Adsorption Isotherm Equation for Coexistence of Two Kinds of Metal Ions in Acidic Solution on Chelating Resin

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Adsorption isotherms for the coexistence of two metal ions (combinations of Zn^{2+}, Cd^{2+}, and Pb^{2+}) in acidic solutions on chelating resins were measured at 25 °C. They were analyzed in relation to the adsorption isotherm equation of a single metal ion, $Q=Q_{max}/(1+AC_M^{-\alpha}C_H^{\beta})$, as was reported in the preceding paper. It is found that the adsorption isotherms of two metal ions (i and j) in acidic solution on chelating resins can be generally expressed by the equation;

$$Q_{i,j}=Q_{max}/\{1+A_iC_i^{-\alpha_i}C_H^{\beta_i}(1+K_{i,j}C_j^{\alpha_j}C_H^{-\beta_j})\}$$

over wide ranges of concentrations of the metal ion, C, and the hydrogen ion, C_H (mol dm^{-3}). Where Q_i and $Q_{i,j}$ are the adsorption amounts (m mol/g-dry resin) of i metal ion in the absence and in the coexistence of j metal ion. Q_{max} is the maximum adsorption amount, α and β are parameters in the adsorption of single metal solution, A and K are correction factors, and subscripts i and j identifing i and j metal ions. The adsorption capacities of two metal ions in acidic solution can be obtained from the isotherms parameters A_i, α_i, α_j, β_i and β_j for an individual single metal ion and only one additional parameter $K_{i,j}$ is needed.

Chelating resins are used to separate a specific metal ion from many coexisting ions in water for removal and analysis of the ion. However, there are few studies on selective adsorption of metal ions on chelating resins under various conditions. In the previous papers,[1,2] the general adsorption isotherm equation and its parameter were given for many systems of chelating resin and single-component heavy metal ion in acidic solution, but no general isotherm equation has been reported for the competitive adsorption of three adsorbates, two metal ions and hydrogen ion. In this study, adsorption isotherms for coexistence of two metal ions (combinations of Zn^{2+}, Cd^{2+}, and Pb^{2+}) in acidic solution on several chelating resins, which have iminodiacetate groups, were measured. They were analyzed by using the adsorption isotherm equation of each single-component heavy metal ion to give a general isotherm equation for selective adsorption of a heavy metal ion in competition with another coexisting metal ion and hydrogen ion.

Experimental

The tested systems of chelating resin and metal ions are shown in Table 1. The chelating resins of UR-40, CR-10, and Dowex A-1 are products of Unitika Ltd., Mitsubishi Chemical Industry Ltd., and Dow Chemical Ltd., respectively. Their properties were described in the preceding paper.[2] The methods for the pretreatments of the resins and the batchwise adsorption tests were similar to those described in the previous paper.[1]

Solutions containing two metal nitrates of various concentrations ranging from 5×10^{-4} to 1×10^{-2} mol dm^{-3} and at constant pH were used for the adsorption tests. The analytical method for determining the metal ions was also similar to that described in the previous papers.[1,2]

TABLE 1. TESTED SYSTEMS OF CHELATING RESIN, METALS, AND pH

Resin	Metals	pH
UR-40	Cd^{2+}–Pb^{2+}	5.1, 3.6
CR-10	Zn^{2+}–Cd^{2+}	5.0, 3.6
CR-10	Zn^{2+}–Pb^{2+}	5.0, 3.6
A-1	Zn^{2+}–Pb^{2+}	5.0, 3.4

Results and Discussion

The adsorbed amount of single i metal ion in acidic solution, Q_i, can be given by the following equation reported in the previous paper.[1]

TABLE 2. PARAMETERS OF Eq. (1) FOR TESTED SYSTEMS

Resin	Metal	Q_{max}	A_i	α_i	β_i
UR-40	Cd^{2+}	2.0	24	0.86	1.0
UR-40	Pb^{2+}	2.0	5.0×10^{-2}	0.80	0.48
CR-10	Zn^{2+}	2.5	6.0	0.76	0.87
CR-10	Cd^{2+}	2.5	20	0.86	1.0
CR-10	Pb^{2+}	2.5	8.4×10^{-3}	0.94	0.46
A-1	Zn^{2+}	2.5	8.6	0.65	0.69
A-1	Pb^{2+}	2.5	9.0×10^{-2}	0.84	0.38

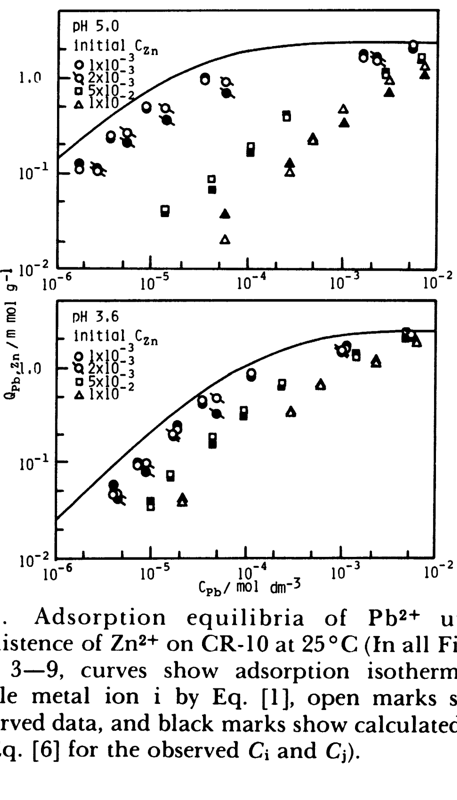

Fig. 1. Adsorption equilibria of Pb^{2+} under coexistence of Zn^{2+} on CR-10 at 25 °C (In all Figs. 1 and 3—9, curves show adsorption isotherms of single metal ion i by Eq. [1], open marks show observed data, and black marks show calculated $Q_{i,j}$ by Eq. [6] for the observed C_i and C_j).

$$Q_i = Q_{max}/(1+A_iC_i^{-\alpha_i}C_H^{\beta_i}) \tag{1}$$

Here, Q_{max} is the maximum adsorption amount which can be given by total ion-exchange capacity of the resin, and C_i and C_H are the concentrations of the i metal ion and hydrogen ion. α_i and β_i are parameters which indicate the degree of influences of C_i and C_H on Q_i. In other words, they show adsorbabilities of i metal ion and hydrogen ion, hence $A_iC_i^{-\alpha_i}C_H^{\beta_i}$ actually means an interfering factor for Q_i. The values of A_i, α_i, and β_i for all the tested systems of chelating resin and metal ion had been obtained in the preceding study.[2] They are listed again in Table 2 because they are needed for the analyses of the results in this study.

Adsorption equilibria of Pb^{2+} under the coexistence of Zn^{2+} on CR-10 at a pH of 5.0 and 3.6 are shown in Fig.1. The adsorbed amount of Pb^{2+} under the coexistence of Zn^{2+} in the acidic solution, $Q_{Pb,Zn}$, was smaller at higher initial concentration of Zn^{2+} and approached Q_{Pb} for a single Pb^{2+} solution at lower concentration of Zn^{2+}.

The interferences of the j metal ion and hydrogen ion to the adsorption of i metal ion were assumed to be represented by Eq. 2 as in the case of the adsorption of a single metal ion.

$$Q_{i,j} = Q_{max}/\{1+A_iC_i^{-\alpha_i}C_H^{\beta_i}(1+K_{i,j}C_j^{\gamma}C_H^{-\delta})\} \tag{2}$$

The interfering factor $K_{i,j}C_j^{\gamma}C_H^{-\delta}$ could be expressed by Eq. 3 from Eq. 2.

$$K_{i,j}C_j^{\gamma}C_H^{-\delta} = (Q_{max}-Q_{i,j})/Q_{i,j}A_iC_i^{-\alpha_i}C_H^{\beta_i} - 1 \tag{3}$$

Therefore, both logarithmic relationships between the values of the righthand side of Eq. 3 and C_j at a constant pH (C_H) and between the values of the righthand side of Eq. 3 and C_H at a constant C_j should be linear. For the adsorption of Pb^{2+} under the coexistence of Zn^{2+} at the constant pH, the former relationships were plotted on a log-log graph as shown in Fig. 2. Straight parallel lines with a slope, γ, of 0.76 were obtained. Also, the log-log plots of the latter relationship at fixed C_{Zn} for the same system showed straight lines with a slope, $-\delta$, of -0.87 as is also shown in Fig. 2. Therefore, the following equation can be obtained

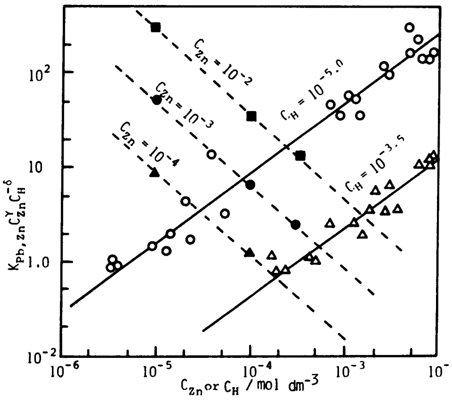

Fig. 2. Logarithmic plots of $K_{Pb,Zn}C_{Zn}^{\gamma}C_H^{-\delta}$ against C_{Zn} at constant C_H or against C_H at constant C_{Zn} for adsorption of Pb^{2+} on CR-10 under coexistence of Zn^{2+}.

for the system of CR-10, Pb^{2+} and Zn^{2+}.

$$Q_{Pb,Zn} = 2.5/\{1+8.4\times10^{-3}C_{Pb}^{-0.94}C_H^{0.46} \times(1+0.44C_{Zn}^{0.76}C_H^{-0.87})\} \tag{4}$$

The calculated values of $Q_{Pb,Zn}$ by Eq. 4 for the same C_{Pb} and C_{Zn} as the observed data were plotted also in the Fig. 1 as black marks, and they are approximately equal to the observed data as open marks. Consequently, the adsorption amount of Pb^{2+} under the coexistence of Zn^{2+} could be obtained by Eq. 4.

The values of γ=0.76 and δ=0.87 for this system were equal to the values of α_i and β_i for Zn^{2+} adsorption in the single solution on CR-10. Furthermore, the adsorption amount of Zn^{2+}, $Q_{Zn,Pb}$, for the same system could be given by Eq. 5.

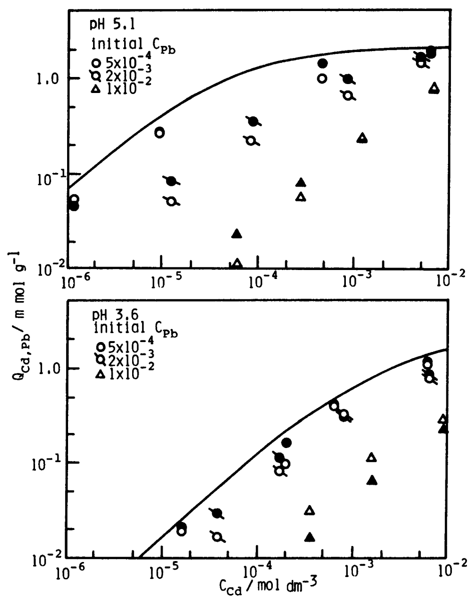

Fig. 3. Adsorption equilibria of Cd^{2+} under coexistence of Pb^{2+} on UR-40 at 25°C.

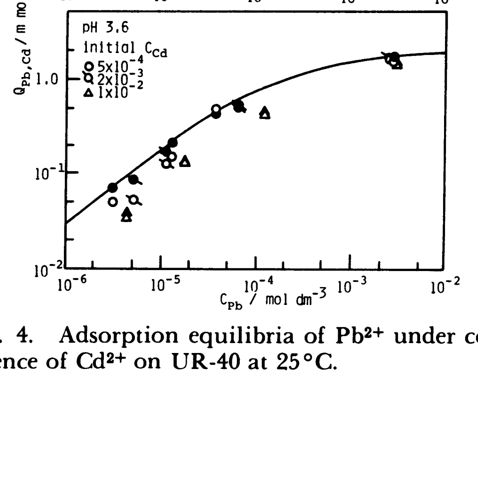

Fig. 4. Adsorption equilibria of Pb^{2+} under coexistence of Cd^{2+} on UR-40 at 25°C.

$$Q_{Zn,Pb} = 2.5/\{1+6.0C_{Zn}^{-0.78}C_{H}^{0.87}(1+50C_{Pb}^{0.94}C_{H}^{-0.46})\} \quad (5)$$

The values of γ=0.94 and δ=0.46 were also equal to the values of α_i and β_i for Pb^{2+} adsorption in the single solution on CR-10.

Therefore, the following equation seems to be valid over a wide concentration range for two metal ions and hydrogen ion.

$$Q_{i,j} = Q_{max}/\{1+A_iC_i^{-\alpha_i}C_H^{\beta_i}(1+K_{i,j}C_j^{\alpha_j}C_H^{-\beta_j})\} \quad (6)$$

For the other tested systems of chelating resin and metal ions, the calculated values of $Q_{i,j}$ by Eq. 6 are compared with the observed data in Figs. 3—9. In these figures, curves show the adsorption isotherms of a single i ion by Eq. 1, open marks show the observed data, and black marks show the calculated $Q_{i,j}$ for the observed C_i and C_j. The computed values of $K_{i,j}$ for all the system are shown in Table 3. Almost all the observed data for the various systems were closely equal to the calculated values over a wide range of conditions. The small deviations of a few data from the calculat-

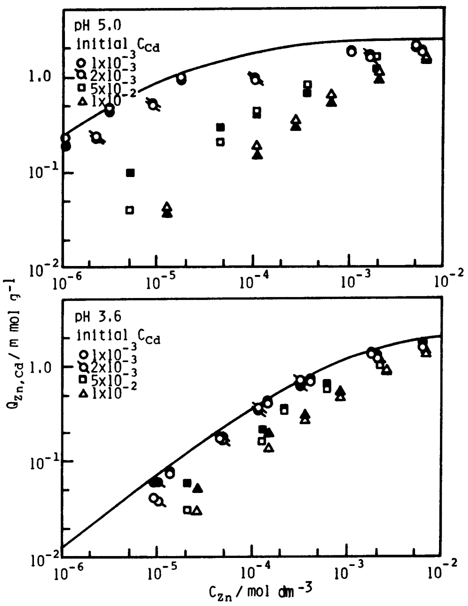

Fig. 5. Adsorption equilibria of Zn^{2+} under coexistence of Cd^{2+} on CR-10 at 25 °C.

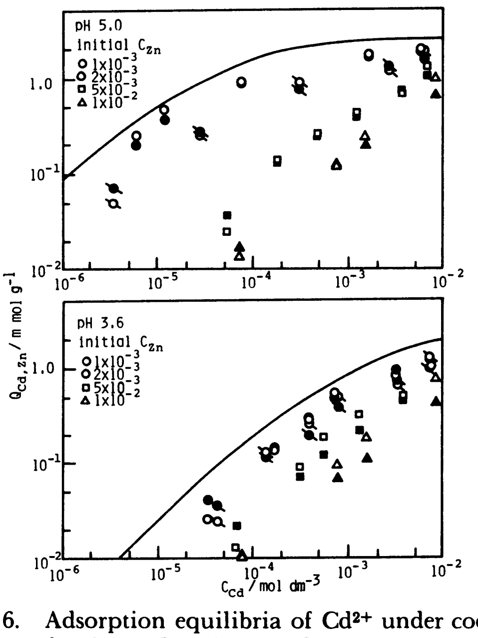

Fig. 6. Adsorption equilibria of Cd^{2+} under coexistence of Zn^{2+} on CR-10 at 25 °C.

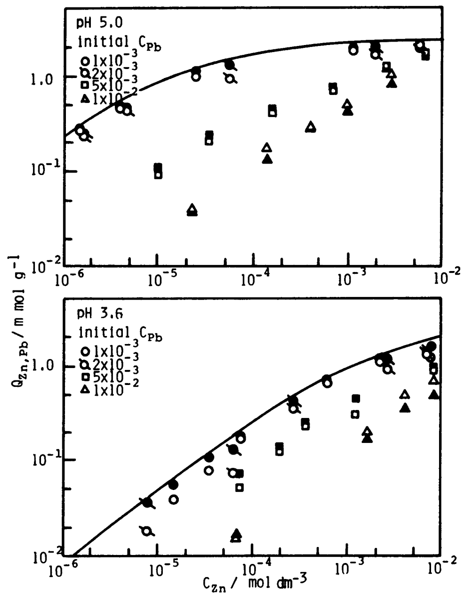

Fig. 7. Adsorption equilibria of Zn^{2+} under coexistence of Pb^{2+} on CR-10 at 25 °C.

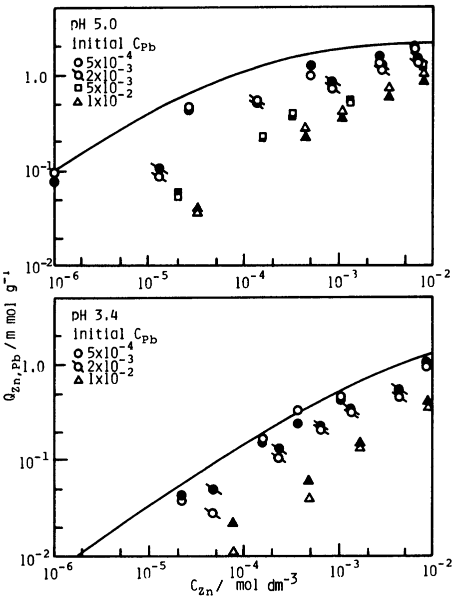

Fig. 8. Adsorption equilibria of Zn^{2+} under coexistence of Pb^{2+} on Dowex A-1 at 25 °C.

TABLE 3. PARAMETER $K_{i,j}$ OF Eq. (6) OBTAINED BY EXPERIMENTS

Resin	Metal i–j	$K_{i,j}$
UR-40	Cd^{2+}-Pb^{2+}	2.7×10^{-2}
	Pb^{2+}-Cd^{2+}	44
CR-10	Zn^{2+}-Cd^{2+}	0.47
	Cd^{2+}-Zn^{2+}	4.3×10^{-2}
	Zn^{2+}-Pb^{2+}	50
	Pb^{2+}-Zn^{2}	0.44
A-1	Zn^{2+}-Pb^{2+}	0.29
	Pb^{2+}-Zn^{2+}	18

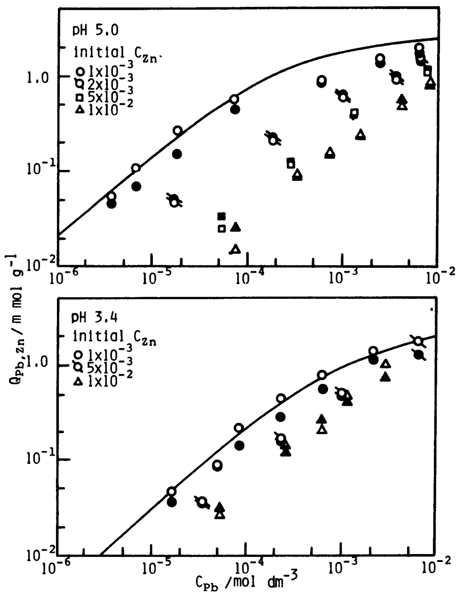

Fig. 9. Adsorption equilibria of Pb^{2+} under coexistence of Zn^{2+} on Dowex A-1 at 25 °C.

ed values will be due to errors of analysis of C_i and of the values of α and β. Consequently, it was confirmed that the selective adsorption isotherm of i ion under coexistence of j ion and hydrogen ion is given by Eq. 6 which contained only one additional correction parameter $K_{i,j}$ with the parameters of the adsorption isotherms for single i and j metal ions. The fact that the adsorption isotherm equation for dual metal ions could be generally expressed by application of the adsorption isotherm equation of single metal ion proves that those adsorption isotherm equations well describe adsorption phenomena on chelating resins.

References

1) K. Urano, V. Chanyasak, and N. Fujii, *J. Colloid Interface Sci.*, **82**, 251 (1981).

2) K. Urano, V. Chanyasak, and N. Fujii, *Bull. Chem. Soc. Japan*, **57**, 2055 (1984).