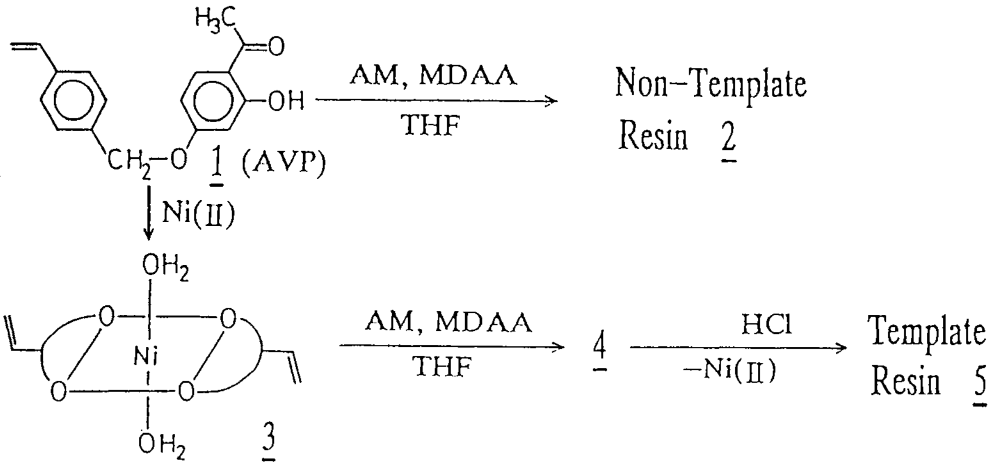
A new chelating resin bearing 2-acetylphenol ligand was synthesized by the copolymerization of 2-acetyl-5-(p-vinylbenzyloxy)phenol, acrylamide, and methylenediacrylamide. The resin adsorbed rapidly Pd(II)[pH 1 - 2.5] and Cu(II)[pH 3.5 - 6] with a high selectivity, and the adsorption ability was promoted by the application of template synthesis method.

Numerous chelating resins have been synthesized for selective separation and recovery of heavy metal ions.[1,2] However, their selectivity is not necessarily so high that many kinds of metal ion are adsorbed on the resins. In order to develop a chelating resin having a high selectivity for certain metal ions, we prepared a new chelating resin bearing 2-acetylphenol ligand, and examined the adsorption properties for several metal ions, together with the effect of a template synthesis. 2-Acetylphenol is an (O,O)-type bidentate ligand, and an analogue of salicylaldehyde (SAL), a well known chelating ligand. SAL is expected to show a high selectivity for Pd(II) and Cu(II) from the complex formation constants ($\log\beta_2 = 14.77$ for Pd(II), 13.31 for Cu(II), whereas, $\log\beta_2 < 9.3$ for Co(II), Ni(II), Pb(II), Zn(II), Fe(II), Mn(II), and Mg(II)),[3] but it is easily oxidized by air, and therefore, air-stable 2-acetylphenol is used here.

The synthetic routes of the resin are shown in Scheme 1. 2-Acetyl-5-(p-vinylbenzyloxy)phenol (AVP) 1 was prepared from 2,4-dihydroxyacetophenone and p-chloromethylstyrene in 40% yield.[4,5] $[Ni(avp)_2(H_2O)_2]$ 3 was prepared by a method similar to salicylaldehydato complex.[6,7] 1 and 3 were copolymerized with acrylamide (AM) and methylenediacrylamide (MDAA) in molar ratios of 1:5:0.15 and 0.5:5:0.15, respectively in tetrahydrofuran (THF) by use of α,α'-azobis(isobutyronitrile) as an initiator. The cross linking polymer 2 (non-template resin) was washed with methanol and water, and dried in vacuo. The cross linking polymer 4 was treated with 6 mol dm^{-3} HCl to form nickel free resin 5 (template resin). It was washed



Scheme 1.

with methanol and water, and dried in vacuo. The white resins 2 and 5 were obtained in ca. 90% yield, and ground and sieved to 100 - 300 mesh. The composition was estimated to be $(Havp)_1(AM)_5(MDAA)_{0.15}$ for both 2 and 5 by elemental analysis.[8)] The maximum loading capacity for Cu(II) was 0.56 (2) and 0.63 (5) mmol/g in bach method at pH 5.5. These values correspond to 80 - 90% of the ligand content estimated as Cu:ligand = 1:2. The swelling capacity was 3.2 (2) and 3.8 (5) in water, respectively.

Figure 1 shows the effect of pH on the distribution coefficient, K_d, in the adsorption of several metal ions, where K_d = (amount of metal adsorbed on one gram of resin)/(amount of metal remaining in 1 cm^3 of the solution). The slopes of the plots for $\log K_d$ vs. pH are 2 for Pd(II), Cu(II), Co(II), Ni(II), and Zn(II), indicating the complex formation ratio between metal and ligand to be 1:2. For Ca(II), Mg(II), Mn(II), Fe(II), Cd(II), and Pb(II), no adsorption was observed in pH 1 to 8. The order of adsorption ability is Ca, Mg, Mn, Fe, Cd, Pb < Zn, Co, Ni < Cu < Pd, and this order is similar to the increasing order of the 1:2-type complex formation constant, β_2-value, of SAL ligand.[3)] Hence, the chelating property of AVP is similar to that of SAL. However, pK_a of AVP is 11.52 in 50% dioxane and is much higher than 9.50 of SAL. Accordingly, it is presumed that the conditional complex formation ability of AVP is lower than that of SAL. In fact, the β_2-values for Cu(II) are 15.80 (AVP) and 13.06 (SAL), respectively, and ΔpK_a is over $\Delta\beta_2$ between AVP and SAL. Therefore, the high pK_a is one of the reasons why AVP-resin adsorbs only a few kind of metal ion. The adsorption pH's are well separated between Pd(II) and Cu(II) (ΔpH = ca. 3.8) and between Cu(II) and M(II) (M = Co, Ni, Zn, Ca, Mg, Mn, Fe, Cd, and Pb) ($\Delta pH \geqq$ ca. 2.5) as shown in Fig. 1. This high selectivity for Pd(II) and Cu(II) may be ascribed to the characteristic property of (O,O)-type bidentate ligand in AVP and SAL. In the cases

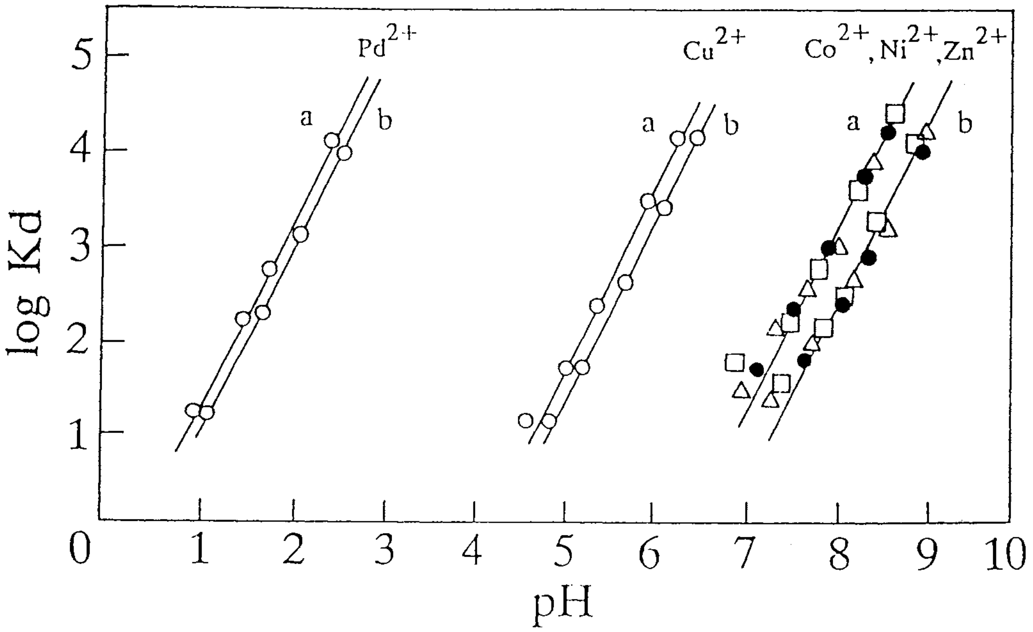


Fig. 1. Effect of pH on the distribution coefficient (K_d). a: Template resin, b:Non-Template resin, ●:Co^{2+}, △:Ni^{2+}, □:Zn^{2+}. [M]=1.0×10^{-4} mol dm^{-3}, Acetate buffer=0.02 mol dm^{-3}, Resin= 0.1 g, Volume=10 cm^3, Shaking time=1 day, 25 °C.

of representative chelating resins bearing iminodiacetic acid (IDA) and 8-hydroxyquinoline (OXIN), the chelators have a nitrogen atom with a strong coordinating ability for many kinds of metal ion. Further, their pK_a's are much lower than that of AVP (2.58 and 9.33 for IDA, 4.91 and 9.81 for OXIN). Thus, they adsorb many kinds of metal ion and their selectivity is not so high as compared with that of AVP.[9,10]

The adsorption pH's of template resin 5 are lower than those of non-

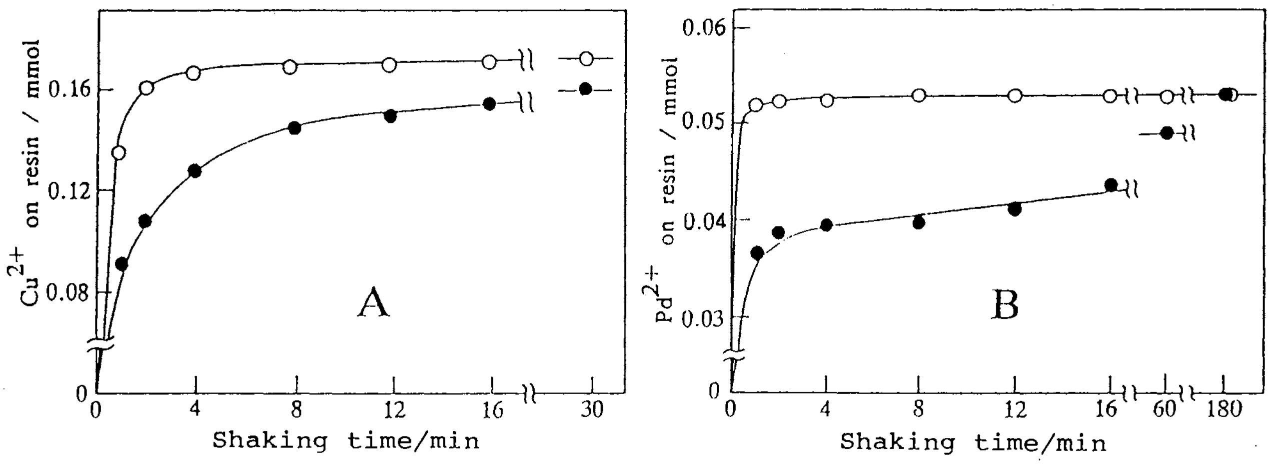


Fig. 2. Time course for the adsorption of Cu(II) and Pd(II) at 25°C. ○:Template resin, ●:Non-Template resin. Resin=0.1 g, Volume=10 cm^3. A:[Cu]=5.0×10^{-3}mol dm^{-3}, pH=5.5. B:[Pd]=5.0×10^{-4}mol dm^{-3}, pH=2.5.

template one 2 for Pd(II), Cu(II), Co(II), Ni(II), and Zn(II) (ΔpH : 0.15 (Pd), 0.20 (Cu), 0.6 (Co, Ni, Zn)). This fact indicates that the adsorption ability is promoted by the template synthesis of the resin; the complex formation of chelating resins depends not only on the property of chelating ligand but also on the disposition of the chelator in the copolymer resins.[11]

The time course for the adsorption of Pd(II) and Cu(II) are shown in Fig. 2. The adsorption rates are very high for both metal ions, and the rates for template resin 5 are higher than those for non-template one 2.

Chromatographic separation of metal ions using the present chelating resins is under investigation.

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