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Adsorption of Metal Ions to Surface-Template Resins Prepared with Amphiphilic Styrene Monomers Bearing Amino Carboxylic Acid

Yoshifumi Koide,* Keigo Tsujimoto, Hideto Shosenji, Mizuo Maeda,† and Makoto Takagi†

Department of Applied Chemistry, Faculty of Engineering, Kumamoto University, Kurokami, Kumamoto 860

†Department of Chemical Science and Technology, Faculty of Engineering, Kyushu University, Hakozaki, Fukuoka 812

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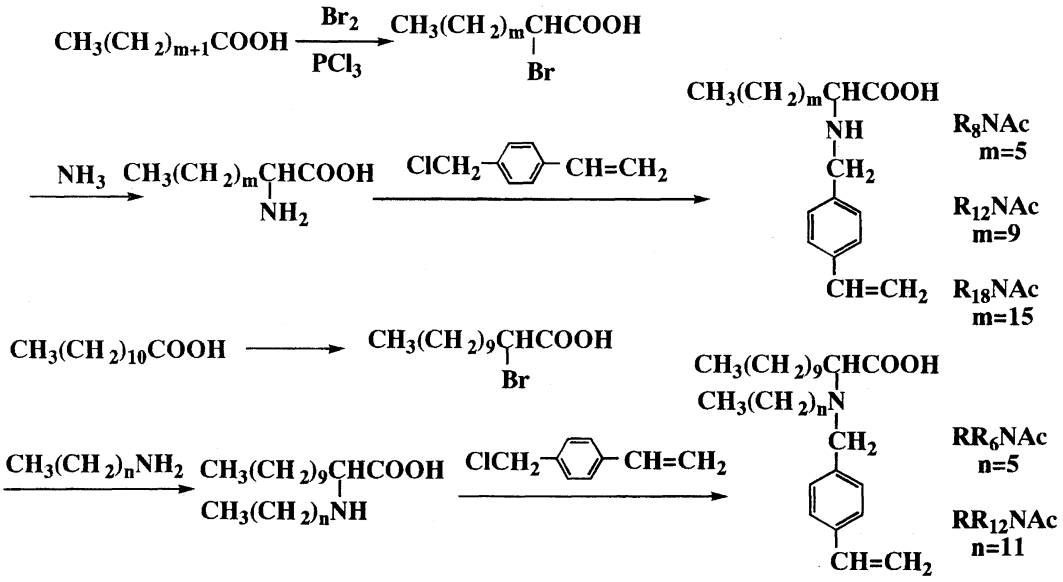
Monomer-type functional surfactants, 2-(*p*-vinylbenzylamino)alkanoic acid (**R_nNAc**) and *N*,*N*-dialkyl derivatives (**RR_nNAc**), have been used as both a ligand and an emulsifier for the preparation of surface-template resins. The surfactants adsorbed at the toluene–water interface and emulsified divinylbenzene–styrene in a Cu^{2+} or Zn^{2+} solution. Emulsion polymerization using a $K_2S_2O_8$ initiator (80 °C) or by irradiation with γ-rays gave fine particles of 200—800 nm in diameter. Metal-imprinted resins prepared with **R_nNAc** and **RR_nNAc** showed a high adsorptive capacity for the metal ion (surface-template effect). Cu-imprinted resins prepared with **R_8NAc** were 2.69-times as effective for Cu^{2+} in competitive sorption from a Cu^{2+}–Zn^{2+} mixture and Zn-imprinted resins were 1.84-times as effective for Zn^{2+}, compared with unimprinted resins. Because of the great emulsifying power, metal-imprinted resins prepared with **R_8NAc** showed the most metal-selective adsorption and the largest capacity among resins prepared with **R_nNAc** and **RR_nNAc**.

The molecular-imprinting technique[1—3] has been noted for selective recoveries of specific molecules.[4—8] Host monomers, with which the guest molecules are combined once, are chemically solidified with matrix monomers by cross-linking polymerization; then, an inner template (molecule-imprinted resins) is formed in the polymer of matrix monomers after the guest molecules are removed. However, the host–guest complexes are required to be soluble in the matrix monomers, and the resins of the inner template must be ground and sieved to produce finely divided resins for separation.

Some surface-template resins have been developed in order to improve such a problem.[9—15] A vinyl monomer-type functional surfactant (emulsifier) capable of binding metal ions orients at the matrix monomers–water interface and emulsify these solutions, so that the surfactant is polymerized with the matrix monomers in the form of the template of a metal complex. A functional surfactant, 10-(*p*-vinylphenyl)decanoic acid (**Rac**), had been applied to surface-template resins,[16] which made the surface-imprinting easy and reliable. The **Rac** at the matrix monomers–water interface became the sites of the template by emulsion polymerization. However, the carboxyl group on the side of **Rac** must be movable because of being a long way (alkyl-chain length) from the fixing vinyl group on the other side, at which the **Rac** is chemically solidified with the matrix monomers. Moreover, the location (depth) at the surface would be affected by the surface activity (emulsification). Emulsification is enhanced by an efficient orientation of a surfactant at the interface. Therefore, an increase in the surface-template effect (selectivity of metal ions) is considered by preparing a resin with a surfactant bearing a vinyl group nearly at the ligand, and by heightening the emulsification upon polymerization. A surfactant of suitable hydrophilic lipophilic balance (HLB) would form a stable emulsion. In the present study, monomer-type surfactants having a wide range of HLB, 2-(*p*-vinylbenzylamino)alkanoic acid (**R_nNAc**) and alkylaminododecanoic acid derivatives (**RR_nNAc**), have been applied to the host monomers as both a ligand and an emulsifier in the preparation of surface-template resins, and having been discussed concerning the relation between the surface-template effect and the emulsification (surface activity) or position of the vinyl group at nearly the amino carboxyl group. The amino carboxyl group in the surfactants would combine with Cu^{2+} or Zn^{2+} at a ratio of 2 : 1 ($M{\cdot}L_2$), and the metal-imprinted resin should have the template of a four-coordinate square plane for Cu^{2+}, and that of a four-coordinate tetrahedron for Zn^{2+}. Template resins prepared with a functional surfactant must show high selectivity. **Rac** had been applied to a surface-imprinting technique[16] and a monomer-type surfactant had been used as an emulsifier in polymerization.[17] However, the preparation of surface-template resins with a functional surfactant adjusted to a suitable HLB has not yet been tried.

Experimental

Functional Surfactants: Monomer-type surfactants (**R_nNAc** and **RR_nNAc**) were prepared through an analogous procedure to that of the synthesis of *N*-(*p*-vinylbenzyl)iminodiacetic acid by Allen et al.[18—20] Alkanoic acids brominated by Br_2 in the presence of PCl_3 were derived to 2-aminoalkanoic acid or 2-alkylaminoalkanoic acid by a reaction with ammonia or alkylamine, and then finally derived to **R_nNAc** or **RR_nNAc** by a reaction with *p*-chloromethylstyrene (Scheme 1). **R_nNAc** IR (KBr) ν_{C-H} 2850 cm^{-1},



Scheme 1. Preparations of $\mathbf{R}_n\mathbf{NAc}$ and $\mathbf{RR}_n\mathbf{NAc}$.

$\nu_{C=O}$ 1590 cm^{-1}, $\nu_{C=C}$ 980, 900 cm^{-1}, ν_{C-H} 810 cm^{-1}. ^{1}H NMR (CD_3OD, NaOD, TMS) δ = 0.9 (3H, $-CH_3$), 1.1—1.8 (10H, 18H, 30H, $-CH_2-$), 3.2 (1H, >CHN–), 3.5—3.9 (2H, $-NCH_2-$), 5.2 (1H, *trans* CH=CAr), 5.7 (1H, *cis* CH=CAr), 6.7 (1H, C=CHAr), 7.3—7.7 (4H, ArH). **R_8NAc** Yield 24%, Mp 206.1—207.1 °C. Found: C, 74.16; H, 8.92; N, 4.62%. Calcd for $C_{18}H_{25}NO_2$: C, 74.18; H, 9.09; N, 5.09%. **R_{12}NAc** Yield 28%, Mp 199.0—200.8 °C. Found: C, 75.68; H, 9.74; N, 4.17%. Calcd for $C_{21}H_{33}NO_2$: C, 76.09; H, 10.03; N, 4.23%. **R_{18}NAc** Yield 30%, Mp 172.0—175.0 °C. Found: C, 77.76; H, 10.65; N, 3.23%. Calcd for $C_{27}H_{45}NO_2$: C, 78.07; H, 10.84; N, 3.37%. **RR_nNAc** IR (KBr) ν_{C-H} 2850, $\nu_{C=O}$ 1590, $\nu_{C=C}$ 980, 900, ν_{C-H} 790 cm^{-1}. ^{1}H NMR (CD_3OD, TMS) δ = 0.9 (6H, $-CH_3$), 1.1—1.8 (26H, 38H, $-CH_2-$), 3.0 (2H, $-CH_2N<$), 3.6 (1H, >CHN–), 4.3 (2H, $-NCH_2Ar$), 5.3 (1H, *trans* CH=CAr), 5.8 (1H, *cis* CH=CAr), 6.7 (1H, C=CHAr), 7.2—7.7 (4H, ArH). **RR_6NAc** Yield 17%, viscous oil. Found: C, 76.95; H, 10.97; N, 3.17%. Calcd for $C_{27}H_{45}NO_2 \cdot 1/2H_2O$: C, 76.42; H, 10.82; N, 3.29%. **RR_{12}NAc** Yield 14%, viscous oil. Found: C, 78.61; H, 11.48; N, 2.64%. Calcd for $C_{33}H_{57}NO_2 \cdot 1/3H_2O$: C, 78.41; H, 11.41; N, 2.77%.

Preparation of Metal-Imprinted Resins: Cu-imprinted resins were obtained by emulsion polymerization using 0.5—1.7 mol% $\mathbf{R}_n\mathbf{NAc}$ or $\mathbf{RR}_n\mathbf{NAc}$ per matrix monomers {= divinylbenzene (DVB) + styrene (St) + 5.4×10^{-4} mol $\mathbf{R}_n\mathbf{NAc}$ or $\mathbf{RR}_n\mathbf{NAc}$}. $\mathbf{R}_n\mathbf{NAc}$ or $\mathbf{RR}_n\mathbf{NAc}$ dissolved in a DVB–St (10 : 1) mixture was added to 60 cm^3 of a $Cu(NO_3)_2$ solution (half or twice as much as the surfactant) containing 1 wt% poly(vinyl alcohol) (n = ca. 1500, Wako Pure Chemicals); then, a mixture of the solutions at pH 5.5 of the isoelectric point of $\mathbf{R}_n\mathbf{NAc}$ or $\mathbf{RR}_n\mathbf{NAc}$ was heated up to 80 °C with stirring at a rate of 300—400 rpm under a nitrogen atmosphere. By adding 1—2 wt% potassium peroxodisulfate ($K_2S_2O_8$) of an initiator to the mixture, the mixing monomers in the emulsion were gradually polymerized and a white polymer (resin) was precipitated upon heating for 6 h. The resins were separated by filtration using a sintered-glass filter (No.5), washed with hot water (90 °C), and finally treated with 5 mol dm^{-3} HCl to remove the Cu of the template from the resins. Zn-imprinted resins and unimprinted resins were also prepared by similar procedures in the presence of $Zn(NO_3)_2$ and in its absence, respectively. Furthermore, metal-imprinted resins were prepared at 0 °C by the irradiation of 1.25×10^4 C kg^{-1} ^{60}Co γ-rays. The use of the ^{60}Co irradiation facility has been made possible by the Inter-University Program for the Common Use JAERI Facilities.

Surface-Template Resin: The adsorption of metal ions to resins was evaluated in a batch operation. The resins prepared with $\mathbf{R}_n\mathbf{NAc}$ or $\mathbf{RR}_n\mathbf{NAc}$ were added to a sample solution of Cu^{2+} or Zn^{2+} (pH 4—6), and then suspended in a metal solution by stirring for 2 h. Since the metal ions adsorb onto the resins, the resins were filtered and then treated with 1 mol dm^{-3} HCl for the determination of the metal ions. After being washed with water, the resins were reused for the next adsorption.

Results and Discussion

Surface Activity: The surface tension was measured with a Wilhelmy surface-tension balance. $\mathbf{R}_n\mathbf{NAc}$ and $\mathbf{RR}_n\mathbf{NAc}$ lowered the surface tension of the alkali solutions and emulsified toluene in water by stirring. The order of the emulsifying ability for a mixture of toluene–water (1 : 1) was $\mathbf{R_{18}NAc} > \mathbf{R_{12}NAc} > \mathbf{R_8NAc} > \mathbf{RR_6NAc} = \mathbf{RR_{12}NAc}$ at 15 °C, and that for a toluene–Cu^{2+} solution at pH 5.5 of the isoelectric point (surfactants: 5.0×10^{-2} mol dm^{-3}, Cu^{2+}: 1.0×10^{-2} mol dm^{-3}) was $\mathbf{R_8NAc} > \mathbf{R_{12}NAc} > \mathbf{R_{18}NAc} > \mathbf{RR_6NAc} = \mathbf{RR_{12}NAc}$. Emulsification is correlated with the interfacial tension. The interfacial tension at the critical micelle concentration (γ_{cmc}), measured with a Du Nouy-type surface tension meter, is shown in Table 1. $\mathbf{R_{18}NAc}$ showed the lowest interfacial tension between toluene and water among these surfactants, while $\mathbf{R_8NAc}$ of a shorter side chain showed the lowest tension at the toluene–Cu^{2+} solution interface.

Complexation: A ligand of amino carboxylic acid should combine with metal ions. Complexations of $\mathbf{R}_n\mathbf{NAc}$ and $\mathbf{RR}_n\mathbf{NAc}$ were confirmed by the extraction of Cu^{2+} with toluene and by back extraction into a 1 mol dm^{-3} HCl. The extraction of Cu^{2+} is shown in Fig. 1. The Cu^{2+} was extracted with the surfactants with the surfactants at a pH above 4. The complexation would be only slightly effective for $\mathbf{R}_n\mathbf{NAc}$ at a

Table 1. Lowering of Interfacial Tension by $\mathbf{R}_n$NAc and $\mathbf{RR}_n$NAc

Surfactant	Liquid (L)[a] of toluene/L interface	γ_{cmc} / mN m^{-1}	cmc[b] / mmol dm^{-3}
R$_8$NAc	Water	4.3	0.22
	Cu^{2+} solution	3.7	0.14
R$_{12}$NAc	Water	3.7	0.20
R$_{18}$NAc	Water	3.5	0.18
	Cu^{2+} solution	4.0	0.32
RR$_6$NAc	Water	5.0	0.32
	Cu^{2+} solution	5.0	0.50
RR$_{12}$NAc	Water	5.0	0.35
	Cu^{2+} solution	5.0	0.63

a) Cu^{2+} solution : 1×10^{-2} mol dm^{-3}, pH 5.5, 15 °C. b) Critical micelle concentration.

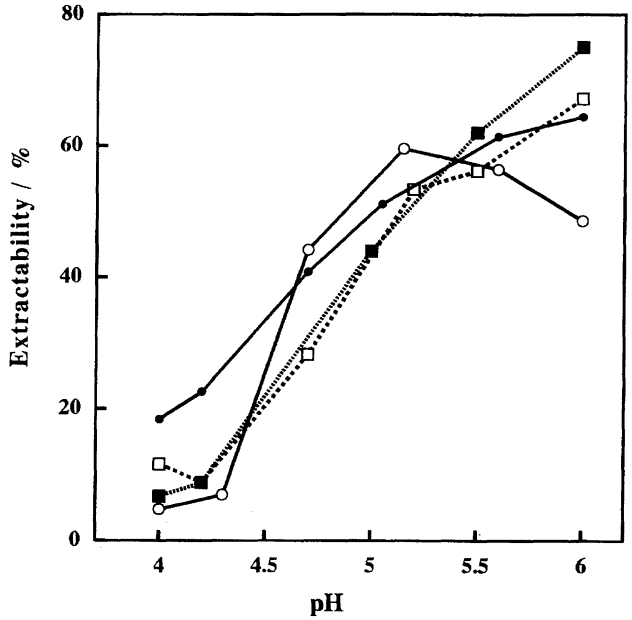


Fig. 1. Extraction of Cu^{2+} with $\mathbf{R}_n$NAc and $\mathbf{RR}_n$NAc. [$\mathbf{R}_n$NAc] and [$\mathbf{RR}_n$NAc] = 1×10^{-4} mol dm^{-3} in toluene, [Cu^{2+}] = 5×10^{-5} mol dm^{-3} in water. ○:**R$_8$NAc**, ●:**R$_{18}$NAc**, □:**RR$_6$NAc**, ■:**RR$_{12}$NAc**.

pH below 5.2, because of the smaller steric hindrance and for $\mathbf{RR}_n$NAc at pH 6.0, because of the larger partition coefficient based on the dialkyl chains. Zn^{2+} was also extracted with the surfactants at a pH above 5.

Emulsion Polymerization: The adsorptive efficiency of the surfactant at the interface between the monomers and metal solution is dominated by the HLB, and the adsorptive orientation affects on the emulsification. Therefore, the surface of resins prepared by emulsion polymerization must be characterized by the surface activity of the surfactant, and the location (depth) of the template at the surface would affect the surface-template effect (selectivity for the target metal ions). **Rac**, as an emulsifier capable of polymerizing and combining with metal ion, brought about a stable emulsion with agitation at 300—400 rpm, and particles of 200—300 nm in diameter were yielded by emulsion polymerization.[16] Since emulsification is correlated with the orientation of the surfactant, the functional surfactants of a wide range of HLB ($\mathbf{R}_n$NAc and $\mathbf{RR}_n$NAc) were examined for the preparation of more efficient resins.

Cu- or Zn-imprinted resins prepared at 0.5—1.7 mol% **R$_{12}$NAc** (per the mixture of DVB–St–**R$_{12}$NAc**) were hard and highly yielded, compared with those at 0.25 mol%. The preparations of resins at 1.7 mol% $\mathbf{R}_n$NAc and $\mathbf{RR}_n$NAc are shown in Table 2. Although Zn-imprinted resins and unimprinted resins were 52—76% yields, the Cu-imprinted resins were slightly lower in yield (28—62%). The resins prepared by the irradiation of γ-rays were more different regarding yields, e.g.; Cu-imprinted resins prepared at twice as much Cu^{2+} as the surfactant were obtained only slightly. The resulting radicals by means of an initiator (or γ-ray) would become inactivate due to the Cu^{2+} of a high reduction potential ($\cdot OSO_3^- + Cu^{2+} \longrightarrow SO_4^{2-} + Cu^+$).

The resins after desorption of the metal ions with 5 mol dm^{-3} HCl were spherical, and the size was 200—800 nm in diameter, the diameter of which was about the same as that prepared by the usual method of emulsion polymerization.[21] However, the blue-green color of the resins means that the complexes were formed in the inner part of the resin, in addition to complexation at the surface. Therefore, the ratio of the ligands ($\mathbf{R}_n$NAc and $\mathbf{RR}_n$NAc) at the surface to those in the inner was estimated from the distribution of the metal ions. The ligands at the surface were taken as the amount of adsorbed metal ions, because of their complexations with the metal ions, while the inner ligands were taken as the amounts of metal ions dissolved in the acidic solution after decomposition of the resins with a mixture of concd HCl–HNO_3–H_2SO_4 (1 : 1 : 1). The number of inner Cu of the resins prepared with **R$_8$NAc** was less than that in resins prepared with **R$_{18}$NAc** or $\mathbf{RR}_n$NAc. Therefore, the inner **R$_8$NAc** must be fewer in number than the inner **R$_{18}$NAc** or $\mathbf{RR}_n$NAc; also, the ratio of the superficial surfactant to the inner one was in the following order: **R$_8$NAc** > **R$_{18}$NAc** > **RR$_6$NAc** > **RR$_{12}$NAc**. Although the Zn-imprinted resins showed a lower surface ratio because of poor complexation (less distribution in the resins), the relation between the surface ratio and the HLB of the surfactant was similar to that for Cu-imprinted resins. Since the hydrophilic **R$_8$NAc** orients more toward the water than do the others, complexation would be effective at the surface of the resin, but not so much at the inner part. The irradiation of γ-rays was also effective for preparing metal-imprinted resins.

The total surfactant at the surface and in the inner part of the resin can be estimated by the added surfactant (5.4×10^{-4} mol), because of the lipophilicity to the resin; also, the sum of both the Cu at the surface and at the inner part can be calculated from the data in Table 2 {= amount ratio of both Cu (mol (g-resin)$^{-1}$) times the amount of resin (= the added monomers time the yield)}. Both Cu at the surface and at the inner part prepared with half as much Cu^{2+} as the surfactant ($\mathbf{R}_n$NAc or $\mathbf{RR}_n$NAc) (1 : 0.5), totaled about half of the surfactant, while both Cu, prepared with twice as much Cu^{2+} to the surfactant (1 : 2), totaled about equal to that of

Table 2. Preparation of Resins with $\mathbf{R}_n$NAc or $\mathbf{RR}_n$NAc[a)]

Surfactant	Imprinting metal ion	Yield %	Color of resins	Amounts of metal: Inner mol g^{-1}	Amounts of metal: Surface mol g^{-1}	Ratio of surface %
Surfactant : Metal ion = 1 : 0.5						
	Cu(II)	48	Yellow-green	4.0×10^{-5}	5.7×10^{-5}	59
R_8NAc	Zn(II)	52	White	2.0	1.0	33
	None	63	White	—	—	—
	Cu(II)	48	Blue-green	7.5	3.3	31 (24*)
R_{18}NAc	Zn(II)	68	White	2.9	0.4	12 (2*)
	None	63	White	—	—	—
	Cu(II)	42	Green	9.6	4.4	31 (42*)
RR_6NAc	Zn(II)	61	White	4.5	0.5	10 (24*)
	None	63	White	—	—	—
	Cu(II)	58	Green	7.8	3.0	28 (35*)
RR_{12}NAc	Zn(II)	68	White	4.6	0.5	10 (18*)
	None	65	White	—	—	—
Surfactant : Metal ion = 1 : 2						
R_8NAc	Cu(II)	52	Yellow-green	5.8	20.7	78
	Zn(II)	76	White	3.0	2.0	40
R_{18}NAc	Cu(II)	30	Blue-green	10.1	27.5	73
	Zn(II)	61	White	2.8	1.0	26 (77*)
RR_6NAc	Cu(II)	28	Yellow-blue	12.6	30.4	71
	Zn(II)	70	White	4.3	1.2	22 (56*)
RR_{12}NAc	Cu(II)	62	Gray-green	8.0	13.5	63
	Zn(II)	65	White	4.3	0.7	14 (30*)

a) Conditions of preparation: surfactant 5.4×10^{-4} mol, DVB 3.76 g (2.8×10^{-2} mol), St 0.30 g (2.8×10^{-3} mol); metal solution 4.5×10^{-3} or 1.8×10^{-2} mol dm^{-3}, 60 cm^3, pH 5.5; initiator $K_2S_2O_8$, stirring at 80 °C for 6 h. * Surface of the resins prepared by irradiation of γ-ray.

the surfactant. These ratios indicate the formation of the Cu·L_2 complex at half as much Cu^{2+} as the surfactant and the formation of the Cu·L complex at twice as much. The composition of complex can be calculated from the stability constant for the alanine–Cu^{2+} complex (pK_1 2.34, pK_2 9.87, log K_{CuL} 8.18, log K_{CuL_2} 6.65);[22)] i.e. Cu·L_2 is 70—100% at half as much Cu^{2+} as the ligand (1 : 0.5) and Cu·L is 45—54% at twice (1 : 2). Therefore, the compositions of the Cu·L_2 and Cu·L complexes in the resins were about consistent with those of the main complexes calculated from the stability constant.

Adsorption of Metal Ion: The adsorption of metal ions to the surface-template resins attained equilibrium in about 1 h. The adsorption for Cu^{2+} and Zn^{2+} at pH 4—6 is shown in Fig. 2. All of the curves were high on the side of neutral pH because of the greater complexation. Although the Cu^{2+} was effectively adsorbed on Cu-imprinted resins prepared with **R_{12}NAc**, the amount of Zn^{2+} was small on the Cu-imprinted resins (middle in Fig. 2). However, the Zn^{2+} was only slightly effectively adsorbed on Zn-imprinted resins (upper), compared with the adsorption to unimprinted resins (lower). The Cu^{2+}- and Zn^{2+}-adsorption must be enhanced by the template effect at the surface of the resin.

The adsorption of metal ions varied with the kind of surfactants in the resin. Fig. 3 shows the relation between the adsorption of Cu^{2+} and the four kinds of resins prepared with the surfactants of different HLB (**R_nNAc** and **RR_nNAc**). The resins in a smaller ratio of the metal ion to the resin show less adsorption, but a greater template effect, because of the unsaturated sites of the surface-template. In order to examine the template effect, the adsorption sites at the surface were set to be still unsaturated under the adsorptive condition (Cu^{2+}: 5×10^{-4} mol dm^{-3}, 5 cm^3; resins: 0.1 g), since the adsorptive amount per g-resin increased at a higher ratio of the initial amount of Cu^{2+} to the resin (cf. the ratio of 25 mmol (g-resin)$^{-1}$ with the 500 mmol (g-resin)$^{-1}$ in Fig. 2). Although these resins showed a high adsorptive capacity for Cu^{2+} (Cu-imprinted resins > Zn-imprinted resins > unimprinted resins) as well as resins prepared with **R_{12}NAc**, the surface-template effect (selectivity) did not increase further. The adsorption of Cu^{2+} to Cu-imprinted resins, prepared with **R_nNAc** and **RR_nNAc**, was 1.2—2.3 times higher at a ratio of 1 : 0.5 (left in Fig. 3), and 1.3—2.5 times higher at a ratio of 1 : 2 than that on unimprinted resins (right). The adsorption of Cu^{2+} on Zn-imprinted resins was also slightly higher. The most effective (highest) adsorption of Cu^{2+} was obtained by Cu-imprinted resins prepared with **R_8NAc**: 0.42×10^{-5} mol (g-resin)$^{-1}$ (1.5 times) at a ratio of 1 : 0.5 and 0.40×10^{-5} mol (g-resin)$^{-1}$ (1.4 times) at a ratio of 1 : 2. The efficiencies of the surfactants in the resin

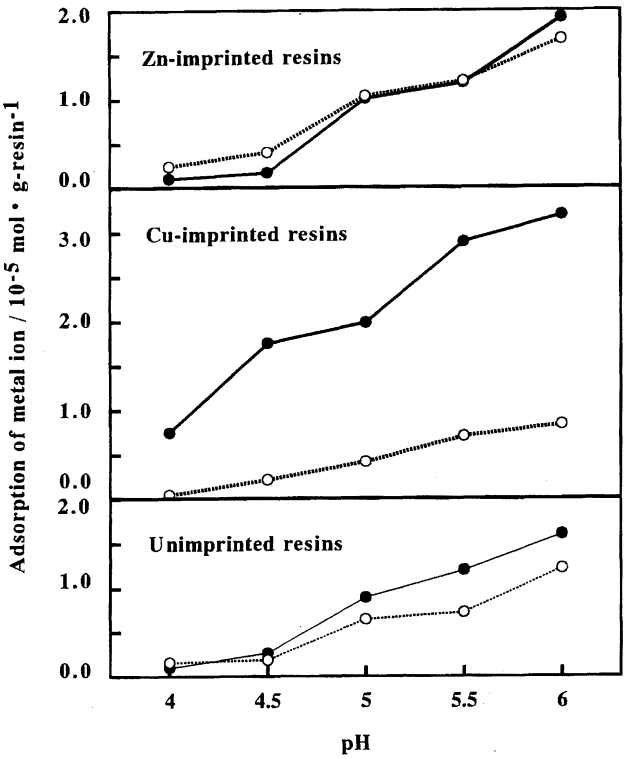


Fig. 2. Adsorption of metal ions on the metal-imprinted resins prepared with $\mathbf{R_{12}NAc}$. $[Cu^{2+}] = [Zn^{2+}] = 5\times10^{-4}$ mol dm^{-3}, 50 cm^3. Resin 50 mg. ●:Cu^{2+}, ○:Zn^{2+}.

were as $\mathbf{R_8NAc} > \mathbf{R_{18}NAc} > \mathbf{RR_6NAc} > \mathbf{RR_{12}NAc}$, and the order was consistent with emulsification in the presence of Cu^{2+} and with complexation at pH 4.8—5.2 (Fig. 1). Thus, Cu^{2+} was adsorbed on Cu-imprinted resins more than on the Zn-imprinted resins or on unimprinted resins. The imprinting sites are specified during emulsion polymerization. The Cu template must be a structure of a four-coordinate square plane. However, the imprinting sites were different in numbers due to the kind of metal complexes because of the difference in the stability constant (the selectivity may be reflected by their numbers). Therefore, the template effect was further confirmed by the adsorption of Zn^{2+} to these resins.

The adsorption for Zn^{2+} was similar to that for Cu^{2+}. Zn^{2+} was effectively adsorbed on metal-imprinted resins prepared at half as much metal ions as the surfactant (1 : 0.5), except for $\mathbf{RR_{12}NAc}$, as shown in Fig. 4 (left). The adsorptive capacity was 1.7—2.7 (mean: 1.97) times higher than that of the unimprinted resins and the most effective (highest) adsorption of Zn^{2+} was 0.34×10^{-5} mol (g-resin)$^{-1}$ (2.3 times) on the Zn-imprinted resins prepared with $\mathbf{R_8NAc}$. Therefore, the Zn-imprinted resins adsorbed the Zn^{2+} preferentially. The selective adsorption for the Zn^{2+} indicates the surface-template effect based on the formation of the Zn-template of a four-coordinate tetrahedral structure, in spite of the question concerning the different numbers of imprinting sites. On the other hand, the adsorption of Zn^{2+} to the Zn-imprinted resins prepared at a ratio of 1 : 2 was 1.0—1.3 (mean: 1.19) times higher than that to the unimprinted resins, while the adsorption on the Cu-imprinted resins was 1.4—2.0 times higher (right in Fig. 4). The unsaturated metal complex (M·L) at a ratio of 1 : 2 (metal) is not the template of the metal ions. Therefore, the difference in the adsorption would be reflected by the number of ligands in the surfactant at the surface, which were formed according to their stability constants (Cu-imprinted resins > Zn-imprinted resins > unimprinted resins). The Zn^{2+} of lower stability constant was less adsorbed on these resins, compared with the Cu^{2+}. Nevertheless, a slightly higher adsorption of Zn^{2+} (1.13 times) was observed for resins prepared with surface-active $\mathbf{R_8NAc}$.

Resins Prepared by Irradiation of γ-Ray: The orientation of the surfactant during polymerization must be disordered by raising the temperature. Therefore, the resins were prepared at 0 °C by irradiation of γ-rays in order to minimize the disorder of the surfactant orientation. Surface-template

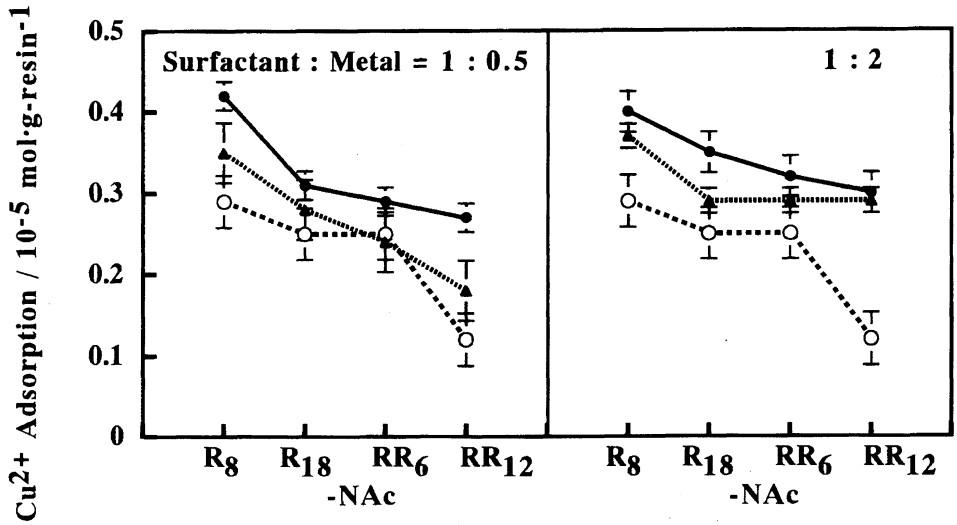


Fig. 3. Adsorption for Cu^{2+}. Initial concn of Cu^{2+}:5×10^{-4} mol dm^{-3}, 5 cm^3, pH 6.0, 25 °C. Resin 0.1 g. ●:Adsorption on Cu-imprinted resins, ▲:Adsorption on Zn-imprinted resins, ○: Adsorption on unimprinted resins.

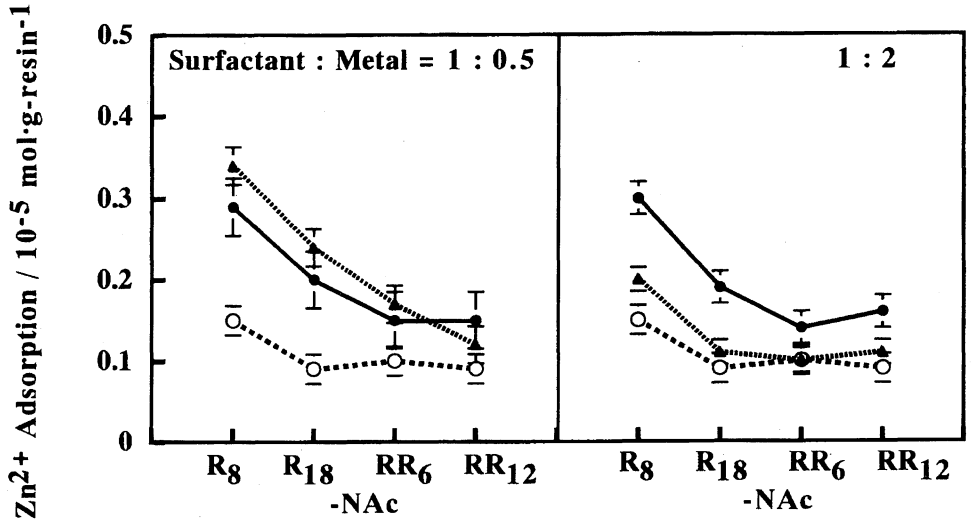


Fig. 4. Adsorption for Zn^{2+}. Initial concn of Zn^{2+}:5×10^{-4} mol dm^{-3}, 5 cm^3, pH 6.0, 25 °C. Resin 0.1 g. ●:Adsorption on Cu-imprinted resins, ▲:Adsorption on Zn-imprinted resins, ○: Adsorption on unimprinted resins.

resins were obtained at greater than 90% yield on being irradiated with 1.25×10^4 C kg^{-1} γ-rays, but not in the presence of twice as much Cu^{2+} as the surfactant. The particles of the resins were slightly larger (below 500 nm in diameter), because of the lack of agitation and the high viscosity at 0 °C. The adsorption of Cu^{2+} and Zn^{2+} to the resins is given in Table 3. The resins showed a high adsorptive capacity for the metal ions of the template, and selective adsorption was observed from a mixture of Cu^{2+} and Zn^{2+}. However, the efficiency of the adsorption was not as high as that on the resins prepared by the initiator of $K_2S_2O_8$. The surfactants would not orient effectively at the interface, since the solubilities at 0 °C were too poor.

Selective Recovery from a Metal Ions Mixture: Since the target metal ions were adsorbed onto the metal-imprinted resins, the selective adsorption from a mixture of Cu^{2+} and Zn^{2+} was examined. The unimprinted resins adsorb the Cu^{2+} more than the Zn^{2+} because of the bigger stability constant of the ligand (chelate effect of amino carboxylic acid). The competitive sorption (Cu^{2+}/Zn^{2+}) on the metal-imprinted resins was compared with that on the unimprinted resins; the relative selectivities to the selectivity of the unimprinted resins $\{(Cu^{2+}/Zn^{2+})_{metal\text{-}imp}/(Cu^{2+}/Zn^{2+})_{unimp}\}$ are shown in Fig. 5. The adsorption of Cu^{2+} on the Cu-imprinted resins (ML_2 complex, left in Fig. 5) was selective (above 1 in relative selectivity), as was the adsorption of Zn^{2+} on the Zn-imprinted resins (below 1), except for the resins prepared with **RR_{12}NAc**. The efficiencies of the surfactants for selective adsorption were **R_8NAc > R_{12}NAc > R_{18}NAc > RR_6NAc > RR_{12}NAc** and the order was consistent with their emulsifications. The Cu-imprinted resins prepared with **R_8NAc** were 2.69-times as effective in selectivity for Cu^{2+} adsorption, and the Zn-imprinted resins were 1.84-times (= 1/0.54) as effective for Zn^{2+} adsorption {relative selectivity for the ratio of Zn^{2+} to Cu^{2+} corresponds to the reciprocal of that (0.54) for the ratio of Cu^{2+} to Zn^{2+}}. **Rac** was 2.31 (= 3.7/1.6)

Table 3. Adsorption to Resins Prepared by Irradiation of γ-Ray[a)]

Surfactant	Composition of template	Adsorption from a metal soln			Adsorption from a mixture		
		Cu^{2+} mol g^{-1}	Zn^{2+} mol g^{-1}	Cu/Zn (rel)	Cu^{2+} mol g^{-1}	Zn^{2+} mol g^{-1}	Cu/Zn (rel)
R_{18}NAc	Zn·L	0.18×10^{-5}	0.14×10^{-5}	1.2 (0.7)	0.18×10^{-5}	0.10×10^{-5}	1.8 (0.9)
	L	0.27	0.15	1.8 (1.0)	0.24	0.12	2.0 (1.0)
	Cu·L_2	0.34	0.10	3.4 (2.0)	0.30	0.10	3.0 (1.2)
RR_6NAc	Zn·L	0.27	0.33	0.8 (0.5)	0.28	0.30	0.9 (0.4)
	L	0.29	0.17	1.7 (1.0)	0.25	0.10	2.5 (1.0)
	Cu·L_2	0.33	0.09	3.7 (1.7)	0.22	0.07	3.1 (1.6)
RR_{12}NAc	Zn·L	0.27	0.14	1.9 (0.9)	0.15	0.13	1.2 (0.6)
	L	0.38	0.18	2.1 (1.0)	0.26	0.14	1.9 (1.0)

a) Preparation of resin: surfactant 1.7 mol% of monomers {=DVB (1.4×10^{-2} mol) +St (1.4×10^{-3} mol) +surfactant (2.7×10^{-4} mol)}, metal solution 9.0×10^{-3} or 3.6×10^{-2} mol dm^{-3}, 15 cm^3, pH 5.5; irradiation of γ-ray 1×10^4 C kg^{-1} at 0 °C. Adsorption of Cu^{2+} and Zn^{2+}: initial concn of metal ions 5×10^{-4} mol dm^{-3}, 5 cm^3, pH 6.0, 25 °C, resin 0.1 g. Rel: relative adsorption of imprinted resins to that of unimprinted resins.

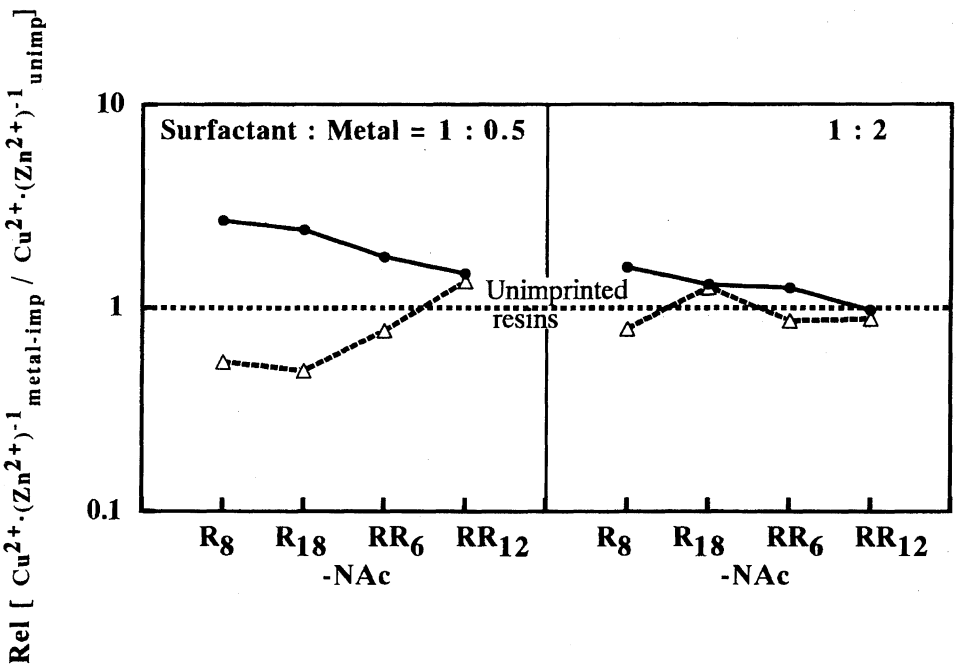


Fig. 5. Competitive sorption on the metal-imprinted resins from a Cu^{2+}–Zn^{2+} mixture. Initial concn of the Cu^{2+}–Zn^{2+} mixture: $[Cu^{2+}] = [Zn^{2+}] = 2.5 \times 10^{-4}$ mol dm^{-3}, 5 cm^3, pH 6.0, 25 °C. Resin 0.1 g. Rel: relative selectivities (Cu^{2+}/Zn^{2+}) of Cu-imprinted resins (●) and Zn-imprinted resins (△) to the selectivity (Cu^{2+}/Zn^{2+}) of unimprinted resins.

times as effective for Cu^{2+} adsorption in relative selectivity; the selectivity of Cu^{2+}/Zn^{2+} was 3.7 for Cu-imprinted resins prepared at 0.25 mol% **Rac** and 1.6 for unimprinted resins.[16] The relative selectivity for Cu^{2+} (2.69) by **R_8NAc** is more effective than that by **Rac**.[16] The high selectivities must be brought about by fixing of the vinyl group almost at the ligands. Moreover, the adsorption capacity of the resins prepared with **R_8NAc** was the greatest, while **RR_nNAc** of poor complexation brought about lower selectivities and a smaller capacity. Much of **R_8NAc** must be present at the surface of the resins and act as the ligand of the surface template, while **RR_nNAc** must be more in the inner part because of the great lipophilicity. Thus, the metal-imprinted resins prepared at twice as much **R_nNAc** as the metal ions (ML_2 complex) showed selective adsorption. On the other hand, the resins prepared at twice as much metal ions as the **R_8NAc** (M·L complex) showed only slight selective adsorption because of the lack of a four-coordinate square plane for Cu^{2+} or the lack of a four-coordinate tetrahedral structure for Zn^{2+} (right in Fig. 5).

The adsorbed metal ions were dissociated quantitatively from the template resins by adding 1 mol dm^{-3} HCl. The metal-imprinted resins prepared at twice as much **R_nNAc** (ML_2 complex) could be used repeatedly after treating with an acidic solution, and showed similar characteristics to those of the originals.

Thus, excellent surface metal-imprinted resins could be prepared by regulating the HLB of the functional surfactant bearing a vinyl group at nearly the ligand; it was concluded that surface metal-template resins can be easily prepared by using a monomer-type ligand having great emulsifying power.

References

1) G. Wulff and A. Sarhan, *Angew. Chem.*, **84**, 364 (1972).
2) G. Wulff, A. Sarhan, and K. Zabrocki, *Tetrahedron Lett.*, **1973**, 4329.
3) G. Wulff, *Angew. Chem., Int. Ed. Engl.*, **34**, 1812 (1995).
4) D. K. Robinson and K. Mosbach, *J. Chem. Soc., Chem. Commun.*, **1989**, 969.
5) G. Vlatakis, L. I. Andersson, R. Müller, and K. Mosbach, *Nature*, **361**, 645 (1993).
6) H. Nishide and E. Tsuchida, *Makromol. Chem.*, **177**, 2995 (1976).
7) H. Nishide, J. Deguchi, and E. Tsuchida, *Chem. Lett.*, **1976**, 169.
8) W. Kuchen and J. Schram, *Angew. Chem., Int. Ed. Engl.*, **27**, 1695 (1988).
9) H. Kido, T. Miyajima, K. Tsukagoshi, M.Maeda, and M. Takagi, *Anal. Sci.*, **8**, 749 (1992).
10) H. Kido, H. Sonoda, K. Tsukagoshi, M. Maeda, M. Takagi, H. Maki, and T. Miyajima, *Kobunshi Ronbunshu*, **50**, 403 (1993).
11) M. Maeda, M. Murata, K. Tsukagoshi, and M. Takagi, *Anal. Sci.*, **10**, 113 (1994).
12) M. Murata, S. Hijiya, M. Maeda, and M. Takagi, *Bull. Chem. Soc. Jpn.*, **69**, 637 (1996).
13) K. Y. Yu, K. Tsukagoshi, M. Maeda, and M. Takagi, *Anal. Sci.*, **8**, 701 (1992).
14) K. Tsukagoshi, K. Y. Yu, M. Maeda, and M. Takagi, *Bull. Chem. Soc. Jpn.*, **66**, 114 (1993).
15) K. Tsukagoshi, K. Y. Yu, M. Maeda, M. Takagi, and T. Miyajima, *Bull. Chem. Soc. Jpn.*, **68**, 3095 (1995).
16) Y. Koide, H. Senba, H. Shosenji, M. Maeda, and M. Takagi, *Bull. Chem. Soc. Jpn.*, **69**, 125 (1996).
17) S. Yamazaki and S. Hattori, *Hyomen*, **25**, 86 (1987).
18) C. F. Allen and M. J. Kalm, *Org. Synth.*, **4**, 398 (1963).

19) C. F. Allen and M. J. Kalm, *Org. Synth.*, **1**, 48 (1967).
20) L. R. Morris, R. A. Rock, C. A. Marshll, and J. H. Home, *J. Am. Chem. Soc.*, **81**, 377 (1959).
21) F. Kitahara and K. Furusawa, "Bunsan·Nyuka-kei No Kagaku," Kogaku-tosho, Tokyo (1991), p. 37.
22) L. E. Maley and D. P. Mellor, *Nature*, **165**, 453 (1950).