

Hydration of Polymer Complexes with Iminodiacetate-Type Chelating Resin

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(Received September 6, 2001)

Hydration of polymer complexes of divalent and trivalent metal ions with an iminodiacetate (IDA)-type chelating resin (-LNa_2) was studied. The hydration numbers of [(-$LH)_2M^{II}$] for Ca^{2+} and [(-$LH)_3M^{III}$] for Y^{3+} and La^{3+}, which are practically the same as those of the respective aqua ions, indicate simple electrostatic interactions between the carboxylates of monoprotonated species of iminodiacetate, (-LH)$^-$, and hydrated metal ions. In contrast, an appreciably smaller hydration number of [(-$LH)_3M^{III}$] for Sc^{3+} than that of the aqua ion suggests involvement of the carboxylates in the coordination sphere. The difference in their interaction modes is discussed.

Adsorption to chelating resins is widely used for the separation and preconcentration of metal ions. Although the stability constants of metal complexes with monomeric ligands corresponding to pendant groups are useful to estimate the adsorption behaviors of chelating resins, some deviation from such estimations is actually observed on occasions. Recently, the reason for the deviation of the adsorption to an iminodiacetate (IDA)-type chelating resin (-LNa_2) was explained quantitatively by the difference in contribution of the auxiliary adsorption species. The species of [(-$LH)_2M^{II}$] enhances the adsorption of Ca^{2+} and Cd^{2+} relative to other divalent metal ions, such as Cu^{2+} and Ni^{2+}, exclusively forming [(-L)M^{II}].[1] Similarly, the species of [(-$LH)_3M^{III}$] enhances the adsorption of Sc^{3+}, Y^{3+} and La^{3+} relative to other trivalent metal ions, such as Al^{3+}, Ga^{3+}, In^{3+}, and Fe^{3+}, exclusively forming [(-L)(-LH)M^{III}].[2] A corresponding species of [(-$LH)_4M^{IV}$] was also suggested in the adsorption of Th^{4+}.[3]

Although the stoichiometry and stability of the adsorbed species are established, the structures of relevant species in the resin phase, including the hydration behaviors, are not well elucidated. Schmuckler et. al. demonstrated that the polymer complex of Cu^{2+} with an IDA-type resin contains three water molecules per metal ion by elemental analysis.[4] Heitner-Wirguin et. al. showed that formation of ion-pairs, $[(-LH_3)^+]_2$-$[MCl_4]^{2-}$ (M^{2+}: Cu^{2+}, Co^{2+}), is responsible for the adsorption from concentrated HCl solutions, while complexation with carboxylates is responsible for the adsorption from neutral solutions, as studied by visible absorption spectroscopy and ESR.[5,6] Reedijk et. al. concluded that the iminodiacetate group coordinates as a tridentate ligand and that the coordination is completed by either water molecules or by carboxylate oxygen atoms from excess neighboring iminodiacetate groups, [(-L)-$M(O)_3$].[7]

The object of this work was to clarify whether a singly protonated iminodiacetate species, (-LH)$^-$, actually coordinates to metal ions through carboxylates or is just located close to hydrated metal ions to neutralize the electric charge, by IR spectroscopy and by the hydration number of the polymer complexes in the resin phase.

Experimental

Reagents. The IDA resin, Amberlite IRC-718 (Rohm and Haas; particle size of 0.40–0.56 mm, Na^+-form) as received and the H^+-form converted by an acid were used; it was confirmed that the original Na^+-form and another Na^+-form reconverted from the H^+-form by an alkali showed the same performances. The polymer complexes with divalent and trivalent metal ions were prepared according to the literature: [(-L)M^{II}] for Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+} and Ca^{2+}; [(-$LH)_2M^{II}$] for Ca^{2+}; [(-L)(-LH)M^{III}] and [(-$LH)_3$-M^{III}] for Sc^{3+}, Y^{3+} and La^{3+}; only one species could be exclusively and quantitatively formed for these metal ions by pH control.[1,2] To evaluate the properties of a polystyrene–divinylbenzene matrix, XAD 4 (Rohm and Haas; particle size of 0.35–0.55 mm) was also subjected to measurement.

Measurement. Thermogravimetric analysis was performed using TG8101D and TG8110D (Thermal Analysis System-300, Rigaku Denki). A glove box equipped with a digital Karl-Fischer titrator (AQ-6, Hiranuma), a balance, a digital thermo/hygrometer, an electric fan, and an electric heater, was used for the determination of water. The temperature was thermostatted at 25 °C, while the humidity was controlled with a suitable desiccant and aqueous solutions of known vapor pressure.

In the determination of water by the Karl-Fischer (K-F) method, a waiting time of three minutes before the start of electrolysis was required for the extraction of water from the resin into an electrolytic solution. Under these conditions, the water content (W), which is expressed by the mass-ratio of water to a resin, did not depend on the sample mass.

The adsorption capacities (C/ mmol g^{-1}) of -LH_2 and -LNa_2 dried over P_2O_5 were determined as follows: the resins were shaken with a solution containing an excess amount of Cu^{2+}. After equilibration and separation, Cu^{2+} was desorbed by an acid. The Cu^{2+} concentrations in the supernatant and in the desorbing solution were determined.

Results

Hydration and Adsorption Capacities of -LH_2 and -LNa_2. The XAD and two forms (-LH_2 and -LNa_2) of IDA resins were dried under ambient conditions, crushed ($<$ 100 mesh), and subjected to thermal analysis up to 250 °C. The XAD resin did not show any reaction within this temperature range, while both IDA resins showed one endothermic reaction centered at around 50 °C and one exothermic reaction at $>$ 150 °C. The IR spectra of the IDA resins taken out of the apparatus at 120 and 200 °C indicated that these correspond to the dehydration and decomposition (decarboxylation) reactions, respectively. The percent weight loss by the dehydration was not reproducible due to the variations in temperature and humidity on the sampling (-4 to -7% for -LH_2 and -5 to -12% for -LNa_2). It was, however, concluded that water molecules were not adsorbed in the polystyrene-divinylbenzene matrix but on the functional groups of iminodiacetate.

The change in mass of these resins in granular forms was iteratively measured as a function of relative humidity (RH) at 25 °C over a period of several months. The mass relative to the mass at the driest condition, RM, is plotted against RH in Fig. 1. The XAD resin showed no change at RH $<$ 50%, while the IDA resins showed slightly concave increases in mass; the change of -LNa_2 was almost twice that of -LH_2. We could not find any stable and definite composition in terms of the hydration Since no hysteresis effects were observed, hydration and dehydration are reversible processes.

The dynamic aspects of the hydration of the IDA resins at 25 °C and at RH of 45% were followed by the increase in mass of the resins, which had been dehydrated over P_2O_5 (Fig. 2). Irrespective of the particle size of the resins, -LH_2 required one day to reach the hydration equilibria. On the other hand, the hydration rate of -LNa_2 depended on the particle size; the ground resin adsorbed water faster than the granular one.

The dynamic aspects of the dehydration over P_2O_5 were also followed by the K-F method. The water content (W) gradually decreased and became constant after one day for -LH_2 and after three days for -LNa_2: the minimum value was 1.47% for -LH_2 and 2.35% for -LNa_2. The adsorption capacities (C) of the resins thus obtained were determined by Cu^{2+}-uptake: 2.19 mmol g^{-1} for -LH_2 and 1.99 mmol g^{-1} for -LNa_2.

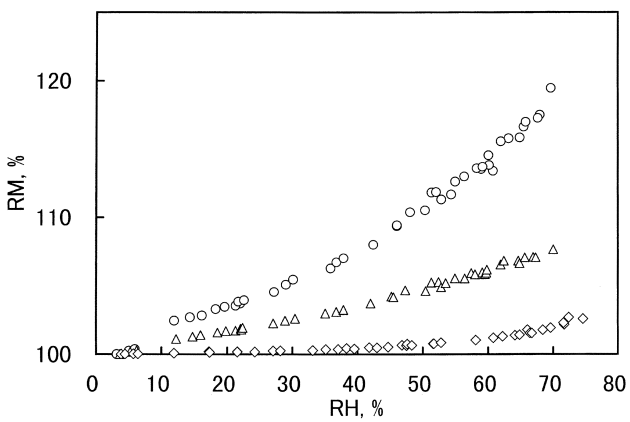

Fig. 1. Relative mass of resins as a function of relative humidity. 25 °C. Resin: -LNa_2 (○); -LH_2 (△); XAD (◇).

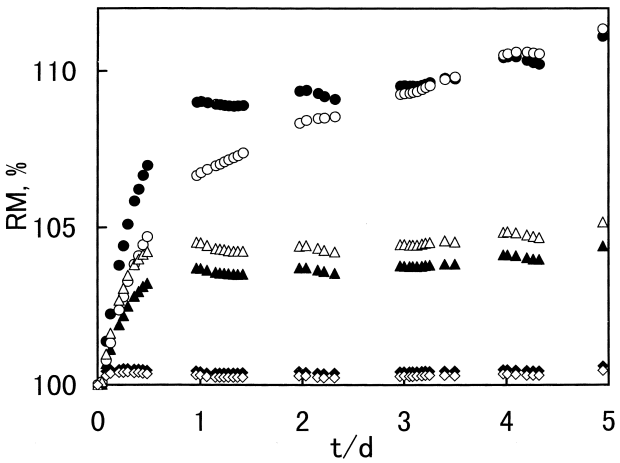

Fig. 2. Time course for hydration of resins. 25 °C. RH: 40%. Resin: -LNa_2 (○,●); -LH_2 (△,▲); XAD (◇,◆). Particle size: granular (○,△,◇); ground (●,▲,◆).

The hydration number (n, average number of water molecules bound to one iminodiacetate group), obtained by the relation of $n = W/(18\times C)$, was 0.37 for -LH_2 and 0.66 for -LNa_2. Provided that X denotes a hypothetical formula weight for [one iminodiacetate dianion + an n-benzyl group + a mean polymer matrix], stoichiometric consideration deduces the following relations for the adsorption capacities of two resins:

$$1/(X + 2\times1 + 0.37\times18) = 2.19\times10^{-3},$$
$$1/(X + 2\times23 + 0.66\times18) = 1.99\times10^{-3}.$$

Consistent values for X (448 and 445) obtained from two resins indicate the validity of this consideration. The actual adsorption capacities, especially of -LNa_2, are seriously affected by RH as shown in Fig. 1.

Hydration of Polymer Complexes. The polymer complexes were dried under ambient conditions and were subjected to thermal analysis and K-F titration. All the complexes underwent endothermic dehydration reactions at similar temperatures as -LH_2 and -LNa_2. The mass of the polymer complexes was hardly affected by RH, and its reduction was much more reproducible than that of -LNa_2 and well agreed with the water content determined by the K-F method.

The water content of a polymer complex of a metal ion M (atomic weight Y), having a general formula of $[(\text{-L})_a\text{-}(\text{H})_b\text{M}(\text{H}_2\text{O})_n]$, is expressed by

$$W = n\times18/(a\times X + b\times1 + Y + n\times18).$$

Thus, the n value is obtained by

$$n = W\times(a\times X + b\times1 + Y)/18(1-W).$$

Representative data are shown in Table 1, and the results are summarized in Table 2.

Infrared Spectra of Polymer Complexes. The wavenumbers of the carbonyl stretching bands observed for polymer complexes are summarized in Table 3. The absorption of

Table 1. Representative Data in the Determination of Hydration Number of Polymer Complexes

Complex/mg	Water/μg	Water/%	*n*
	[-LCa]		
0.9	107.4	11.9	3.7
0.6	71.4	11.9	3.7
0.8	83.2	10.4	3.1
1.2	120.1	10.0	3.0
0.8	86.5	10.8	3.3
0.7	71.7	10.2	3.1
1.1	122.7	11.2	3.4
	[(-LH)$_2$Ca]		
0.7	71.7	10.2	5.9
0.7	68.8	9.8	5.7
0.6	61.4	10.2	5.9
0.4	40.9	10.2	5.9
	[(-L)(-LH)Sc]		
0.6	55.9	9.3	5.4
0.7	62.8	9.0	5.1
1.0	91.8	9.2	5.3
1.2	113.9	9.5	5.5
0.8	75.9	9.5	5.5
1.2	117.3	9.8	5.7
	[(-LH)$_3$Sc]		
1.0	51.2	5.1	4.2
1.0	51.0	5.1	4.2
1.0	51.7	5.2	4.2

Table 2. Hydration Number of Polymer Complexes with IDA Resin

Metal ion	Hydration number			Ionic radius[c]
	Polymer complex[a]		Aqua ion[b]	pm
	[-LM^{II}]	[(-LH)$_2$M^{II}]		
Ni^{2+}	5.2 ± 0.3(7)	—[d]	6	69
Cu^{2+}	3.65 ± 0.3(7)	—[d]	4 + 2	73
Zn^{2+}	4.0 ± 0.3(6)	—[d]	6	74
Cd^{2+}	3.4 ± 0.2(7)	—[d]	6	95
Ca^{2+}	3.3 ± 0.3(7)	5.9 ± 0.1(4)	6–7	100
	[(-L)(-LH)M^{III}]	[(-LH)$_3$M^{III}]		
Sc^{3+}	5.4 ± 0.2(6)	4.2 ± 0.1(3)	—[e]	75
Y^{3+}	7.0 ± 0.3(7)	7.2 ± 0.2(6)	8	90
La^{3+}	4.8 ± 0.1(5)	8.0 ± 0.2(5)	8–9	103

a) Number of data in parentheses; b) Hydration number of aqua ions determined by scattering methods[8]; c) Ionic radius for hexa-coordination in pm[9]; d) Not measurable because of their minor contribution to the adsorption; e) Not reported.

-LNa$_2$ at 1590 cm^{-1} was found for these polymer complexes containing the (-L)$^{2-}$ species, such as [(-L)M^{II}] and [(-L)(-LH)M^{III}]. The wavenumber was shifted by 30–40 cm^{-1} for the complexes with metal ions of smaller atomic weights and higher affinities, such as Cu^{2+} and Sc^{3+}, while being unchanged for the complexes with metal ions of larger atomic weights, such as Cd^{2+}, Y^{3+} and La^{3+}, or of lower affinities like Ca^{2+}.

Table 3. Characteristic IR Band (cm^{-1}) of Polymer Complexes with IDA Resin

Metal ion	Polymer complex		
H^+	[-LNa$_2$]	[-LHNa]	[-LH$_2$]
	1590	1620	1620, 1720
	[-LM^{II}]	[(-LH)$_2$M^{II}]	
Cu^{2+}	1620	—[a]	
Cd^{2+}	1590	—[a]	
Ca^{2+}	1590	1620	
	[(-L)(-LH)M^{III}]	[(-LH)$_3$M^{III}]	
Sc^{3+}	1630	1640	
Y^{3+}	1600	1620	
La^{3+}	1600	1620	

a) Not measurable because of minor contribution to the adsorption.

The [-LHNa] resin did not show any band characteristic of carboxylic acids but a band characteristic of carboxylates, shifted to 1620 cm^{-1} (Table 3); this indicates the protonation at an imino nitrogen atom. The IR spectra of the polymer complexes containing only (-LH)$^-$ as an iminodiacetate species, like [(-LH)$_2$M^{II}] and [(-LH)$_3$M^{III}], were similar to that of [-LHNa]. This indicates that the interaction of (-LH)$^-$ with metal ions, if any, occurs only through carboxylates. The wavenumber was shifted by 20 cm^{-1} for [(-LH)$_3$M^{III}] of Sc^{3+}.

The [-LH$_2$] resin showed another band at 1720 cm^{-1} as well as 1620 cm^{-1}; this is characteristic of carboxylic acids with hydrogen-bonding.

Discussion

Structures of Polymer Complexes. The hydration numbers of [(-L)M^{II}] for Cu^{2+}, Zn^{2+}, Cd^{2+}, and Ca^{2+} range from 3 to 4, which seems reasonable by taking into account the hexacoordination of these metal ions and a denticity of three for iminodiacetate; less than one water molecule may be adsorbed. The hydration numbers of [(-L)(-LH)M^{III}] for Sc^{3+} and La^{3+}, which are around 5, agree with greater coordination numbers of these trivalent metal ions, compared with divalent metal ions. The reason for the appreciably higher values of the complexes with Ni^{2+} and Y^{3+} is not clear.

The hydration numbers of [(-LH)$_2$M^{II}] for Ca^{2+} and of [(-LH)$_3$M^{III}] for Sc^{3+} and La^{3+} are much greater and rather close to the hydration numbers of aqua ions of the respective metals. Moreover, the IR spectra of these species are practically the same as that of [-LHNa]. These results indicate that carboxylates of (-LH)$^-$ do not strongly interact with central metal ions but are just located close to the hydrated metal ions. In contrast, the hydration number of [(-LH)$_3$M^{III}] for Y^{3+} is around 4, which is appreciably smaller than that of the aqua ion. The IR spectrum showed an appreciable shift. These suggest the involvement of carboxylates in the coordination sphere of a rather small and highly charged cation. This agrees well with the result that the adsorption constant of [(-LH)$_3$M^{III}] for Sc^{3+} is much larger than those for Y^{3+} and La^{3+}; log K_{33} (= [(-LH)$_3$M^{III}][H$^+$]^3/[M^{3+}][-LH$_2$]^3): −0.74 for Sc^{3+}, −4.50 for Y^{3+}, −4.51 for La^{3+}.[2] Such a striking difference is reasonably

ascribed to the difference in affinity of each metal ion to carboxylate: $\log K_1$ ($= [M^{III}(CH_3COO)^{2+}]/[M^{3+}][CH_3COO^-]$) for the acetato complex at 25 °C and at an ionic strength of 0.1 mol dm^{-3}: 3.48 for Sc^{3+}, 1.68 for Y^{3+}, 1.82 for La^{3+}, 0.53 for Ca^{2+}.[10]

Recently, the hydration number of the polymer complexes of Eu^{3+} with strongly acidic cation-exchange resins [SCR], its linear analogue of poly(4-styrenesulfonic acid) [PSA], weakly acidic cation-exchange resins [WCR], and its linear analogue of poly(acrylic acid) [PAA] were studied by time-resolved fluorescence spectroscopy.[11] In Eu^{3+}–WCR and Eu^{3+}–PAA systems, 5.5–6.5 out of 9 water molecules are expelled between pH 4–9, due to the complexation by carboxylates, and the hydration numbers range 3.5–2.5. In Eu^{3+}–SCR and Eu^{3+}–PSA systems, on the other hand, practically 0 and only 1 water molecule is respectively expelled, and the hydration numbers range 9–8. Although the monoprotonated iminodiacetate species of ($-LH^-$) can be considered to be a kind of WCR, the hydration state of $[(-LH)_3M^{III}]$ for La^{3+} is rather close to those of Eu^{3+}–SCR and Eu^{3+}–PSA systems. This may be explained by the difference in flexibility of the polymer matrix: polystyrene-divinylbenzene for SCR, PSA and IDA resin and polyethylene for WCR and PAA.

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