Effects of Functional Group Density in Styrene-Divinylbenzene Copolymer Phase and of Supporting Electrolyte Concentration in Aqueous Phase on Performance of Iminodiacetate-type Chelating Resin in Terms of Contribution of Ion-Exchange Mechanism

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The effects of the functional group density in the styrene-divinylbenzene copolymer phase and of the supporting electrolyte concentration in the aqueous phase on the performance of the iminodiacetate (IDA)-type chelating resin were studied in terms of contribution of an ion-exchange mechanism. High hydrophobicity of the resin having a low functional group density interfered with penetration of aqueous solutions into the resin phase to slow the acid-base reaction and the adsorption reaction. Uptake of the cation in the supporting electrolyte into the resin phase was clearly indicated in each of two acid dissociation reactions. The high concentration of the supporting electrolyte enhanced acid dissociation of the IDA group, and a singly deprotonated species interacting with the supporting electrolyte cation strongly interfered with adsorption by the ion-exchange mechanism, while only slightly interfering with adsorption by the complexation. Both the complexed and ion-exchanged species respectively involving two or more IDA groups were destabilized to reduce the adsorption capacity of the resin having the low functional group density.

Keywords Chelating resin, iminodiacetate, functional group density, supporting electrolyte concentration

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divalent metal ion. Only one study examined the effects of the IDA density of agarose-based resins on preconcentration and matrix elimination and suggested advantages of the low-density resin for removal of matrix elements.10

Such an ion exchange mechanism works for even sodium or potassium ion at a high concentration. The effects of the inert electrolyte concentration on the acid-base behaviors of IDA resins have been studied to a certain degree,11–14 while those on the metal adsorption behaviors having been little studied.15 This paper describes the effects of the density of IDA groups in the conventional PS-DVB resin as well as the effects of the supporting electrolyte concentration on the acid-base and metal adsorption reactions.

**Experimental**

**IDA resins**

The IDA resins of low exchange capacities were prepared by modifying a previous method.15 After swelling of a Merrifield resin (cross linking degree of 1%, Cl content of 1.8 mmol g⁻¹, 200–400 mesh) in toluene, 10-times excess of diethyl iminodiacetate (IDA-diEt) relative to the Cl content of the resin was added, and the suspension was refluxed for 2 days. The ester-type resin obtained was filtered off and was washed successively with acetone, ethanol, and water. The resin was then hydrolyzed by reflux in a 1.0 mol L⁻¹ NaOH aqueous ethanol solution for 2 days (IDA-1.3; hereinafter, digits after the resin name are expressed in terms of mmol g⁻¹). The same procedures using another Merrifield resin (cross linking degree of 2%, Cl content of 0.9 mmol g⁻¹, 100–200 mesh) with 10-times excess of and an equivalent amount of IDA-diEt respectively gave IDA-0.7 and IDA-0.3. In the case of IDA-0.3, hydrolysis was of and an equivalent amount of IDA-diEt respectively gave a third portion of each resin was equilibrated with a 0.5 mol L⁻¹ HNO₃ solution overnight, was filtered off, and was dried without washing (IDA-As). A second portion of each resin was equilibrated with a 1.0 mol L⁻¹ NaOH solution overnight, was filtered off, was washed with water, and was dried (IDA-Bs). A third portion of each resin was equilibrated with a 0.5 mol L⁻¹ NaOH solution overnight, was filtered off, was washed thoroughly with water, and was dried (IDA-Cs). A fourth portion of each resin was equilibrated with a 0.5 mol L⁻¹ NaOH solution overnight, was filtered off, and was dried without washing (IDA-Ds). The resulting resins were stored in a glove box kept at 25°C and at relative humidity of 50%. The results of elemental analysis and the densities of IDA groups (D idi / mmol g⁻¹) based on the nitrogen content and on the metal adsorption of the IDA-Cs form [(-LHNa) form as described below] are summarized in Table S1 (Supporting Information). The IR spectra of the resins were recorded by a KBr disk method.

**pH titration**

Respective suspensions of the IDA-Bs forms [(-LH₂) form as described below] of IDA-2.1, IDA-1.3, and IDA-0.7 (w g; total amount of IDA group in terms of mmol, TAₓ = D idi × w) in V mL of a supporting electrolyte solution (10⁻²⁰, 10⁻¹⁵, 10⁻¹⁰, 10⁻⁶, or 10⁻¹⁰ mol L⁻¹ NaNO₃) (an apparent IDA concentration, C idi /mol L⁻¹ = TAₓ/V) were potentiometrically titrated with a standard NaOH solution (C oH/mol L⁻¹) under nitrogen atmosphere in a water jacket thermostatted at 25°C. The pH-meter was calibrated in advance by a concentration scale, and the ionic product of water, K w, was experimentally determined for each reaction system; log(K w/mol L⁻²), C NaNO₃/mol L⁻¹: -14.0, 10⁻⁶, and 10⁻¹; -13.9, 10⁻¹⁰; -13.8, 10⁻⁴, and 10⁻¹. Three to twelve hours were required for the equilibration after addition of the NaOH solution to the respective suspensions of IDA-2.1 and IDA-1.3, and more than 20 h for the suspension of IDA-0.7. The average number of protons attached to IDA, n idi, was calculated by Eq. (1):

\[
n_{\text{ idi}} = 2 \times C_{\text{ L}} - C_{\text{ OH}} - (\text{[H}^+) - K_{\text{w}}(\text{H}^+))/C_{\text{ L}}.
\]

In contrast, the theoretical average number of protons attached to IDA, n th, is given by Eq. (2):

\[
n_{\text{ th}} = (1/K_{\text{a,2}} \times \text{[H}^+] + 2 \times 1/K_{\text{a,2}} \times \text{[H}^+]^2)/\left(1 + 1/K_{\text{a,2}} \times \text{[H}^+] + 1/K_{\text{a,1}} \times \text{[H}^+]^2\right)
\]

where \(K_{\text{a,1}}\) and \(K_{\text{a,2}}\) respectively denote first and second acid dissociation constants:

\[
K_{\text{a,1}} = ([\text{LH}^-][\text{H}^+])/[\text{L}]
\]

\[
K_{\text{a,2}} = ([\text{L}^2^-][\text{H}^+])/[\text{L}^-]
\]

Here, \(-\text{LH}^-\) and \(-\text{L}^2^-\) respectively include the species interacting with Na⁺ as a component of the supporting electrolyte, and the concentrations of such resin species are expressed in terms of mmol g⁻¹. The acid dissociation constants were optimized to give a minimum error square sum about n, U = \(\sum(n_{\text{ brid}} - n_{\text{ th}})^2\).

**Metal adsorption**

By taking into consideration the previous findings,14,25 nickel and calcium were examined respectively as a more reactive and a less reactive divalent metal ion, and indium and lanthanum respectively as a more reactive and a less reactive trivalent metal ion. Respective suspensions of the IDA-Cs of IDA-2.1 and IDA-1.3 in a series of solutions containing a metal ion (the total amount of which is twice that of IDA (TASₐ = Cₐ × V = 2 × TAₓ)) at various pH (in such a range that hydrolysis of a metal ion is negligible) and supporting electrolyte concentrations were shaken at 125 strokes/min and at 25°C for 2 days with regard to the divalent metal ion and for 3 days with regard to the trivalent metal ions. In the case of IDA-0.7, reproducible adsorption data could not be obtained, due to the low adsorption ability and the longer equilibration time. After equilibration, each of the supernatants was subjected to pH measurement and determination of the metal ion by AAS or ICP-AES, and the experimental adsorption capacity A C brid was calculated.

The adsorption of divalent metal ions to IDA resins is expressed by Eqs. (5) and (6):24,25

\[
\text{(-LH}^-\text{)} + \text{M}^{2+} = ([\text{-L}])\text{M} + 2\text{H}^+ ; \quad K_{\text{10}}
\]

\[
2\text{(-LH}^-\text{)} + \text{M}^{2+} = ([\text{-L}^2\text{-}]\text{M} + 2\text{H}^+ ; \quad K_{\text{12}}
\]

The mass balances with reference to the IDA group and the metal ion are respectively given by Eqs. (7) and (8):

\[
C_{\text{L}} = (m/V)\times([\text{-LH}^-] + [\text{-L}^-]) + ([\text{-L}]\text{M} + 2([\text{-L}^2\text{-}]\text{M})
\]

\[
C_{\text{M}} = (m/V)\times([\text{-L}])\text{M} + ([\text{-L}^2\text{-}]\text{M})
\]
The calculated adsorption capacity is given by Eq. (9):

$$AC_{\text{calc}} = [(–L)M] + [(–LH)2M] \quad (9)$$

The adsorption of trivalent metal ions is expressed by Eqs. (10) and (11):23

$$2(–LH2) + M^{3+} = [(–L)(–LH)M] + 3H^+; \quad K_{21} \quad (10)$$

$$3(–LH2) + M^{3+} = [(–LH)3M] + 3H^+; \quad K_{33} \quad (11)$$

The mass balances are given by Eqs. (12) and (13):

$$C_L = \left(\frac{m}{V}\right) \times \left([–LH2] + [–LH–] + [–L2–] + 2[(–L)(–LH)M] + 3[(–LH)3M]\right) \quad (12)$$

$$C_M = [M^{2+}] + \left(\frac{m}{V}\right) \times \left([(–L)(–LH)M] + [(–LH)3M]\right) \quad (13)$$

The calculated adsorption capacity is given by Eq. (14):

$$AC_{\text{calc}} = [(–L)(–LH)M] + [(–LH)3M] \quad (14)$$

The adsorption constants were optimized to give a minimum error square sum about $AC$, $U = \sum (AC_{\text{obsd}} – AC_{\text{calc}})^2$.

**Results and Discussion**

**IR examination in preparing IDA resins having low functional group densities**

Changes in IR spectrum accompanied by derivatization of two Merrifield resins to give IDA-1.3, IDA-0.7, and IDA-0.3 are shown in Fig. S1 (a – c) (Supporting Information). Both the two Merrifield resins had an absorption at around 1260 cm$^{-1}$ assigned to an H–C–Cl stretching;36 the resin containing more C–Cl groups to be derivatized had the higher intensity. After the derivatization with IDA-diEt, the H–C–Cl band disappeared and a new absorption appeared at around 1740 cm$^{-1}$ assigned to a C–O stretching of the ester groups in Fig. S1 (a, b). This indicates that the IDA-diEt group was introduced at a benzyl position. In contrast, both these two bands were observed in Fig. S1(c). This indicates that C–Cl groups were partly derivatized with IDA-diEt. After hydrolysis of the ester-types with 1.0 mol L$^{-1}$ NaOH in aqueous ethanol (v/v = 1), the band at around 1740 cm$^{-1}$ disappeared, and new bands at 1635 cm$^{-1}$ assignable to an antisymmetric stretching mode of COO$^-$ and at 1400 cm$^{-1}$ assignable to a symmetric stretching mode appeared in Fig. S1 (a,b). This indicates that the ester-types were hydrolyzed to give carboxylate-types with regard to IDA-1.3 and IDA-0.7. In contrast, hydrolysis for IDA-0.3 was not achieved by a 1.0 mol L$^{-1}$ aqueous ethanol solution of NaOH but required a 1.0 mol L$^{-1}$ tetrabutylammonium hydroxide in toluene (Fig. S1(c)).

**Characterization of four species at different protonation degrees by IR in solid state**

The IR spectra of the respective four resin forms were recorded for IDA-2.0, IDA-1.3, IDA-0.7, and IDA-0.3 (Fig. 1). The respective resin forms of IDA-2.0, IDA-1.3, and IDA-0.7 showed substantially the same spectra. The following assignments were used as benchmarks: (i) 1730 cm$^{-1}$ characteristic for –COOH, (ii) 1635 cm$^{-1}$ characteristic for free –COO$^-$, and (iii) 1590 cm$^{-1}$ characteristic for –COO$^–$Na$^+$ (Scheme S1, Supporting Information). The IDA-As showed strong absorption (i) together with a sharp strong band at 1380 cm$^{-1}$ due to NO$_3^–$ and weak absorption (ii). The resins contained (–LH$_3^+$,NO$_3^–$) as a major species and (–LH$_2$) as a minor one. The IDA-Bs showed both absorption (i) and (ii) of comparable strength. The resins contained (–LH$_2$) with one of two protons located on an amino nitrogen atom; i.e., zwitter ionic form. The IDA-Cs showed absorption (ii) and (iii) of comparable strength. The resins contained (–LHNa) with the proton located on the amino group; i.e., zwitter ionic form. The IDA-Ds showed only absorption (iii). The resins contained (–LNa$^2$).

In contrast, no spectral changes were observed for IDA-0.3 even after the contact with strong acids, strong bases, or metal ions. The most hydrophobic resin phase of IDA-0.3 expelled aqueous solutions, such that neither acid-base nor ion-exchange nor complexation reactions accompanied by elution of the tetrabutylammonium ion may have proceeded.

**Acid-base properties of IDA resins**

The $n$ values plotted against $–\log[H^+]$ for IDA-2.1, IDA-1.3, and IDA-0.7 at different concentrations of the supporting
electrolyte, NaNO₃, are shown in Fig. S2 (Supporting Information). The formation function of each IDA resin shifted to the lower pH region with an increase in the supporting electrolyte concentration. The acid dissociation constants evaluated as described in the experimental section are summarized in Table 1, while the literature values are shown in Table S2 (Supporting Information). Previous studies qualitatively suggested the higher acidities of IDA resins (smaller $pK_{a1}$ and $pK_{a2}$ values) at the higher supporting electrolyte concentration (Table S2). When the $pK_a$ values obtained in this study are plotted against log $C_{NaNO_3}$ (Fig. 2), linear relationships are observed with a slope of –1. It is impracticable to directly compare the equilibrium constants at different ionic strengths in the strict sense. The actual changes in acid dissociation constants are, however, much larger than the changes expected from changes in activity coefficients, and the slope clearly indicates uptake of one Na⁺ ion into the resin phase from the aqueous phase by deprotonation (characteristic of ion-exchange), and (-LH⁻) and (-L²⁻) in the resin phase are to be expressed as (-LHNa⁺) and (-LNa₂), respectively.

The large difference between $pK_{a1}$ and $pK_{a2}$ values is attributed to the difference in the positions of the relevant protons as described above, irrespective of the functional group density; one proton on the carboxylate oxygen atom and one proton on the amino nitrogen atom in (-LH₂⁻). The $pK_{a1}$ values of the IDA resins are appreciably larger than the corresponding value of IDA (2.21) in an aqueous solution, since Na⁺ is unlikely to penetrate into the hydrophobic IDA resins; this trend is more remarkable for the resin of the lower IDA density. In contrast, the $pK_{a2}$ values of the IDA resins are slightly larger than the corresponding value (8.90) in an aqueous solution. Replacement of the first proton by Na⁺ may reduce the hydrophobicity of the resin phase and reduce the difficulty in uptake of Na⁺ in association with dissociation of the second proton.

### Table 1 Effects of supporting electrolyte concentration and functional group density on acid dissociation constants of IDA resins

<table>
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<tr>
<th>$\log C_{NaNO_3}$</th>
<th>IDA-2.1</th>
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<th>IDA-0.7</th>
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<td>$pK_{a1}$</td>
<td>$pK_{a2}$</td>
<td>$pK_{a1}$</td>
</tr>
<tr>
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<td>5.6</td>
<td>11.2</td>
<td>5.4</td>
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<td>4.9</td>
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<td>4.7</td>
</tr>
<tr>
<td>−0.5</td>
<td>4.1</td>
<td>9.6</td>
<td>4.2</td>
</tr>
<tr>
<td>0.0</td>
<td>3.6</td>
<td>9.1</td>
<td>3.9</td>
</tr>
</tbody>
</table>

a. ±0.1.
b. Not determined.

### Fig. 2 Effects of supporting electrolyte concentration on acid dissociation constants. Resin: IDA-2.1 (●, ○); IDA-1.3 (●, □); IDA-0.7 (■, □). Broken lines indicate $pK_a$ values of IDA in aqueous solutions.

### Fig. 3 Adsorption curves of divalent metal ions to IDA resins. M²⁺: (a,b) Ni²⁺, (c,d) Ca²⁺. Resin: (a,c) IDA-2.1, (b,d) IDA-0.7. Black solid line, calculated curves using the constants in Table 2; red broken line, contribution of [(-LH)₂M]; red dotted line, contribution of [(-LM)]. The horizontal line at 50% corresponds to the unique formation of [(-LH₂)M].
10^{-2} mol L^{-1} are shown in Fig. 3 with the adsorption capacity normalized by the density of IDA group, AC_{obsd}/D_{IDA}, as ordinate. The data for Ni^{2+} showed single sigmoidal curves in relatively narrow pH ranges, while the data for Ca^{2+} showed two-step sigmoidal curves in wider pH ranges. The adsorption constants were determined as described in the experimental section and are summarized in Table 2. The adsorption curves calculated by using the obtained constants and the contributions of two species are also shown in Fig. 3. The species [(–L)M] involving only one IDA group is responsible for adsorption of both the metal ions on both the resins. In contrast, the species [(–LH)2M] formed in an acidic medium contributes more to adsorption of the less reactive Ca^{2+} ion. Because a multiple-interacting species (M:IDA=1:2) is more favorable and the stability of [(–LH)2M] relative to [(–LM)] is higher for the resin of the higher IDA density, the species [(–LH)2M] is formed in a wider pH range on IDA-2.1 than on IDA-0.7.

The adsorption curves of In^{3+} and La^{3+} to IDA-2.1 and IDA-0.7 are shown in Fig. 4. The adsorption curves of both the metal ions to IDA-2.1 are spread over wider pH ranges than those expected for complexation only and suggest contribution of the ion-exchange mechanism. In contrast, the adsorption curve to IDA-0.7 was negligible for In^{3+} and reached only up to 33% for La^{3+}. The adsorption constants similarly evaluated are included in Table 2, and the calculated curves and the contributions of two species by use of these constants are shown in Fig. 4. With respect to adsorption of the trivalent metal ions, only multiple-interacting species (M:LI=1:2 and 1:3) are relevant to the adsorption, unlike the divalent metal ions. The complexed species [(–L)(–LH)M] contributes to the adsorption of both In^{3+} and La^{3+} on IDA-2.1 but not on IDA-0.7. With regard to [(–L)(–L)H]M, the doubly deprotonated IDA (–L2–) is expected to strongly attract the metal ions within the shell of an IDA unit. The second and singly deprotonated IDA (–LH–) may reach the complexed metal center in the resin of the high IDA density but not in the resin of the low IDA density. The ion-exchanged species [(–LH)2M] may contribute to the adsorption of both In^{3+} and La^{3+} on IDA-2.1, while contributing to the adsorption of only La^{3+} but not to the adsorption of In^{3+} on IDA-0.7 of the lower IDA density. The reason for such a difference is not clear at this stage.

**Effects of supporting electrolyte concentration on adsorption of divalent metal ions**

The adsorption curves of Ni^{2+} and Ca^{2+} to IDA-2.1 at the supporting electrolyte concentrations of 10^{-2} and 1 mol L^{-1} are shown in Fig. 5. The relative adsorption decreased with an increase in supporting electrolyte concentration including 10^{-2} mol L^{-1} (Fig. 3), and the trend is more marked for Ca^{2+}. The equilibrium was similarly analyzed. The optimized constants are summarized in Table 2, and the calculated curves and the contributions of the respective species including [(–LH)Na] and [(–LNa)2] are shown in Fig. 5. The adsorption constants are substantially independent of the supporting electrolyte concentration as shown in Table 2. A remarkable change in relative adsorption of Ca is attributed to the difference in extent of formation of [(–LH)Na]. The abundance of [(–LH)Na] at −log[H^{+}] around 6 is 0, 15, and 70%, and the abundance of [(–LH)Ca] is 50, 42 and 15% at the supporting electrolyte concentrations of 10^{-2}, 10^{-4}, and 1 mol L^{-1}, respectively. Thus,
the increase in the supporting electrolyte concentration enhances the acid dissociation or the ion-exchange with Na\textsuperscript{+}, and the resulting species (–LHNa) interferes with the adsorption by ion-exchange.

Conclusions

The higher hydrophobicity of the resin having the lower functional group density interfered with hydrolysis of a precursor ester as found for IDA-0.3 or slowed the acid-base and adsorption reactions to reach equilibrium as found for IDA-0.7. Uptake of the cation in the supporting electrolyte in each of two acid dissociation reactions was clearly indicated. Thus, the high concentration of the supporting electrolyte such as 1 mol L\textsuperscript{-1} enhances acid dissociation of the IDA group, and the resulting singly deprotonated species (–LH\textsuperscript{−}) strongly interferes with the adsorption by the ion-pair mechanism but not the adsorption by complexation. Both the complexed and ion-exchanged species respectively involving two or more IDA groups are destabilized to reduce the adsorption ability of a low density resin (IDA-1.3) compared with the conventional resin (IDA-2.1).

Acknowledgements

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Supporting Information

Additional tables (properties of resins, literature values of pK\textsubscript{a}), additional scheme (IR band assignment of IDA resins), and additional figures (IR change in derivatization, formation function of IDA resins). This material is available free of charge on the Web at http://www.jsac.or.jp/analsci/.

References