Selective Adsorption of Metal Ions to Surface-Template Resins Prepared by Emulsion Polymerization Using 10-(*p*-Vinylphenyl)decanoic Acid

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A monomer-type surfactant, 10-(*p*-vinylphenyl)decanoic acid (**1**), has been prepared and applied to an emulsifier for the preparation of surface-template resins. The hydrophobicity of **1** corresponded to that of $C_{15}H_{31}COONa$ on the basis of the cmc values, while that of **1** on the emulsification corresponded to that of $C_{12}H_{25}COONa$. The monomers (DVB + St + **1**) were copolymerized in a metal ion solution and the resulting polymers were evaluated for their surface-template effects. The suspension polymerization gave resins 0.08 mm in diameter and the adsorption of metal ions on Cu^{2+}-imprinted resins attained equilibrium in 2 h. The surface-template effects based on the oriented **1** exceeded the inner-template resins in selective adsorption. On the other hand, the emulsion polymerization gave fine particles 200—300 nm in diameter. The resins showed excellent surface-template effects. The adsorption of metal ions was 50—100 times as much as that on the resins prepared by suspension polymerization (see Fig. 2 and Table 3). The metal-imprinted resins was 1.88 times more effective than the unimprinted resins, and the Zn^{2+}-imprinted resins showed more effective adsorption for Zn^{2+} than for Cu^{2+} and for Ni^{2+}. Such surface-template effects were also seen for Cu^{2+}- and Ni^{2+}-imprinted resins. The selectivity (Cu^{2+}/Zn^{2+}) from the mixture of both metal ions was 3.7 for the Cu^{2+}-imprinted resins prepared at 0.25 mol% **1**. Furthermore, the metal-imprinted resins could be used repeatedly.

The molecular imprinting technique[1] has been noted for the selective recoveries of specific molecules such as organic compounds[2] and metal ions.[3] However, the techniques reported so far seem less general, especially for water-soluble guests. Since host monomers binding to the specific guest molecules were chemically solidified with matrix monomers by cross-linking polymerization, the host–guest complexes are required to be soluble in the matrix monomers. When target molecules are polar, the complexes would be hardly soluble in the matrix monomers. Moreover, the resulting molecular-imprinted resins should be ground and sieved to produce finely divided resins, because most of the imprintings are formed in the inner parts of bulk resins. For the same reason, the resins would require a long time for separation.

Two types of novel imprinting techniques that took advantage of an oil-water interface have been proposed to improve the conventional techniques for rapid and selective recovery.[4,5] The first surface-template resins were obtained by polymerization of *p*-divinylbenzene (DVB) in an aqueous metal ion solution, using oleic acid as a host monomer. It was suggested by a potentiometric study that metal-selective cavities were formed at the surface of the resins. However, the selective recovery of a specific guest from a metal ion mixture has not been examined. The long-term stability should also be examined since oleic acid (host monomer) may be just anchored but not chemically bound to the bulk resins.[4] The second example was prepared by the seeded emulsion polymerization of DVB, styrene (St), butyl acrylate, and methacrylic acid. Metal ions were combined with the carboxyl groups of the methacrylic acid moiety on the surface of the seed copolymer through their reorganization, and then the metal complexes were fixed by cross-linking copolymerization of DVB and butyl acrylate.[5] The surface metal-imprinted microspheres selectively adsorbed the imprinted metal ions. However, the reorganizations of carboxyl groups at the surface must be incomplete since the metal ion selectivity was not very satisfactory. This may be attributed to insufficient mobility of the surface-bound groups.

Now, we propose a third technique as an efficient method for the preparation of surface-template resins. A functional surfactant (emulsifier) that is capable of binding metal ions and functions as vinyl monomer must orient at the interface between the matrix monomers and water, and emulsify these solutions. The surfactant should be polymerized with the matrix monomers in the form of a metal complex. Therefore, a functional surfactant should make the surface imprinting easy and reliable. A monomer-type surfactant named New Frontier A-229ER, which is a phosphonic ester of acrylate oligomer (Dai-Ichi Kogyo Seiyaku Co., Ltd.), has been used as an emulsifier in emulsion polymerization by S. Yamasaki et al.[6] However, the surface-imprinting technique has not been tried yet.

In this paper, 10-(*p*-vinylphenyl)decanoic acid (**1**) bearing carboxylic acid as a simple ligand has been prepared. The characteristics of the surface metal-imprinted resins, prepared by emulsion polymerization using **1**, have been investigated.

Experimental

Materials. A monomer-type surfactant **1** was obtained through an analogous procedure to the synthesis of branched 10-(*p*-vinylphenyl)undecanoic acid by Freedman et al. (Scheme 1).7)

9-Benzoylnonanoic acid was prepared from sebacic acid by the method of Hill7,8) and the carbonyl group was reduced with zinc amalgam by Clemmensen reduction.9) The reduced compound, 10-phenyldecanoic acid, was extracted with ethyl ether and distilled at 210 °C/0.4 mmHg (1 mmHg = 133.322 Pa). 10-Phenyldecanoic acid was converted to methyl 10-phenyldecanoate,10) and then acetylated in 46% yields.7) The product, 10-(*p*-acetylphenyl)decanoate, was treated with aluminium isopropoxide in 2-propanol and the reduction afforded methyl 10-[*p*-(1-hydroxylethyl)phenyl]decanoate in 45% yield.7) The hydroxylethyl group was dehydrated over fused potassium hydrogensulfate by distillation at 220—240 °C/0.4 mmHg.7) The distilled methyl 10-(*p*-vinylphenyl)decanoate was in turn saponified to **1** in 77% yield.7)

10-Phenyldecanoic Acid: Mp 30.1—30.6 °C. IR (KBr) $\nu_{C=O}$ 1710 cm^{-1}. ^{1}H NMR (CCl_4, TMS) $\delta = 1.3$ (14H, $-CH_2-$), 2.3 (2H, $-CH_2Ac$), 2.6 (2H, $-CH_2Ar$), 7.2 (5H, ArH), 10.5 (1H, COOH). Found: C, 76.91; H, 9.39%. Calcd for $C_{16}H_{24}O_2$: C, 77.3; H, 9.74%.

1: Mp 55.3—57.2 °C. IR (KBr) $\nu_{C=O}$ 1690 cm^{-1}. ^{1}H NMR (CCl_4, TMS) $\delta = 1.3$ (14H, $-CH_2-$), 2.2 (2H, $-CH_2Ac$), 2.4 (2H, $-CH_2-Ar$), 4.9—5.1 (1H, trans CH=CAr), 5.5—5.7 (1H, cis CH=CAr), 6.5—6.7 (1H, C=CHAr), 7.2 (4H, ArH), 10.4 (H, COOH). Found: C, 78.1; H, 9.00%. Calcd for $C_{18}H_{26}O_2$: C, 78.8; H, 9.55%.

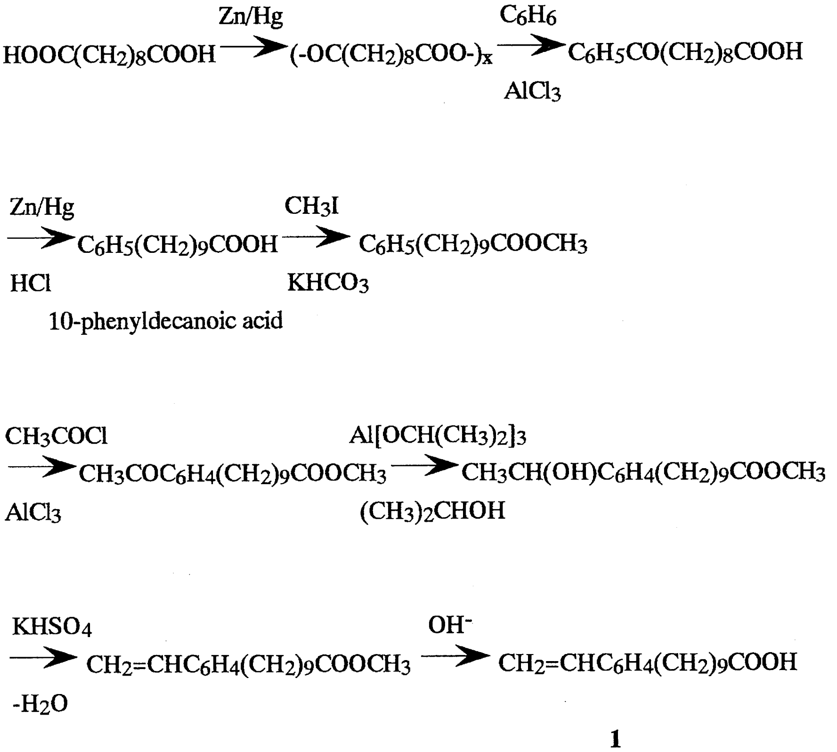
Metal-Imprinted Resins: Surface-template resins were prepared by the usual suspension polymerization and by emulsion polymerization using **1**. The latter method is as follows. The monomer-type surfactant **1** was dissolved in 80 cm^3 of Cu^{2+} solution (pH 6.0) containing 1 wt% poly(vinyl alcohol) (n = ca. 1500, Wako Pure Chemicals). Then, the Cu^{2+} solution was added to a DVB–St (10 : 1) mixture and stirred at a rate of 300—400 rpm. The emulsion was heated up to 75 °C under nitrogen atmosphere and potassium peroxodisulfate ($K_2S_2O_8$) as an initiator was added to it. The monomers in emulsion were gradually polymerized and the polymer (resins) was left for a long time (6 h). After the decantation, the resins as a white solid were separated by filtration using a sintered-glass filter (No.5). The resins were washed with hot water (90 °C) and then treated with 0.1 mol dm^{-3} HNO_3 for 1 h. As the metal ions in the resins were dissolved in the HNO_3 solution, the resins were washed with cold water and dried in a vacuum (Fig. 1). Unimprinted resins were also prepared by similar procedures in the conditions without metal ions.

Polymerization by γ-ray was examined instead of the emulsion polymerization using $K_2S_2O_8$. The emulsion in an ampule was irradiated with 1.25×10^4 C kg^{-1} ^{60}Co γ-ray at room temperature. The use of the ^{60}Co irradiation facility has been made possible by the Inter-University Program for the Common Use JAERI Facilities.

Adsorption of Cu^{2+}: Ten mg of resins were placed in a flask containing 50 cm^3 of 5×10^{-5} mol dm^{-3} Cu^{2+} solution (pH 5.0 and 6.0) and then the suspension was stirred for 2 h. The resins in the solution were filtered and then treated with 50 cm^3 of 0.1 mol dm^{-3} HCl for the desorption. After being washed with 500 cm^3 water, the resins could be reused for the adsorption. The amounts of Cu^{2+} in the remaining solution and in the HCl washing-solution were measured with an atomic-absorption spectrophotometer (Hitachi 170-30).

Results and Discussion

Surface Activities: An alkali solution of **1**, measured by a Wilhelmy surface tension balance, caused lowering of surface tension (γ_{cmc}: 41 mN m^{-1}, cmc: 1.25×10^{-3} mol dm^{-3}



$$\mathrm{HOOC(CH_2)_8COOH} \xrightarrow{\mathrm{Zn/Hg}} \mathrm{(\text{-}OC(CH_2)_8COO\text{-})_x} \xrightarrow[\mathrm{AlCl_3}]{\mathrm{C_6H_6}} \mathrm{C_6H_5CO(CH_2)_8COOH}$$

$$\xrightarrow[\mathrm{HCl}]{\mathrm{Zn/Hg}} \underset{\text{10-phenyldecanoic acid}}{\mathrm{C_6H_5(CH_2)_9COOH}} \xrightarrow[\mathrm{KHCO_3}]{\mathrm{CH_3I}} \mathrm{C_6H_5(CH_2)_9COOCH_3}$$

$$\xrightarrow[\mathrm{AlCl_3}]{\mathrm{CH_3COCl}} \mathrm{CH_3COC_6H_4(CH_2)_9COOCH_3} \xrightarrow[\mathrm{(CH_3)_2CHOH}]{\mathrm{Al[OCH(CH_3)_2]_3}} \mathrm{CH_3CH(OH)C_6H_4(CH_2)_9COOCH_3}$$

$$\xrightarrow[\mathrm{-H_2O}]{\mathrm{KHSO_4}} \mathrm{CH_2{=}CHC_6H_4(CH_2)_9COOCH_3} \xrightarrow{\mathrm{OH^-}} \underset{\mathbf{1}}{\mathrm{CH_2{=}CHC_6H_4(CH_2)_9COOH}}$$

Scheme 1. Preparation of **1**.

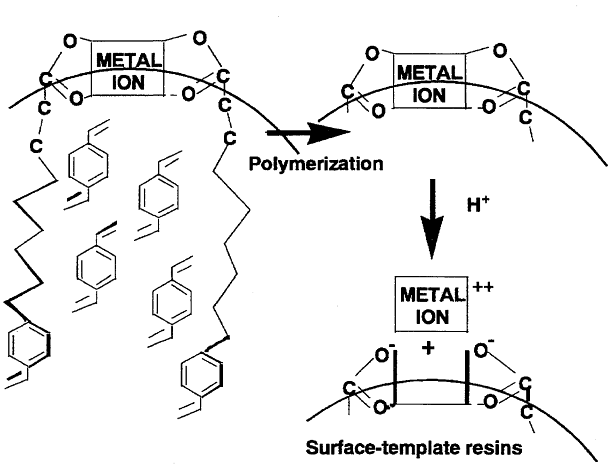


Fig. 1. Preparation of metal-imprinted resins.

at pH 12). The cross-sectional area of a molecule, calculated from the Gibbs adsorption equilibrium, was 0.57 nm^2. The cmc of **1** was lower than those of $C_{11}H_{23}COONa$ (above 1×10^{-2} mol dm^{-3}), $C_{13}H_{27}COOK$ (6×10^{-3} mol dm^{-3}),[11] and $C_{15}H_{31}COONa$ (3.2×10^{-3} mol dm^{-3} at 52 °C).[11] The hydrophobicity of **1** based on the cmc values should nearly correspond to that of $C_{15}H_{31}COONa$. Hydrophobicity of a phenyl group is known to be equivalent to about three and one-half methylene groups.[12] Therefore, the sum of the carbon number of **1** was estimated to be $C_{12+3.5}$ ($C_{14}H_{29}COONa$ or $C_{15}H_{31}COONa$). The monomer-type surfactant **1** was easily polymerized by heating, and an alkali solution of the polymer (polysoap) showed the lowering curve of surface tension without the break point corresponding to cmc (γ: 47 mN m^{-1} at 2.5×10^{-3} unit mol dm^{-3}).

Three cm^3 of water containing 0.2 mol% **1** (sodium salts) was mixed with a 3 cm^3 of toluene in a 50 cm^3 of test tube and the toluene–water (1 : 1) mixture was emulsified by stirring vigorously. The volume (height) of the resulting emulsion was measured at intervals of five minutes and compared with those by 0.2 mol% sodium dodecyl sulfate (DS) and some sodium alkanoates. The order of emulsifying ability at pH 12 was the following: hexadecanoate > tetradecanoate >**1** > DS > dodecanoate ≫ octadecanoate. Therefore, the chain length of **1** seems to correspond to the alkyl chain of 13 carbon number of sodium alkanoate. This is shorter than 15.5—16 of carbon number estimated from the cmc values and the calculation. The smaller oleophilicity (larger hydrophilicity) on emulsification would be ascribed to the large partition of vinylbenzene moiety between the two liquid phases, since styrene is sparingly soluble in water.

Suspension Polymerization: Monomer-type surfactant **1** in the matrix monomers (DVB + St) should adsorb at the monomers–Cu^{2+} solution interface and form the Cu^{2+} complex. The polymer (resins) of these monomers prepared by using benzoyl peroxide (BPO) as an initiator would have the same cavities at the surface as the structures of the Cu^{2+} complexes. The conditions of the preparation are summarized in Table 1. Excess DVB (10-fold of the St) was copolymerized with the St and **1** to prepare the resins of tight structure and to prevent the carboxyl groups from moving.

The suspension polymerization gave fine resins of about 0.08 mm (0.04—0.16 mm) diameter in 31—66% yields, while the polymerization without **1** gave coarse resins with diameter of 0.4 mm in 70—80% yields. The monomer-type surfactant **1** would make the monomer particles divide finely because **1** lowers the interface tension.

After the combined Cu^{2+} was eluted from the surface-template resins by stirring in a HNO_3 solution, adsorption of Cu^{2+} and Zn^{2+} was examined at pH 5—6. The adsorption of Cu^{2+} on the resins attained equilibrium in 2 h. The amounts of the adsorbed metal ions (mmol/g-resins) increased with increasing the molar ratios of **1**, as is shown in Fig. 2.

The amount of **1** at the interface should increase with the addition of **1** at the time of polymerization. However, the relative amount of **1** at the interface would be larger than those in the two liquids when **1** was polymerized at the lower concentration, and smaller when at the higher concentration because of the dissolution of **1** in the two liquids in the forms of aggregate, micelle, etc. The efficiencies per additive **1** de-

Table 1. Preparation of Cu^{2+}-Imprinted Resins by Suspension Polymerization[a)]

1·(DVB+St+**1**)$^{-1}$/mol%	**1**/mol	Cu^{2+}·**1**$^{-1}$/mol mol^{-1}	Yield/g	Yield/%
0.04	7.3×10^{-6}	0.5	0.92	41
0.08	1.7×10^{-5}	2	1.68	60
0.19	3.5×10^{-5}	2	1.56	65
0.30	1.8×10^{-5}	1	0.35	44
0.33	3.6×10^{-5}	2	0.68	48
0.34	1.9×10^{-5}	1	0.22	31
0.39	1.8×10^{-5}	1	0.19	31
0.04	7.3×10^{-6}	0	1.47	66
0.17	1.5×10^{-5}	0	0.49	44
0.25	1.9×10^{-5}	0	0.47	45
0.30	1.7×10^{-5}	0	0.23	31
0.39	1.8×10^{-5}	0	0.15	25

a) Conditions of suspension polymerization: DVB/St = 10 (mol/mol), BPO 1 wt%, PVA 2.5 wt%, Cu^{2+} solution 80 cm^3, pH 6.0. Reaction mixture was stirred at a rate of 300—400 rpm, 85 °C for 6 h.

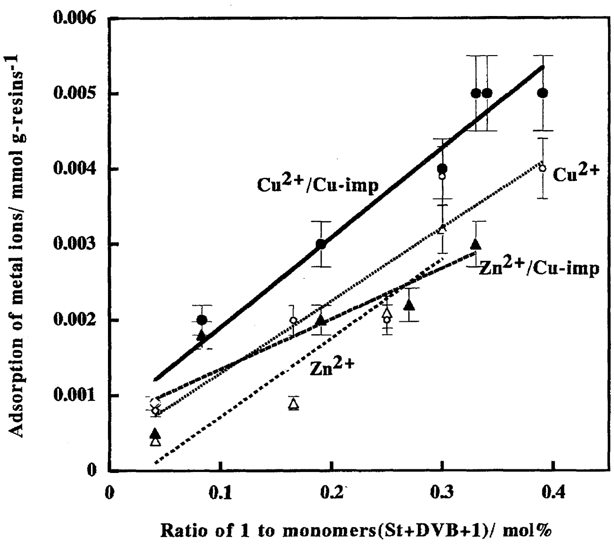


Fig. 2. Adsorption of Cu^{2+} and Zn^{2+} on the Cu-imprinted resins prepared by suspension polymerization. Initial concn of Cu^{2+} and Zn^{2+}: 5×10^{-5} mol dm^{-3}, 50 cm^3, pH 6.0. Resins: 1 g. ●: adsorption of Cu^{2+} on Cu-imprinted resins, ▲: Zn^{2+} on Cu-imprinted resins, ○: Cu^{2+} on unimprinted resins, △: Zn^{2+} on unimprinted resins.

creased at the high concentration; the adsorbed Cu^{2+} on the resins was 0.021 mmol g^{-1} mol%$^{-1}$ at 0.04 mol% **1**, 0.019 mmol g^{-1} mol%$^{-1}$ at 0.08 mol% **1**, 0.014 mmol g^{-1} mol%$^{-1}$ at 0.19—0.30 mol% **1**, and 0.013 mmol g^{-1} mol%$^{-1}$ at 0.39 mol% **1**. Figure 2 shows that the amounts of the adsorbed Cu^{2+} on the Cu^{2+}-imprinted resins were larger than those on the unimprinted resins, too. Moreover, the adsorption of Zn^{2+} on the Cu^{2+}-imprinted resins was a little larger than that on the unimprinted resins in the range of 0.04—0.25 mol% **1**. The fixation of **1** at the interface would be effective during the polymerization in the presence of Cu^{2+} because of the orientation of the carboxyl group toward the Cu^{2+} solution, and much of the Zn^{2+} would also be adsorbed on the resins at the lower concentration by cation exchange. The size and the coordination number of the imprinted metal ions should change the conformation of the metal complex at the interface. Therefore, a large adsorption of Cu^{2+} would be brought about by the template effects at the surface. However, the resins were too large to use for the separation and the amounts of the adsorbed Cu^{2+} per g-resins were not high. Moreover, the lower yields of the resins may weaken the template effects, since the conformation during the polymerization is changeable. Therefore, emulsion polymerization was examined for the preparation of finer resins.

Emulsion Polymerization: A monomer-type surfactant **1** as an emulsifier made stable emulsions with agitation at 300—400 rpm. Three monomers (DVB + St + **1**) in a metal-ions solution were copolymerized by using an initiator of water-soluble $K_2S_2O_8$ or by irradiation with γ-rays as an initiator. The conditions of the preparation are shown in Table 2.

The resins prepared at 0.04—0.33 mol% **1** were hard, but those at 1 mol% **1** were rubberlike polymers. The polymerization at 0.25 mol% **1** gave fine particles and the size of resins was 200—300 nm in diameter, as long as that by the usual emulsion polymerization. However, the Cu^{2+}-imprinted resins were the lowest in yield; yields were about 3% for the Cu^{2+}-imprinted one, 37% for the Zn^{2+}-imprinted one, 15% for the Ni^{2+}-imprinted one, and 32% for the unimprinted one. The radicals of the initiator would be inactivated by the Cu^{2+} because of the high reduction potential

$$\cdot OSO_3^- + Cu^{2+} \rightarrow SO_4^{2-} + Cu^+.$$

Adsorption of Metal Ions: The adsorbed Cu^{2+} on 1 g of the resins was 50—100 times as much as that on the resins prepared by suspension polymerization (see Fig. 2 and

Table 2. Preparations of Metal-Imprinted Resins by Emulsion Polymerization[a)]

		Metal-imprinting		Initiator	
1·(DVB+St+**1**)$^{-1}$/mol%	**1**/mol	Metal·**1**$^{-1}$/mol mol^{-1}		$K_2S_2O_8$/mg	γ-ray/C Kg^{-1}
0.25	2.0×10^{-5}	Cu^{2+}	1	20	
0.25	2.0×10^{-5}	Zn^{2+}	1	20	
0.25	2.0×10^{-5}	Ni^{2+}	1	20	
0.25	2.0×10^{-5}	None	0	20	
0.33	3.6×10^{-5}	Cu^{2+}	1	31	
0.33	2.7×10^{-5}	Zn^{2+}	1	21	
0.33	1.8×10^{-5}	Ni^{2+}	1	14	
0.33	3.6×10^{-5}	None	0	31	
1.0	4.0×10^{-5}	Cu^{2+}	1	10	
1.0	4.0×10^{-5}	Zn^{2+}	1	10	
1.0	4.0×10^{-5}	Ni^{2+}	1	10	
1.0	4.0×10^{-5}	None	0	10	
0.04	3.7×10^{-6}	Cu^{2+}	1		1.25×10^4
0.04	3.7×10^{-6}	Ni^{2+}	1		1.25×10^4
0.04	3.7×10^{-6}	None	0		1.25×10^4

a) Conditions of emulsion polymerization: DVB/St = 10 (mol/mol), metal solution 80 cm^3, pH 6.0, $K_2S_2O_8$ 75 °C, γ-ray 15—20 °C.

Table 3).The metal ions would be combined with the carboxyl groups on the wider surface of the finer resins. Moreover, the amounts of the adsorbed $\mathrm{Cu^{2+}}$ at pH 6.0 were much more than those at pH 5.0. The monomer-type surfactant **1** must dissociate at pH 4—5 and should complex more easily with the $\mathrm{Cu^{2+}}$ at pH 6.0, since the acid dissociation of hexanoic acid is $\mathrm{p}K_\mathrm{a}$ 4.63 at 25 °C (I=0.1).[13] The adsorption sites on the unimprinted resins were still unsaturated with the metal ions under the conditions described in Table 3 because of the increase of the amount of $\mathrm{Cu^{2+}}$-adsorption at the high concentration.

The adsorption of $\mathrm{Cu^{2+}}$ on the $\mathrm{Cu^{2+}}$-imprinted resins was 1.2—4.5 times (mean: 1.88) higher than that on the unimprinted resins. The $\mathrm{Zn^{2+}}$- and the $\mathrm{Ni^{2+}}$-imprinted resins also showed high adsorption for $\mathrm{Zn^{2+}}$ and $\mathrm{Ni^{2+}}$, respectively. In addition to the high adsorption, the $\mathrm{Zn^{2+}}$-imprinted resins showed more effective adsorption for $\mathrm{Zn^{2+}}$ than for $\mathrm{Cu^{2+}}$ and for $\mathrm{Ni^{2+}}$; 1 g of $\mathrm{Zn^{2+}}$-imprinted resins prepared at 0.25 mol% **1** adsorbed 0.062 mmol $\mathrm{Cu^{2+}}$, 0.138 mmol $\mathrm{Zn^{2+}}$, and 0.095 mmol $\mathrm{Ni^{2+}}$ at pH 5. Such template effects were also seen for $\mathrm{Cu^{2+}}$- and $\mathrm{Ni^{2+}}$-imprinted resins. The highly effective adsorption for the imprinted metal ions clearly indicates the surface-template effect based on the orientation of **1**, and the surface-template effects exceeded those of the inner-template

Table 3. Adsorption of Metal Ions on Metal-Imprinted Resins Prepared by Emulsion Polymerization

			Amount of metal ion per g-resins		
Resins	**1**[a]/mol%	pH	$\mathrm{Cu^{2+}}$/mmol g^{-1}	$\mathrm{Zn^{2+}}$/mmol g^{-1}	$\mathrm{Ni^{2+}}$/mmol g^{-1}
Suspension polymerization[b]					
$\mathrm{Cu^{2+}}$-imprinted	0.33	6.0	0.005±0.001	—	—
$\mathrm{Zn^{2+}}$-imprinted	0.33	6.0	—	0.003±0.001	—
Emulsion polymerization (Initiator of $\mathrm{K_2S_2O_8}$, 75 °C)					
$\mathrm{Cu^{2+}}$-imprinted	0.25	5.0	0.105±0.011 (1.6)[d]	—	—
$\mathrm{Cu^{2+}}$-imprinted	0.33	5.0	0.318±0.032 (4.5)[d]	—	—
$\mathrm{Cu^{2+}}$-imprinted	0.25	6.0	0.234±0.024 (1.2)[d]	—	—
$\mathrm{Zn^{2+}}$-imprinted	0.25	5.0	0.062±0.006	0.138±0.014 (1.8)[d]	0.095±0.010
$\mathrm{Zn^{2+}}$-imprinted	0.33	5.0	0.074±0.008	0.192±0.019 (1.4)[d]	0.108±0.011
$\mathrm{Zn^{2+}}$-imprinted	0.25	6.0	0.134±0.014	0.165±0.017 (1.8)[d]	0.019±0.002
$\mathrm{Ni^{2+}}$-imprinted	0.25	5.0	—	0.052±0.005	0.127±0.013 (1.8)[d]
$\mathrm{Ni^{2+}}$-imprinted	0.33	5.0	0.065±0.007	0.120±0.012	0.150±0.015 (1.5)[d]
$\mathrm{Ni^{2+}}$-imprinted	0.25	6.0	0.210±0.021	0.060±0.006	0.167±0.017 (1.4)[d]
Unimprinted	0.25	5.0	0.066±0.007	0.075±0.008	0.070±0.007
Unimprinted	0.33	5.0	0.069±0.007	0.139±0.014	0.103±0.010
Unimprinted	0.25	6.0	0.203±0.020	0.093±0.009	0.121±0.012
Emulsion polymerization (Irradiation of γ-ray,[c] room temperature)					
$\mathrm{Cu^{2+}}$-imprinted	0.04	6.0	0.139±0.014 (1.5)[d]	0.127±0.013	0.043±0.005
$\mathrm{Ni^{2+}}$-imprinted	0.04	6.0	0.073±0.008	0.053±0.006	0.121±0.012 (1.6)[d]
Unimprinted	0.04	6.0	0.092±0.009	0.066±0.007	0.076±0.008

Resins: 10 mg, Metal ion: 5×10^{-5} mol dm^{-3}, 50 cm^3. a) Ratio of **1** to the total monomers (DVB+St+**1**), b) Resins: 1 g, c) 1.25×10^4 C Kg^{-1} γ-ray, d) ( ): Ratio of adsorbed metal ion on metal-imprinted resins to that on unimprinted one.

Table 4. Selective Adsorption from a $\mathrm{Cu^{2+}}$–$\mathrm{Zn^{2+}}$ Mixture

			Adsorption of metal ions per g-resins		
Resins	**1**[a]/mol%	pH	$\mathrm{Cu^{2+}}$/mmol g^{-1}	$\mathrm{Zn^{2+}}$/mmol g^{-1}	$\mathrm{Cu^{2+}/Zn^{2+}}$
Suspension polymerization[b]					
$\mathrm{Cu^{2+}}$-imprinted	0.25	5.0	0.052±0.008	0.015±0.002	3.5
$\mathrm{Cu^{2+}}$-imprinted	0.33	5.0	0.068±0.010	0.029±0.004	2.4
Unimprinted	0.25	5.0	0.002±0.001	0.002±0.001	1.0
Emulsion polymerization					
$\mathrm{Cu^{2+}}$-imprinted[b]	0.04	5.0	0.090±0.014	0.030±0.005	3.0
$\mathrm{Cu^{2+}}$-imprinted	0.25	6.0	0.609±0.091	0.165±0.025	3.7
$\mathrm{Cu^{2+}}$-imprinted	1.0	6.0	0.227±0.034	0.126±0.019	1.8
Unimprinted[b]	0.04	5.0	0.021±0.003	0.015±0.002	1.4
Unimprinted	0.25	6.0	0.475±0.071	0.287±0.043	1.6

Resins: 10 mg, $\mathrm{Cu^{2+}}$–$\mathrm{Zn^{2+}}$ mixture: each 5×10^{-5} mol dm^{-3}, 50 cm^3. a) Ratio of **1** to the total monomers (DVB+St+**1**), b) Resins: 20 mg.

resins (1.3—1.5 times) reported by Nishide et al.[3a)]

The orientation of **1** during polymerization must be disordered by the high temperature (75 °C). To minimize the disorder of the oriented **1**, the monomers were copolymerized by irradiation with γ-rays at room temperature. The resins were obtained in above 90% yield on being irradiated with 1.25×10^4 C kg^{-1} γ-rays. However, the lack of the agitation plus the addition of small amounts of **1** (0.04 mol%) should make the resins a little larger. The particles were below 500 nm in diameter and the efficiencies of adsorption was not as high as those of the resins prepared by initiation with $K_2S_2O_8$. The former resins also had similar surface-template effects (see the bottom column of Table 3).

Selective Recovery from a Metal-Ions Mixture: The metal-imprinted resins adsorbed the target metal ions most, as demonstrated in the previous section, so selective adsorption can be expected. The adsorption of the metal ions from a mixture of Cu^{2+} and Zn^{2+} is shown in Table 4.

The selectivity of the resins prepared by suspension polymerization were similar to those of the resins prepared by emulsion polymerization, except for their smaller adsorption capacities. The Cu^{2+} was adsorbed selectively on the Cu^{2+}-imprinted resins much more than on the unimprinted resins. The greatest adsorption capacity and the highest selective adsorption for Cu^{2+} were obtained by the Cu^{2+}-imprinted resins prepared by emulsion polymerization at 0.25 mol% **1**; the selectivity of Cu^{2+}/Zn^{2+} was 3.7 for the Cu^{2+}-imprinted resins and 1.6 for the unimprinted resins. However, the resins prepared at 1 mol% **1** showed a lower selectivity ($Cu^{2+}/Zn^{2+}=1.8$). The Zn^{2+}-imprinted resins prepared by emulsion polymerization also showed the selectivity at pH 5.0 ($Cu^{2+}/Zn^{2+}=1.1$). Moreover, the metal-imprinted resins could be used repeatedly after treating with a acidic solution, since the carboxyl groups are chemically bound to the resins and the metal complex should be dissociated in the acidic solution. The reproducible resins prepared by the simple imprinting method showed the similar characteristics to the originals; the amounts of Cu^{2+} on the Cu^{2+}-imprinted resins (0.25 mol% **1**, pH 5.0) were 0.105 mmol g^{-1} in the first adsorption, 0.102 mmol g^{-1} in the second, and 0.110 mmol g^{-1} in the third.

Resins of the same order in size should be prepared by controlling the emulsion, and the ion-exchange capacities should be discussed more. However, a small difference in the size and in ion-exchange capacities did not affect the selectivity very much. Therefore, the selective adsorption of surface-template resins is apparent.

Thus, it was concluded that the surface-template resins, prepared by emulsion polymerization using a functional surfactant able to be polymerized, selectively adsorb the imprinted metal ions.

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