Chelating resins have been prepared by introducing formazane derivatives with acid groups (X) to polyacrolein (X=COOH, OH, AsO3H2 etc.). For the resins, the distribution coefficients (Kd) of metal ions and their pH dependency, and exchange capacity have been examined. The resins show high selectivity to Cd²⁺, Zn²⁺ and Cu²⁺, log Kd being 4.20-5.54 for Cd²⁺, 4.03-4.70 for Cu²⁺ and 3.57-4.50 for Zn²⁺. The exchange capacities (meq/g) are 1.63-2.42 for Cu²⁺, 1.70-2.41 for Cd²⁺ and 1.73-2.41 for Zn²⁺.

Keywords Chelating resins, formazane derivatives, ion exchange, distribution coefficients, exchange capacity

Chelating resins are playing increasingly important roles in the preconcentration and separation of trace elements. These sorbents are especially useful in the trace analysis of natural water, and in preconcentrating noble metals from complex samples. Chelating resins are characterized by high selectivity, which depends mainly on the chelating groups.

Other features (e.g. capacity, kinetics) depend rather on the characteristics of polymeric matrices. Various matrices are used in the synthesis of chelating resins, such as: copolymers of styrene and divinylbenzene; polystyrene; polymethacrylate; and fibrous materials such as cellulose.

In addition to a well-known resin Chelex-100 based on a styrene-divinylbenzene copolymer with iminodiacetate groups, numerous chelating resins have already been synthesized by using various chelating agents: oxine³-⁴, dithiocarbamates⁷-⁸, Rhodamine, thio-oxine and thiourea⁹, nitrosonaphthols¹⁰,¹¹, N-substituted hydroxylamines¹²,¹³, PAR¹⁴, arsonic acid¹⁵, triazolethiol¹⁶, cysteine¹⁷, ketoiminocarboxylic acids¹⁸ and 2-(3-sulfo benzoyl) pyridine-2-pyridyldrazine.¹⁹

In the present work, novel chelating resins were synthesized by introducing a series of formazane chelate compounds (see Fig. 1), which has been investigated extensively as colorimetric reagents²⁰-²³, to polyacrolein according to methods given in the literature²⁴-²⁶.

Furthermore, the properties of the prepared resins, such as the distribution coefficients of metal ions and the exchange capacity, have also been examined.

Experimental

Apparatus

An IL-300 inductively coupled plasma atomic emission spectrophotometer was used for the determination of metal ions under standard operating conditions. A Denki Kagaku Keiki Model HG-3 Digital pH Meter with a glass and calomel electrode pair was used for pH measurements.

Reagents

Metal stock solutions. Dissolve an appropriate amount of each metal in nitric acid. Add perchloric acid and evaporate nearly to dryness. Dissolve the residue with water to yield a 0.1 M metal solution.

Buffer solutions. Prepare the buffer solutions for pH 1.10-6.90 by mixing a 0.1 M perchloric acid solution and a 0.1 M hexamaine solution and those for pH 7.6-8.5 by mixing a 0.1 M perchloric acid solution with a 0.05 M borax solution.
Synthesis of the chelating resins

The PF, PCF and PHF resins were prepared according to procedures described in the literature. The procedure for the preparation of the PAF resin is described here: Suspend 1.5 g of polyacroleinphenylhydrazone in a mixture comprising 350 ml of pyridine and 50 ml of tetrahydrofuran–ethanol (1:1); then add 3.4 g of sodium acetate to the resulting suspension and keep the mixture below 0°C. Diazotize 3.47 g of 2-aminophenyl arsonic acid by mixing with 7 ml of hydrochloric acid and 1.2 g of sodium nitrite in the usual way. Then slowly add the diazonium salt to the polyacroleinphenylhydrazone solution while keeping the latter below 0°C and alkaline (pH 10–14) to run coupling. After allowing the reaction mixture to stand for 5 h below 10°C, add water to the mixture followed by filtration of the product. Extract the compound with benzene for 5 h in a Soxhlet extractor in order to remove any remaining starting materials and dry under reduced pressure. The CHF resin was synthesized in almost the same way.

Table 1 summarizes the analytical results for nitrogen and the mole-substitution rate of formazane groups.

Measurement of distribution coefficients for metal ions

The distribution coefficients (Kd) of metal ions were measured by a batch method.

Accurately weigh 20–30 mg of resin (dried under reduced pressure at 60°C for 10 h) into a stoppered test tube. To this resin add 0.5 ml of a 1 M sodium perchlorate solution, 0.5 ml of a 0.001 M metal ion solution and 4 ml of a buffer solution adjusted to pH 1.1–8.5. Shake for 96 h at 27±1°C and then determine the metal-ion content remaining in the solution phase by ICP–AES. Kd should be calculated by using of the following equation:

\[
K_d \text{ (ml/g)} = \frac{[M^{n+}_s]}{[M^{n+}_r]}
\]

where s and r stand for the solution phase and the resin phase, respectively.

Results and Discussion

Distribution coefficients of metal ions

Table 2 shows Kd values for the transition-metal ions on each resin prepared at 0.1 M ionic strength; maximum adsorption was observed for each metal. Generally, all the resins give high Kd values. Among the metal ions tested, zinc, cadmium and copper showed extremely high Kd values, whereas cobalt, nickel and iron had somewhat low values. The Kd value decreases in the order: Cd2+>Cu2+>Fe3+>Zn2+>Co2+ for the PF resin, Cd2+>Fe3+>Cu2+>Zn2+>Ni2+ for the PCF resin, Cd2+>Cu2+>Zn2+>Ni2+>Co2+ for the PAF resin, Cd2+>Cu2+>Zn2+>Ni2+>Co2+ for the PHF resin and Cd2+>Cu2+>Zn2+>Ni2+>Co2+ for the CHF resin.

Effect of pH on the adsorption of metal ions on chelating resins

The effect of pH on the adsorption behavior of Co2+, Ni2+, Cu2+, Zn2+ and Cd2+ was investigated. The obtained results are shown in Figs. 2–4, where the adsorption (defined as \([\text{the amount of metal ion adsorbed on the resin}/(\text{the total amount of metal ion added})])\times100\) is plotted against the pH values. For all resins tested, the pH range of the adsorption maximum of copper exceptionally shifted to the far acidic side. As can be seen in Fig. 2, the pH at the adsorption maximum on the PAF resin shifts to the more acidic side than that of the PF resin by one pH unit for Cu2+, 0.4 pH unit for Cd2+ and 0.3 pH unit for Ni2+ and Zn2+ so that the adsorbability of metal ions on the PAF resin seems to be larger than that on the PF resin. The difference in the coordinating group appears to affect

Table 1  Elementary analysis of prepared resins

<table>
<thead>
<tr>
<th>Resin</th>
<th>Nitrogen, wt %</th>
<th>Formazane, mol %</th>
</tr>
</thead>
<tbody>
<tr>
<td>PF</td>
<td>1.74</td>
<td>1.85</td>
</tr>
<tr>
<td>PCF</td>
<td>3.99</td>
<td>7.00</td>
</tr>
<tr>
<td>PAF</td>
<td>2.95</td>
<td>3.60</td>
</tr>
<tr>
<td>PHF</td>
<td>4.19</td>
<td>5.00</td>
</tr>
<tr>
<td>CHF</td>
<td>7.16</td>
<td>10.30</td>
</tr>
</tbody>
</table>

* For abbreviations, see Fig. 1.

Table 2  Distribution coefficients (Kd(ml/g)) of metal ions on the prepared chelating resins

<table>
<thead>
<tr>
<th>Resin</th>
<th>Co(II)</th>
<th>Ni(II)</th>
<th>Cu(II)</th>
<th>Zn(II)</th>
<th>Cd(II)</th>
<th>Fe(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>log Kd pH</td>
<td>log Kd pH</td>
<td>log Kd pH</td>
<td>log Kd pH</td>
<td>log Kd pH</td>
<td>log Kd pH</td>
</tr>
<tr>
<td>PF</td>
<td>4.0</td>
<td>5.4</td>
<td>3.9</td>
<td>5.4</td>
<td>4.4</td>
<td>5.4</td>
</tr>
<tr>
<td>PCF</td>
<td>3.1</td>
<td>5.4</td>
<td>3.5</td>
<td>5.4</td>
<td>4.0</td>
<td>4.9</td>
</tr>
<tr>
<td>PAF</td>
<td>3.1</td>
<td>5.4</td>
<td>3.7</td>
<td>5.4</td>
<td>4.5</td>
<td>4.8</td>
</tr>
<tr>
<td>PHF</td>
<td>2.8</td>
<td>5.5</td>
<td>3.9</td>
<td>5.5</td>
<td>4.5</td>
<td>4.9</td>
</tr>
<tr>
<td>CHF</td>
<td>3.0</td>
<td>5.7</td>
<td>3.1</td>
<td>5.7</td>
<td>4.7</td>
<td>5.0</td>
</tr>
</tbody>
</table>

μ (ionic strength)=0.1 M.
the adsorbabilities of metal ions; in the PF resin two nitrogen atoms (N, N coordination) of the imino group (=NH) and the azo group (−N=N−) can take part in coordination bond formation while in the PAF resin oxygen atoms of arsonic acid group (−AsO(OH)₂) also take part in bond formation. This is also consistent with the fact that in the PAF resin the pH range of the adsorption maximum for each metal ions is slightly different from each other (pH dependent), while in the PF resin cadmium, zinc and nickel, except copper, show adsorption maxima within almost the same pH range. The coordination atoms of the PCF, PHF and CHF resins seem to be N,N,O, N,N,O and N,N,O,O, respectively, where the oxygen atoms of the carboxyl group (−COOH) and/or hydroxyl group (−OH) participate in bond formation. It is known that a chelate with more

![Fig. 2 Adsorption behavior of metal ions on the PF and PAF resins. Metal ion, 0.5 µmol; chelating resin, 20 mg; (●) Cu²⁺; (□) Cd²⁺; (○) Zn²⁺; (▲) Ni²⁺; (■) Co³⁺.](image)

![Fig. 3 Adsorption behavior of metal ions on the PCF and PHF resins. Metal ion, 0.5 µmol; chelating resin, 20 mg; (●) Cu²⁺; (□) Cd²⁺; (○) Zn²⁺; (▲) Ni²⁺; (■) Co³⁺.](image)

![Fig. 4 Adsorption behavior of metal ions on the CHF resins. Metal ion, 0.5 µmol; chelating resin, 20 mg; (●) Cu²⁺; (□) Cd²⁺; (○) Zn²⁺; (▲) Ni²⁺; (■) Co³⁺.](image)
coordinating atoms is generally more stable, though the adsorbabilities of Ni\(^{2+}\) and Co\(^{2+}\) on the CHF resin are markedly low (see Fig. 4). This is due to the steric hindrance caused by a polymer matrix situated outside the coordination spheres of the metal complexes.

**Exchange capacity of metal ions**

The exchange capacities of metal ions are listed in Table 3. All prepared resins show high exchange capacities. Especially, higher capacities have been observed for Cu\(^{2+}\), Zn\(^{2+}\) and Cd\(^{2+}\). Resins containing one acid group (such as the PCF, PAF and PHF resins) have higher capacities, whereas a resin containing two acid groups (the CHF resin) has a lower one.

In conclusion, the PCF, PHF and PAF resins which were prepared by introducing one acid group (such as a carboxyl, hydroxyl or arsonic acid group) to the formazane nucleus have been found to have high exchange capacities as well as pH-dependent adsorbabilities for metal ions. They also show potential for practical use. PF resins without an acid group have remarkably high K\(_d\) values (log K\(_d\), 5.54) for Cd\(^{2+}\). A further investigation of the adsorption behavior of metal ions would most likely extend the utility of these resins in the field of inorganic analysis.

**References**


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**Table 3 Exchange capacities (meq/g) of the prepared resins**

<table>
<thead>
<tr>
<th>Resin</th>
<th>Co(II)</th>
<th>Ni(II)</th>
<th>Cu(II)</th>
<th>Zn(II)</th>
<th>Cd(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PF</td>
<td>0.30(5.40)</td>
<td>0.21(5.40)</td>
<td>2.40(5.36)</td>
<td>2.11(6.83)</td>
<td>2.00(6.96)</td>
</tr>
<tr>
<td>PCF</td>
<td>1.00(5.40)</td>
<td>0.71(5.40)</td>
<td>1.92(4.86)</td>
<td>1.73(6.15)</td>
<td>2.23(6.61)</td>
</tr>
<tr>
<td>PAF</td>
<td>1.62(5.40)</td>
<td>1.53(5.40)</td>
<td>2.42(4.81)</td>
<td>2.41(6.21)</td>
<td>2.41(6.44)</td>
</tr>
<tr>
<td>PHF</td>
<td>1.20(5.50)</td>
<td>1.10(5.50)</td>
<td>2.41(4.89)</td>
<td>2.25(6.54)</td>
<td>2.40(6.74)</td>
</tr>
<tr>
<td>CHF</td>
<td>0.70(5.74)</td>
<td>0.35(5.74)</td>
<td>1.63(4.99)</td>
<td>1.82(6.79)</td>
<td>1.70(7.00)</td>
</tr>
</tbody>
</table>

μ (ionic strength)=0.1 M; temperature, 27±1°C; equilibration time: 96 h. Numerals in the parentheses indicate the pH values at which exchange capacities were measured.