# Electron Spin Resonance and Some Spectral Studies on Coordination Behaviors of Paramagnetic Metal Ions for Chelating Resins

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Coordination behaviors of VO(II), Cr(III), Mn(II), Fe(III), Cu(II), and Gd(III) ions for the iminodiacetato group in the chelating ion-exchange resin Dowex A-1 were studied with the aid of ESR, infrared absorption, and Mössbauer spectroscopies. A comparative investigation also was made with the o-hydroxybenzyliminodiacetato group in the chelating resin Unicellex UR-50. The iminodiacetato group in Dowex A-1 is considered to coordinate as a tridentate ligand and form 1 : 1 chelates with metal ions, whereas the o-hydroxybenzyliminodiacetato group in Unicellex UR-50 coordinates as a quadridentate ligand in alkaline media and forms 1 : 1 chelates. Elucidation of spin-spin exchange interaction has led to a conclusion that the iminodiacetato groups present in the coordination pore of Unicellex UR-50 are closer to one another than those of Dowex A-1. For Fe(III) ions adsorbed in concentrated HCl media, besides the species $[FeCl_4]^-$, lower symmetric species are considered to be adsorbed with the anion exchange effect, from results of resin phase ESR and Mössbauer spectra.

Recently, new type chelating resins which are highly selective for certain metal ions have been synthesized and selective separation of metal ions has been investigated. As the selectivity is considered to depend on the chelating functional group, an investigation of the coordination behavior of metal ions for the group is of great importance in synthesis of metal ion specific resin. Commercially-available resins, Dowex A-1 and Unicellex UR-50, have different functional groups and show different coordination behaviors.

The chelating resin Dowex A-1 consists of a styrene–divinylbenzene copolymer to which iminodiacetato group is attached as chelating group. Cohen and Heitner-Wirguin suggested Cu(II) ion species adsorbed on Dowex A-1 by infrared and ESR measurements.[1,2] They assumed that Dowex A-1 acts only as an anion exchanger in concentrated HCl media and Cu(II) ion is adsorbed as $[CuCl_4]^{2-}$ or $[CuCl_3(H_2O)]^-$. In neutral and alkaline solution the functional group acts as bidentate and tridentate ligands, respectively. Their assumption was supported by Umezawa and Yamabe[3] considering the mobility of Cu(II) ions adsorbed on the resin phase and the effect of the water molecules involved in the resin phase by means of ESR spectroscopy. More recently, Hoek and Reedijk[4] suggested from ESR and electronic spectra measurements that the iminodiacetato group in Chelex 100 (analytical grade Dowex A-1) coordinates as a tridentate chelating ligand to metal ions, such as Co(II), Ni(II), and Cu(II), and that the distorted octahedral is completed by either water molecules or by carboxylate oxygens from excess neighboring iminodiacetato groups.

The chelating resin Unicellex UR-50 was made by polycondensation of N-(o-hydroxybenzyl)iminodiacetic acid with phenol and formaldehyde. Tomoshige et al.[5] compared the coordination behavior of the resin with that of Chelex 100 and suggested, by considering chelate stability constants of the resin with metal ions, that the phenolic hydroxyl group plays an important role in the chelating behavior. However, they gave no discussion of the adsorption structure of metal ions on the resin phase. To investigate the adsorption structure of metal ions on the resin phase would give significant information

about the coordination behavior of the resin. Thus, we have made a comparison of coordination behaviors of Dowex A-1 and Unicellex UR-50 in connection with the adsorption structure of metal ions on the resins from the viewpoint of synthesis of metal ion specific resin. This paper presents a study of resin phase ESR spectra of paramagnetic metal ions, such as VO(II), Cr(III), Mn(II), Fe(III), Cu(II), and Gd(III) ions, distributions of these metal ions between the resin and solution phases, and adsorption structures of these metal ions. Furthermore, chelating behaviors of monomers, such as iminodiacetic acid (IDA) and N-benzyliminodiacetic acid (BIDA), are also compared with those of the resins.

## Experimental

*Reagents and Materials.*     All reagents used were of analytical grade. Stock solutions of VO(II), Cr(III), Mn(II), Fe(III), and Cu(II) ions were prepared by dissolving vanadyl dichloride, chromium(III) nitrate, manganese(II) chloride, iron(III) chloride, and copper(II) chloride in dilute hydrochloric acid solution, respectively. Their concentrations were standardized by EDTA titration. Standard solution of metal ions of desired concentration were prepared by diluting the stock solutions. The buffer solutions were as follows: pH 1 to 2, potassium chloride–hydrochloric acid; pH 3 to 6, sodium acetate–acetic acid; pH 7 to 9, tris(hydroxymethyl)-aminomethane–hydrochloric acid; pH 10, ammonium chloride–ammonia water. Deionized distilled water was used. The chelating ion-exchange resins used were Dowex A-1 (Dow Chemical Co.) in the sodium form as 50—100 mesh beads and Unicellex UR-50 (Unitika, Ltd.) in the hydrogen form as 20—50 mesh beads. The resins were conditioned and transformed into the hydrogen and sodium forms in a conventional manner, respectively. The cation exchange capacities of Dowex A-1 and Unicellex UR-50 were 3.74 and 3.57 mequiv. per g of dry resin, based upon the uptake of tetra-amminecopper(II) ion which was formed in 2 mol dm$^{-3}$ ammonia water. Nonaqueous ion-exchanger Amberlyst A-26 (Rohm and Haas) in the chloride form was used without further treatment.

*Preparation of Samples and Reference Compounds.*     About 500 mg of dry resin, 10 cm$^3$ of metal ion solution and 40 cm$^3$ of 0.1 mol dm$^{-3}$ buffer solution were placed in a flask and

agitated for 24 h at $20\pm1$ °C. Metal ion concentration was 100 μg/cm³. After equilibration, the pH value was measured, the solution was filtered, and the wet resin phase (dried in a silica gel desiccator for 12 h) and the dry resin phase (dried for 2 d) were subjected to ESR spectral measurements. Only for estimation of distribution ratio the resin was rinsed rapidly with deionized distilled water except resins immersed in concentrated HCl media, then the solution and rinse were combined and analyzed for metal ion concentration by atomic absorption spectrometry except Gd(III) ion (colorimetry). Distribution ratio, $D$, is defined as follows and evaluated by determining the metal ion concentration in an equilibrated solution:

$$D = \frac{\text{amt. of metal ion per g of dry resin}}{\text{amt. of metal ion per cm}^3\text{ of solution}}.$$

The amount of metal ions adsorbed on the resin phase was also analyzed after elution with 2 mol dm⁻³ HCl except Cr(III) ion. The amount of Cr(III) ions on the resin phase was analyzed after ashing the resin.

[FeCl₄]⁻ ion was prepared by extraction into diisopropyl ether from aqueous acidic chloride solution.[6] This chlorocomplex was adsorbed on the anion exchanger Amberlyst A-26 in diisopropyl ether media and compared with that on Dowex A-1 in concentrated HCl media. Other reference compounds such as (CH₃NH₃)₂[MnCl₄], [(CH₃)₄N]₂[MnCl₄], (CH₃NH₃)₃[FeCl₆]·CH₃NH₃Cl, (NH₄)₂[FeCl₅(H₂O)], and (CH₃)₄N[FeCl₄] were prepared by addition of counter ion's chloride to a concentrated HCl solution containing chlorocomplex of Mn(II) or Fe(III).[7,8] IDA and BIDA complexes of Cu(II) ion were prepared by the following method: To 50 cm³ of solution containing 0.01 mol of CuCl₂·2H₂O was added 100 cm³ of solution containing 0.01 or 0.02 mol of IDA or BIDA. The resulting solution was adjusted to pH 7 with 0.02 mol of NaHCO₃ and HCl and warmed nearly to boiling point and then absolute ethanol was added until a slight turbidity appeared. Finally, the solution was cooled in an ice-bath. The resulting crystalline material was filtered and recrystallized from a water–ethanol mixture. The obtained complexes were identified by elemental analysis as CuIDA·3H₂O (Found: C, 19.39; H, 4.87; N, 5.59%. Calcd for complex: C, 19.32; H, 4.45; N, 5.63%), Na₂Cu(IDA)₂·2.5H₂O (Found: C, 23.00; H, 3.36; N, 6.62%. Calcd for complex: C, 23.06; H, 3.62; N, 6.72%), and Na₂Cu(BIDA)₂·2H₂O (Found: C, 44.54; H, 4.09; N, 4.74%. Calcd for complex: C, 44.94; H, 4.46; N, 4.76%).

*Physical Methods and Analysis.* The pH value of equilibrated solutions was measured on a Hitachi-Horiba D-5 pH meter. A Nippon Jarrell-Ash AA-781 atomic absorption and flame emission spectrophotometer was used in determination of metal ion concentration. First derivative ESR spectra were recorded on a JEOL JES-ME-3X spectrometer at X-band frequencies at room and liquid nitrogen temperatures. Resin particle samples without grinding were packed in JEOL quartz cells and their ESR spectra were measured. No change in ESR spectral shape between the wet and dry resin phases was observed, hence it follows that resin phase spectra can be obtained with the equilibrium state kept. As the amount of metal ion in the solution phase in the resin can be neglected, ESR spectra obtained are regarded as corresponding to the metal ion on the resin phase. For measurement of solution ESR spectra, a JEOL capillary cell (0.05 cm³) was used. Care was taken to keep all settings of the spectrometer knobs unchanged within a series of intensity measurements except for receiver gain amplitude.[9] Relative ESR signal intensity is defined by $(R.I.)=h_{\mathrm{pp}}(\Delta H_{\mathrm{pp}})^2/\text{Gain}$, where $h_{\mathrm{pp}}$ is peak-to-peak height in dm and $\Delta H_{\mathrm{pp}}$ is peak-to-peak width in

mT. Magnetic field was reassessed by DPPH or Mn²⁺/MgO powder marker. Mössbauer spectra were measured by the constant acceleration method on an Austin Science Associates, Inc. Mössbauer spectrometer at room and liquid nitrogen temperatures, with a source of cobalt-57 (5 mCi) diffused into a palladium foil. The scan speed of spectrometer was calibrated using a pure iron foil, which was also used as a reference for isomer shift. All spectra were fitted to Lorentzian line shapes by computer calculation. Infrared spectra were measured in KBr pellets on a JASCO Model DS-403 G grating infrared spectrophotometer in the range 4000—200 cm⁻¹.

## Results and Discussion

*General.* pH dependences of distribution ratio, amount of metal ions adsorbed on the resin phase, and ESR signal intensity of metal ions for Dowex A-1 and Unicellex UR-50 are shown in Fig. 1. The variation in $D$ values with pH for Dowex A-1 is in the same tendency as that obtained by Leyden and Underwood and obviously different from that for Unicellex UR-50.[10] This difference seems to reflect the effect of the phenolic hydroxyl group at $o$- or $p$-position in Unicellex UR-50. Amounts of metal ions adsorbed on the resin phase are expressed in $(M)_R$, metal ion μg per g dry resin. With Dowex A-1 the decrease in $(Mn)_R$ values above pH 9 may suggest an inhibition of adsorption due to hydrolysis, and on the contrary, the increase in $(Fe)_R$ values above pH 8 may suggest adsorption or adherence of hydroxyl complexes and hydroxide due to hydrolysis. With Unicellex UR-50, however, the variation in $(M)_R$ values due to hydrolysis was found in higher pH regions than that for Dowex A-1. ESR signal intensities are expressed in $(R.I.)_m$, signal intensity per g of metal ion in the dry resin. The following signals were used for the estimation of $h_{\mathrm{pp}}$ and $\Delta H_{\mathrm{pp}}$: The $M_I=-1/2$ line for VO(II), the $g_{\mathrm{eff}}\simeq2$ signal for Cr(III), Mn(II), and Gd(III), the $g_{\mathrm{eff}}\simeq4$ signal for Fe(III), and the $g_\perp$ line for Cu(II). The order of signal intensities was Mn(II)> Cu(II)>VO(II)≈Cr(III)≈Fe(III)≈Gd(III) in all of the pH regions. For each metal ion, there was no marked difference in signal intensity between Dowex A-1 and Unicellex UR-50, except for Gd(III) ion.

Table 1 shows infrared spectral data, of which assignments were made according to the literature.[11] The method is based on the simple rule that the unionized and uncoordinated COO stretching band occurs at 1750—1700 cm⁻¹ and 1200—1220 cm⁻¹, whereas the ionized and coordinated COO stretching band is at 1650—1590 cm⁻¹. For example, sodium form resin was suggested to be Type III+Type IV, having a strong absorption band at 1585 cm⁻¹ and a weak absorption band at 1210 cm⁻¹. The acting resin forms are found to transform from Type I to Type IV depending on the pH of media. As described above, resin phase infrared spectra are very efficient in suggesting the acting resin form. It should be noted that all infrared spectra have the absorption due to H₂O molecule around 3400 cm⁻¹. From the weight loss after drying at 100 °C, the water content of hydrogen form Dowex A-1 was found to be 11.03%. These H₂O molecules may influence adsorption behaviors of the metal ions, together with the buffer salts, onto the resin phase.
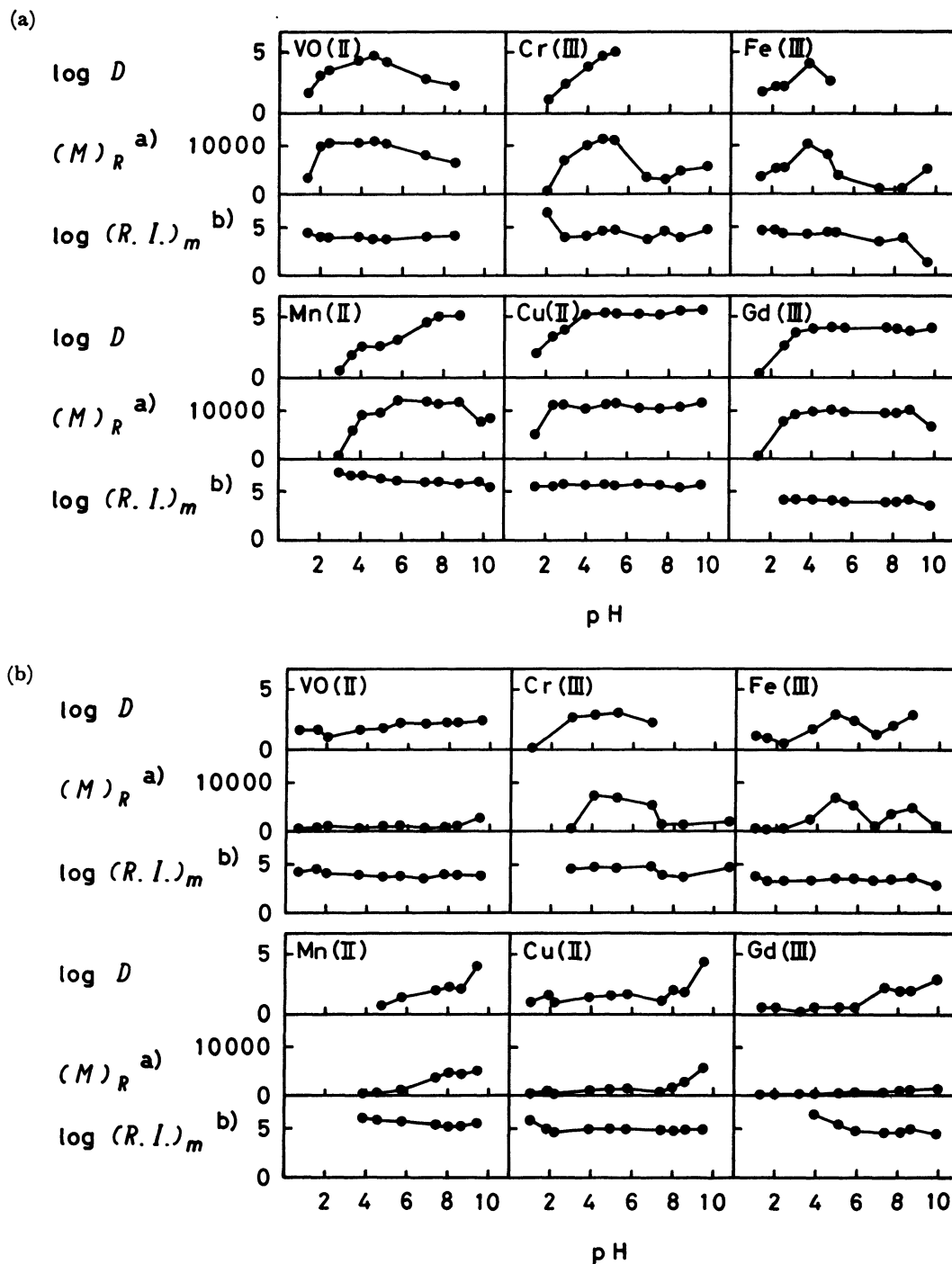
Fig. 1.  pH Dependences of distribution ratios, amounts of metal ions adsorbed on (a) Dowex A-1 and (b) Unicellex UR-50 and their ESR signal intensities.  a): Metal ion μg per g dry resin, b): signal intensity per g of metal ion in the dry resin.

*Cu(II) Ions Adsorbed on the Resin Phase.*    From the results of infrared absorption bands, with both Dowex A-1 and Unicellex UR-50 acting resin forms were suggested to be Type I in concentrated HCl media, Type II+Type III in the media of pH 4, and Type III+Type IV in the media of pH 9. ESR spectra and parameters of Cu(II) ions adsorbed on the resin phase and of some reference compounds are shown in Fig. 2 and Table 2.

In concentrated HCl media, the suggested resin form

of Type I is supported by the similarity of the resin phase ESR spectra to those of anion exchanger Dowex 1 × 4.[2] Comparing ESR spectra of Cu(II) ions adsorbed on Dowex A-1 and Unicellex UR-50 in concentrated HCl media, we find no significant change except for the free radical signal of Unicellex UR-50. Although the cation exchange capacities of these resins are approximately the same, the amount of Cu(II) ions adsorbed on Unicellex UR-50 is about one seventieth that on Dowex A-1.  This fact seems to reflect the steric

TABLE 1.   INFRARED ABSORPTION BANDS $(cm^{-1})$ OF DRY RESIN PHASES

| Sample | Equilibration conditions[a] | Carboxyl group[b] | | | Suggested resin forms[e] |
|--------|------------------------------|--------|---------|---------|-------------|
| | | -COOH | COO-M | -COOH | |
| A-1 | Na-form | | 1585 | $1210_{vw}$ | III+IV |
| A-1 | blank, concd HCl | $1730_s$ | 1600 | $1200_s$ | I |
| A-1 | blank, pH 4.40 | 1720 | 1620 | $1210_w$ | II+III |
| A-1 | blank, pH 8.58 | | $1630_{vs}$ | $1215_{vw}$ | III+IV |
| A-1 | metal, concd HCl | $1730—1710_s$ | 1610—1600 | $1210—1180_s$ | I |
| A-1 | metal, ≈pH 4 | 1720—1210 | 1625—1600 | $1210—1200_w$ | II+III |
| A-1 | metal, ≈pH 9 | | $1625—1600_{vs}$ | $1210—1200_{vw}$ | III+IV |
| UR-50 | H-form | $1700_s$ | 1620 | $1210_s$ | I |
| UR-50 | blank, concd HCl | $1725_s$ | 1590 | $1190_s$ | I |
| UR-50 | blank, pH 4.01 | 1700 | 1620 | $1200_w$ | II+III |
| UR-50 | blank, pH 8.08 | | $1610_{vs}$ | $1210_{vw}$ | III+IV |
| UR-50 | metal, concd HCl | $1725—1720_s$ | 1600—1590 | $1200—1180_s$ | I |
| UR-50 | metal, ≈pH 4 | 1720—1690 | 1620—1590 | $1210—1190_w$ | II+III |
| UR-50 | metal, ≈pH 9 | | $1620—1590_{vs}$ | $1210—1200_{vw}$ | III+IV |

a) Metal: VO(II), Cr(III), Mn(II), Fe(III), Cu(II), and Gd(III).   b) vs: Very strong, s: strong, w: weak, vw: very weak.

c) 
$$RN\begin{array}{c} CH_2COOH \\ H \\ CH_2COOH \end{array} \longrightarrow RN\begin{array}{c} CH_2COO^- \\ H \\ CH_2COOH \end{array} \longrightarrow RN\begin{array}{c} CH_2COO^- \\ H \\ CH_2COO^- \end{array} \longrightarrow RN\begin{array}{c} CH_2COO^- \\ \\ CH_2COO^- \end{array}$$

pH 1.2          pH 4.0          pH 7.4          pH 12.3
Type I          Type II          Type III          Type IV

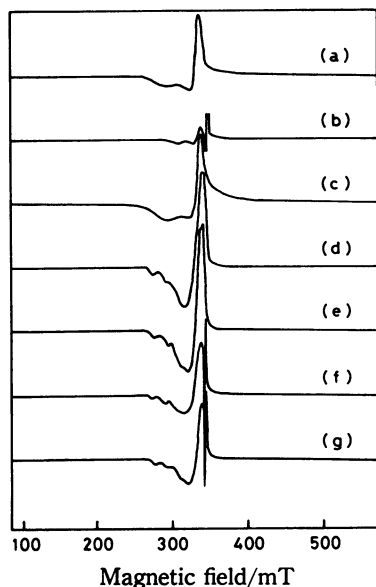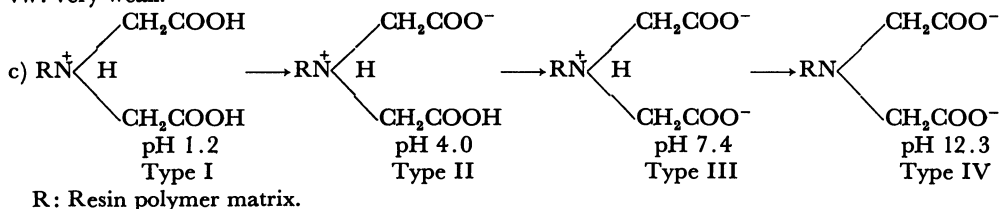R: Resin polymer matrix.



100   200   300   400   500
Magnetic field/mT

Fig. 2.   ESR spectra of Cu(II) ions adsorbed on the resin phases.
(a): A-1, concd HCl, dry, (b): UR-50, concd HCl, dry, (c): 1×4, concd HCl, dry, (d): A-1, pH 4.32, dry, (e): A-1, pH 9.30, dry, (f): UR-50, pH 3.87, dry, (g): UR-50, pH 8.60, dry.

hindrance of the phenolic hydroxyl group in Unicellex UR-50. Waki et al.[12] suggested from distribution measurements that $[CuCl_3(H_2O)]^-$ and $[Cu_2Cl_7]^{3-}$ species are present in Dowex 1 resin phases in concentrated HCl media. However, on the basis of the ESR spectra of Cu(II) ions adsorbed on the resin phase in concentrated HCl media in this work, it is not possible

TABLE 2.   ESR PARAMETERS FOR Cu(II) IONS ADSORBED ON THE RESIN PHASES

| Sample | $(Cu)_R$[a] | Parameter | | |
|--------|-------------|-----------|------|------|
| | | $A_{//}$/mT | $g_{//}$ | $g_\perp$ |
| A-1, concd HCl, wet | | | 2.27 | 2.09 |
| dry | $0.29 \times 10^4$ | | 2.29 | 2.08 |
| 1×4, concd HCl, wet | | | 2.32 | 2.09 |
| dry | $0.14 \times 10^4$ | | 2.31 | 2.09 |
| UR-50, concd HCl, wet | | | 2.25 | 2.08 |
| dry | $0.004 \times 10^4$ | | 2.23 | 2.08 |
| A-1, pH 4.32, wet | | 18.6 | 2.29 | 2.07 |
| dry | $1.58 \times 10^4$ | 18.4 | 2.31 | 2.09 |
| A-1, pH 9.30, wet | | 18.0 | 2.27 | 2.08 |
| dry | $1.09 \times 10^4$ | 19.1 | 2.29 | 2.08 |
| UR-50, pH 3.87, wet | | 16.9 | 2.30 | 2.08 |
| dry | $0.09 \times 10^4$ | 16.1 | 2.31 | 2.08 |
| UR-50, pH 8.60, wet | | 15.0 | 2.28 | 2.07 |
| dry | $0.25 \times 10^4$ | 16.9 | 2.28 | 2.07 |

a) Cu(II) ion μg per g dry resin.

to differentiate $[CuCl_3(H_2O)]^-$ and $[Cu_2Cl_7]^{3-}$ species. ESR spectra of Cu(II) ions adsorbed on the resin phase in concentrated HCl media are different from powder ESR spectra of $[CuCl_4]^{2-}$ species in solid samples.

In the media of pH 4 and pH 9, no conclusive difference in the dependence of chelation on the transformation of acting resin forms was indicated in the resin phase ESR spectra. The resin phase ESR spectra of Cu(II) ions exhibited axial spectra with $g_{//}$ and $g_\perp$ parts and Cu(II) ions on the resin phase were expected to be of distorted tetragonal structure. ESR parameters of the wet resin phase are almost identical with those of the dry resin phase, independent of the pH of media

TABLE 3.  ESR PARAMETERS OF THE RESIN PHASES
AND THE POWDERS AND FROZEN SOLUTIONS OF
Cu(II) COMPLEXES WITH IDA AND BIDA

| Sample | Parameters $g$ values ($\Delta H_{pp}$/mT) |
|---|---|
| A-1, pH10.00, $(Cu)_R = 8.93 \times 10^4$ [a] | $g_{iso} = 2.12(13.4)$ |
| UR-50, pH10.00, $(Cu)_R = 1.90 \times 10^4$ [a] | $g_{iso} = 2.10(19.6)$ |
| CuIDA·3H$_2$O powder | $g_{iso} = 2.14(17.7)$ |
| Na$_2$Cu(IDA)$_2$·2.5H$_2$O powder | $g_{//} = 2.27$, $g_{\perp} = 2.07$ |
| Cu(II) : IDA=1 : 1 frozen solution | $g_{iso} = 2.12(13.4)$ |
| 1 : 2 frozen solution | $g_{//} = 2.29$, $g_{\perp} = 2.07$ |
| Na$_2$Cu(BIDA)$_2$·2H$_2$O powder | $g = 2.08(9.3)$ |
| Cu(II) : BIDA=1 : 1 frozen solution | $g_{iso} = 2.10(14.6)$ |
| 1 : 2 frozen solution | $g_{//} = 2.24$, $g_{\perp} = 2.05$ |

a) Cu(II) ion μg per g dry resin.

and different from those of aqua complex and cation exchange resin phase.

Other comparative investigations with some reference compounds were done. Chelating behaviors of monomers, such as iminodiacetic acid (IDA) and N-benzyliminodiacetic acid (BIDA), were compared with those of the resins. ESR parameters of Cu(II) ion on the resin phase and of powders and frozen solutions of Cu(II) complexes with the monomers are listed in Table 3. The chelate stability constants of IDA with Cu(II) ions were reported as $\log K_1 = 10.55$ and $\log K_2 = 5.65$, and structures of the chelates were assumed.[13] The 1 : 1 Cu–IDA chelate shows an isotropic ESR spectrum and the 1 : 2 chelate shows an anisotropic ESR spectrum. Since the resin phase ESR spectra of Cu(II) ions are similar to the powder and frozen solution ESR spectra of the 1 : 1 chelate, the iminodiacetato group in Dowex A-1 was concluded to form the 1 : 1 chelate with Cu(II) ion.

From the above results, it seems that the iminodiacetato group must chelate as a tridentate ligand to Cu(II) ions to form the 1 : 1 chelate in all of the pH regions. However, no conclusive evidence is found for chelation through the nitrogen atom. Although coordination of the phenolic hydroxyl group in Unicellex UR-50 was indicated from the increase in $(Cu)_R$ values above pH 8, the resin phase ESR spectra seemed unchange. Thus, it may be suggested that the phenolic hydroxyl group does not contribute so significantly to the structure of Cu(II) ions on the resin phase.

The hyperfine structure of the $g_{//}$ part became obscure with the increase in $(Cu)_R$ values and the isotropic spectra with $g_{iso} = 2.12$ and $\Delta H_{pp} = 13.4$ mT for Dowex A-1 and $g_{iso} = 2.10$ and $\Delta H_{pp} = 19.6$ mT for Unicellex UR-50 were observed. In the isotropic spectra, when the gain became 100 times, the peak presumably based on $\Delta M_s = \pm 2$ could be observed at $g = 4.38$ and $g = 4.60$ for Dowex A-1 and Unicellex UR-50, respectively. This fact clearly indicates that exchange interaction must be present.

Spin-spin interaction affect the line width either as broadening (dipole-dipole interaction) or as narrowing (exchange interaction). For purely dipolar interactions between identical spins in the field of cubic symmetry, the expected line width for polycrystalline powder is
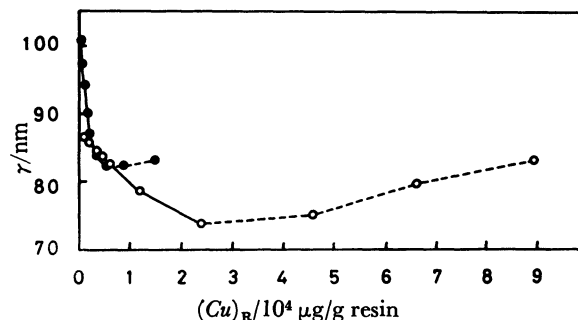


Fig. 3.  Variation of distance between the neighboring spins with amount of Cu(II) ions adsorbed on the resin phases.
○: Dowex A-1, ●: Unicellex UR-50.

given by the expressions:[14]

$$r^6 = \frac{3}{5} S(S+1) g^2 \beta^2 \frac{8.5}{\langle \Delta H^2 \rangle},$$

and

$$\langle \Delta H^2 \rangle = \frac{1}{4}(\Delta H_{pp})^2,$$

where, $r$ is the distance between the neighboring spins. On the basis of the above discussion and on the assumption that the expressions be applicable to the resin phase, the distance between the neighboring spins for Cu(II) ions on the resin phase may be estimated. The variation in the distance with $(Cu)_R$ values is shown in Fig. 3. Exchange interactions may be concluded to be present above $(Cu)_R = 2.4 \times 10^4$ μg/g resin phase for Dowex A-1 and above $0.6 \times 10^4$ μg/g resin phase for Unicellex UR-50. As previously described, nearly the same cation exchange capacities of these resins mean that the resins have almost the same amount of iminodiacetato groups. Therefore, the difference in $(Cu)_R$ value between Dowex A-1 and Unicellex UR-50 is demonstrated to be attributable mainly to the polymer matrix, that is to say, the iminodiacetato groups present in a coordination pore of Unicellex UR-50 are closer to one another than those of Dowex A-1.

*Mn(II) Ions Adsorbed on the Resin Phase.*     In concentrated HCl media, Mn(II) ion is considered to be adsorbed on the resins with anion exchange effect in the same way as Cu(II) ion. From a comparison of resin phase ESR spectra of Mn(II) ions with powder ESR spectra of $[(CH_3)_4N]_2[MnCl_4]$ and $(CH_3NH_3)_2$-$[MnCl_4]$,[15] of which ESR parameters are listed in Table 4, Mn(II) ions adsorbed on the resin phase in concentrated HCl media were suggested to be predominantly tetrahedral $[MnCl_4]^{2-}$.

ESR spectra of Mn(II) ions adsorbed on Dowex A-1 and Unicellex UR-50 in the media of pH 4 and pH 9 are shown in Fig. 4. In the resin phase ESR spectra of Mn(II) ions adsorbed in the media of pH 4, peaks with $g = 5$ and $g = 3$ were observed besides the sextet lines with $g = 2$, whereas in the media of pH 9, the sextet ones smeared out and signal intensities of the peak resulting from the zero-field splitting increased. This change in ESR spectra means that Mn(II) ions in low symmetry sites increased with increasing pH of the media. The resin phase ESR spectra of Mn(II) ions

TABLE 4. ESR PARAMETERS FOR Mn(II) IONS ADSORBED ON DOWEX A-1, DOWEX 1×4, AND UNICELLEX UR-50 IN CONCENTRATED HCl MEDIA AND SOME REFERENCE COMPOUNDS

| Sample | $(Mn)_R$[a] | Parameters | |
| --- | --- | --- | --- |
| | | $g$ | $\Delta H_{pp}/mT$ |
| Mn(II)-A-1, wet | | 2.00 | 47.4 |
| dry | $0.01 \times 10^4$ | 2.00 | 47.2 |
| Mn(II)-1×4, wet | | 2.00 | 44.6 |
| dry | $0.07 \times 10^4$ | 2.00 | 43.8 |
| Mn(II)-UR-50, wet | | 2.00 | 49.3 |
| dry | n.d. | 2.00 | 49.8 |
| $[(CH_3)_4N]_2[MnCl_4]$ powder | | 2.02 | 22.8 |
| $(CH_3NH_3)_2[MnCl_4]$ powder | | 2.01 | 3.3 |

a) Mn(II) ion μg per g dry resin.
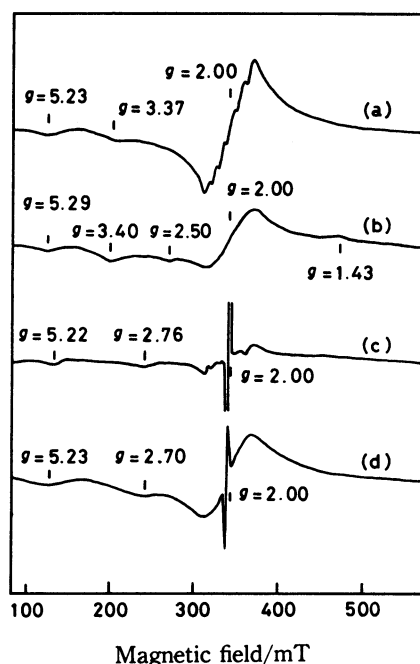


Fig. 4. ESR spectra of Mn(II) ions adsorbed on Dowex A-1 and Unicellex UR-50.
(a): A-1, pH 4.33, dry, (b): A-1, pH 9.65, dry, (c): UR-50, pH 3.83, dry, (d): UR-50, pH 8.59, dry.

adsorbed in the media above pH 4 show very interesting patterns. Dowsing et al.[16-19] interpreted several ESR spectra of high-spin $d^5$ system in terms of a spin Hamiltonian of the form

$$\mathcal{H} = g\beta HS + D[S_z^2 - \frac{1}{3}S(S+1)] + E(S_x^2 - S_y^2),$$

theoretically discussed the change of ESR spectra according to the distortion parameters, $D$ and $\lambda$ ($E/D$), and compared with observed spectra. Through analysis of the resin phase ESR spectra of Mn(II) ions in the media above pH 4, distortion parameters $D$ and $\lambda$ were tentatively assigned by their energy diagram. The data may fit $D=0.17$ cm$^{-1}$ and $\lambda=0.167$ cm$^{-1}$ for Mn(II) ions on Dowex A-1, and $D=0.29$ cm$^{-1}$ and $\lambda=0.244$ cm$^{-1}$ on Unicellex UR-50. Blumberg[20] showed that if $\lambda=0$ represents axial symmetry, $0<\lambda<1/3$ represents a departure toward rhombic symmetry, $\lambda=1/3$ represents the maximum possible rhombic symmetry, $1/3<\lambda<1$ represents a convergence toward axial symmetry again and $\lambda=1$ represents entirely axial symmetry. On the basis of the above discussion, therefore, Mn(II) ions adsorbed on the resin phase in the media above pH 4 were suggested to be of rhombic symmetry lowered from octahedral and axial symmetries perhaps by the substitution of coordinated $H_2O$ molecules for hydroxide ions. The difference between the ESR spectra of Dowex A-1 and Unicellex UR-50 resin phases shows that the phenolic hydroxyl group in Unicellex UR-50 strongly influences the coordination structure of Mn(II) ions.

*Fe(III) Ions Adsorbed on the Resin Phase.* The dry resin phase ESR spectra of Fe(III) ions adsorbed in concentrated HCl media and $[FeCl_4]^-$ adsorbed on Amberlyst A-26 in diisopropyl ether media are shown in Fig. 5 and the analyzed data are listed in Table 5. For comparison, powder ESR spectral parameters of $(CH_3NH_3)_3[FeCl_6]\cdot CH_3NH_3Cl$, $(NH_4)_2[FeCl_5(H_2O)]$, and $(CH_3)_4N[FeCl_4]$ and solution ESR spectral parameters of $[FeCl_4]^-$ in diisopropyl ether media are included in Table 5. The resin phase ESR spectra of Fe(III) ions adsorbed on Dowex A-1 in concentrated HCl media seem to have patterns with $g_{eff}=4$ and $g_{eff}\cong2$ similar to those on Dowex 1×4 and of $[FeCl_4]^-$ adsorbed on Amberlyst A-26. The $g_{eff}\cong2$ signal is

TABLE 5. ESR PARAMETERS FOR Fe(III) IONS ADSORBED ON THE RESIN PHASES IN CONCENTRATED HCl MEDIA AND $[FeCl_4]^-$ ADSORBED ON AMBERLYST A-26 IN DIISOPROPYL ETHER MEDIA

| Sample | $(Fe)_R$[a] | Parameters | |
| --- | --- | --- | --- |
| | | $g$ values | ($\Delta H_{pp}/mT$) |
| Fe(III)-A-1, dry | $0.68 \times 10^4$ | 4.41(18.1), | 2.02(24.4) |
| Fe(III)-A-1, dry[b] | $4.80 \times 10^4$ | 4.36(19.0), | 2.03(73.1) |
| Fe(III)-1×4, dry | $0.74 \times 10^4$ | 4.42(20.0), | 2.00(32.5) |
| Fe(III)-1×4, dry[b] | $8.80 \times 10^4$ | 4.45( 5.2), | 2.04(70.9) |
| Fe(III)-UR-50, dry | $0.31 \times 10^4$ | 4.17(22.6), | 2.02(55.8) |
| $[FeCl_4]^-$-A-26, dry | $0.47 \times 10^4$ | 4.32(16.9), | 2.02(62.4) |
| $H[FeCl_4]$ diisopropyl ether solution | | | 2.02(25.2) |
| $(CH_3)_4N[FeCl_4]$ powder | | | 2.02(21.3) |
| $(NH_4)_2[FeCl_5(H_2O)]$ powder | | | 2.02(25.1) |
| $(CH_3NH_3)_3[FeCl_6]\cdot CH_3NH_3Cl$ powder | | | 2.02( 8.8) |

a) Fe(III) ion μg per g dry resin.    b) The column method.
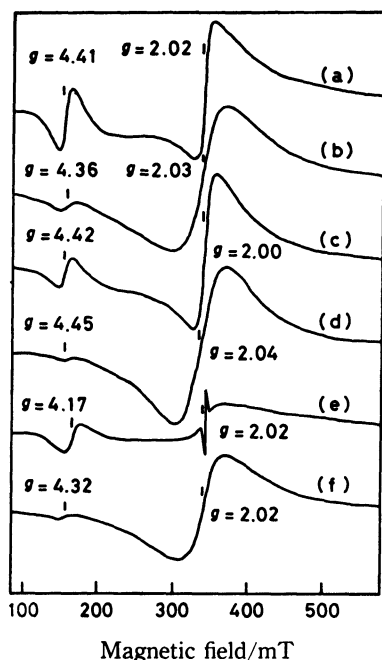
Fig. 5. ESR spectra of Fe(III) ions adsorbed on the resin phases in concentrated HCl media and [FeCl$_4$]$^-$ adsorbed on Amberlyst A-26 in diisopropyl ether media. (a): Fe(III)–A-1, dry, (b): Fe(III)–A-1, dry (column method), (c): Fe(III)–1×4, dry, (d): Fe(III)–1×4, dry (column method), (e): Fe(III)–UR-50, dry, (f): [FeCl$_4$]$^-$–A-26, dry.
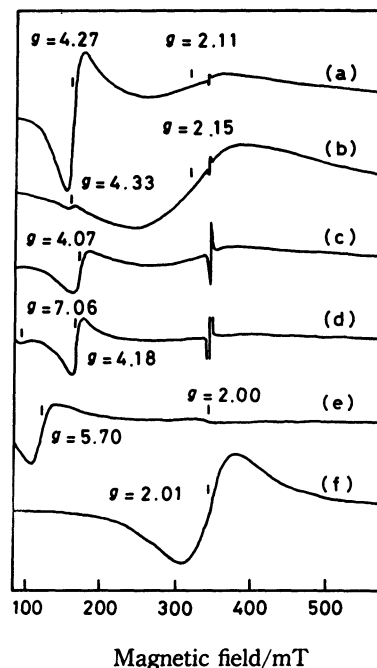


Fig. 6. ESR spectra of Fe(III) ions adsorbed on Dowex A-1 and Unicellex UR-50 and reference compounds. (a): A-1, pH 4.32, dry, (b): A-1, pH 10.05, dry, (c): UR-50, pH 5.00, dry, (d): UR-50, pH 8.80, dry, (e): Fe(III)–meso-tetraphenylporphine chloride, (f): Fe(III) hydroxide.

considered to be due to [FeCl$_4$]$^-$ species. On the other hand, with the resin phase ESR spectrum of Fe(III) ions adsorbed on Unicellex UR-50 in concentrated HCl media, the intensity of the $g_{eff}\cong2$ signal is not so large as that of Dowex A-1. It is apparent that the $g_{eff}\cong4$ signal is not attributable to the coordination by the iminodiacetato group because of the similarity to the resin phase ESR spectra of Fe(III) ions adsorbed on Dowex 1×4 in concentrated HCl media and on Amberlyst A-26 in diisopropyl ether media, as can be seen in Fig. 5.

ESR signals close to $g=4$ often occur in biological materials and clay minerals. Castner et al.[21] proposed $D=0$ and $E\neq0$ to account for the $g=4.27$ spectrum found for iron(III) ions in glass. Griffith[22] showed that d$^5$ ion is in special environments, then $D$ need not be zero but shall be small. The special environments are tetrahedral MA$_2$B$_2$, distorted octahedral MA$_6$, and octahedral MA$_3$B$_3$. Of these environments, the $g_{eff}\cong4$ signal is attributable to tetrahedral MA$_2$B$_2$. From the above discussion, since the resin phase ESR spectrum of Fe(III) ions adsorbed in concentrated HCl media shows two signals with $g_{eff}\cong4$ and $g_{eff}\cong2$, the MA$_2$B$_2$ species, in addition to the MA$_4$ species, [FeCl$_4$]$^-$ is considered to be present. That is, besides the species [FeCl$_4$]$^-$ simply adsorbed with the anion exchange effect, lower symmetric anion species such as a mixed ion cluster bridging by Cl atoms may be considered to be adsorbed.

Figure 6 shows the ESR spectra of Fe(III) ions adsorbed on Dowex A-1 and Unicellex UR-50 in the media of pH 4 and pH 9. In the resin phase ESR

spectra of Fe(III) ions adsorbed on Dowex A-1 in the media above pH 8, a broad signal with $g_{eff}\cong2$ and $\Delta H_{pp}\cong100$ mT and a weak signal with $g_{eff}\cong4$ were observed. As this broad signal is similar to that of Fe(III) hydroxide powder, of which a spectrum is included in Fig. 6, most of Fe(III) ions on the resin phase are considered to exist as hydroxyl complex or hydroxide. In the resin phase ESR spectra of Fe(III) ions adsorbed on Unicellex UR-50, however, a broad signal with $g_{eff}\cong2$ was not observed and the $g_{eff}\cong4$ signal intensity increased in the pH region where hydroxide forms. The $g_{eff}\cong4$ signal in the media of pH 4 was analyzed in the same way with Mn(II) ion. The data may be $D>0.23$ cm$^{-1}$ and $\lambda=-1/3$ cm$^{-1}$. Therefore, the Fe(III) ions adsorbed on the resin phase in the media of pH 4 are suggested to be of rhombic symmetry similarly to Mn(II) ions. For comparison, an ESR spectrum of Fe(III)–porphine complex, which is characterized by strong axial symmetry, is also shown in Fig. 6.[16] Although the $g_{eff}\cong4$ signal for pH 4 is apparently similar to that for concentrated HCl media, it must be emphasized that the adsorbed species are different.

Especially for Fe(III) ions, resin phase Mössbauer spectra were observed by using metallic iron-57 and spectral parameters at room temperature are listed in Table 6. The Mössbauer parameters suggest that the iron adsorbed on the resin phase in concentrated HCl media is trivalent of high-spin configuration and of tetrahedral symmetry[23] and a small peak that shows lower symmetric species was observed in a Mössbauer spectrum at liquid nitrogen temperature, whereas those for the iron adsorbed in the media of pH 4 suggest that

Table 6. Mössbauer parameters for iron
adsorbed on the resin phases

| Sample | I.S.[a] | Q.S.[a] | L.W.[a] |
| | mm s⁻¹ | mm s⁻¹ | mm s⁻¹ |
|---|---|---|---|
| A-1, concd HCl | 0.19 | 0.36 | 0.24 |
| A-1, pH 4.00 | 0.37 | 0.65 | 0.72 |
| A-1, pH 9.00 | 0.37 | 0.80 | 0.53 |
| UR-50, concd HCl | | n.d. | |
| UR-50, pH 4.00 | 0.45 | 0.82 | 0.76 |
| UR-50, pH 9.00 | 0.41 | 0.87 | 0.56 |

a) I.S.: Isomer shift; Q.S.: quadrupole splitting; L.W.: line width.

the iron on the resin phase is trivalent of high-spin configuration and very distorted symmetry of tetrahedron rather than octahedron as judged from the value of isomer shift. In the media of pH 9 the parameters are similar to those of iron(III) hydroxide.[24] This fact suggests the adherence of hydroxide in addition to the adsorption of hydroxyl complex and accounts for the increase in $(Fe)_R$ values and for the appearance of the broad ESR signal with $g_{eff} \cong 2$.

The Mössbauer parameters at room temperature for the iron adsorbed on Unicellex UR-50 in the media of pH 4 suggest that the iron on the resin phase is trivalent of high-spin configuration and distorted octahedral symmetry. All Mössbauer spectra were also measured at the liquid nitrogen temperature but no significant suggestion was obtained.

From the above discussion, it may be concluded that the iminodiacetato group in Dowex A-1 coordinates as a tridentate ligand to Fe(III) ion and a distorted tetrahedron is completed by water molecules, whereas in

Unicellex UR-50 the phenolic hydroxyl group also coordinates in alkaline media and a distorted octahedron is completed by water molecules.
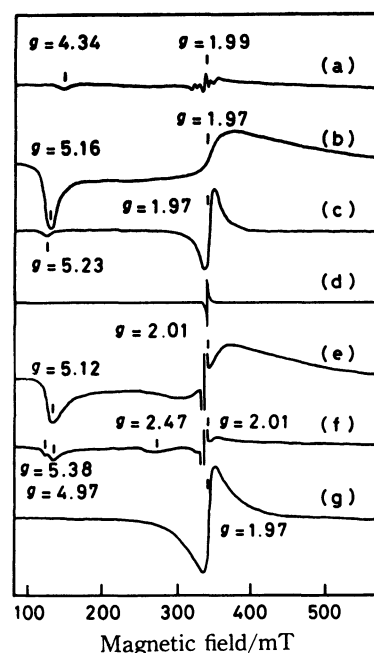


Fig. 8. ESR spectra of Cr(III) ions adsorbed on Dowex A-1 and Unicellex UR-50 and hydroxide.
(a): A-1, concd HCl, dry, (b): A-1, pH 3.90, dry, (c): A-1, pH 8.50, dry, (d): UR-50, concd HCl, dry, (e): UR-50, pH 4.04, dry, (f): UR-50, pH 8.38, dry, (g): Cr(III) hydroxide.
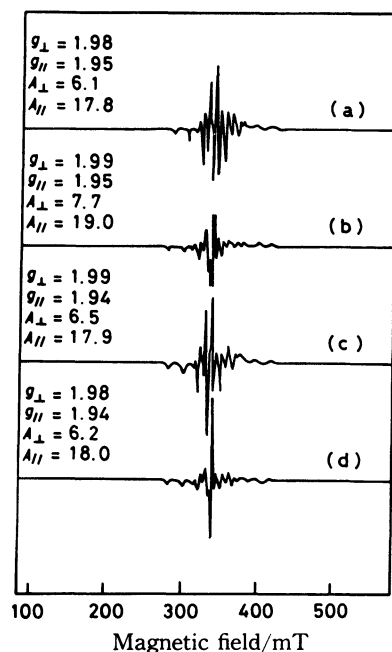


Fig. 7. ESR spectra of VO(II) ions adsorbed on Dowex A-1 and Unicellex UR-50.
(a): A-1, concd HCl, dry, (b): UR-50, concd HCl, dry, (c): A-1, pH 3.82, dry, (d): UR-50, pH 3.58, dry. $A$ values are expressed in mT.
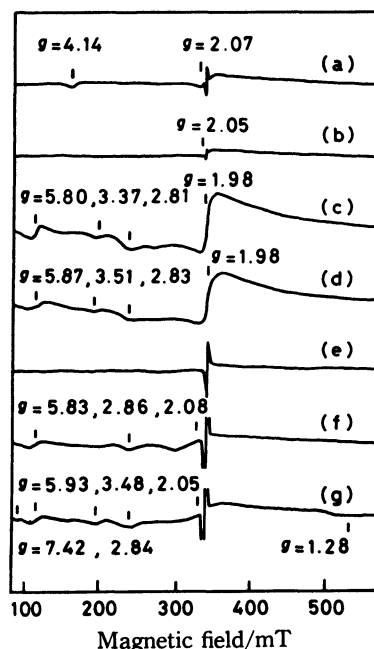


Fig. 9. ESR spectra of Gd(III) ions adsorbed on Dowex A-1, Dowex 1 × 4 and Unicellex UR-50.
(a): A-1, concd HCl, dry, (b): 1 × 4, concd HCl, dry, (c): A-1, pH 3.91, dry, (d): A-1, pH 8.55, dry, (e): UR-50, concd HCl, dry, (f): UR-50, pH 3.84, dry, (g): UR-50, pH 8.59, dry.

*Other Paramagnetic Metal Ions Adsorbed on the Resin Phase.*
ESR spectra of VO(II), Cr(III), and Gd(III) ions adsorbed on the resin phase are shown in Figs. 7, 8, and 9. VO(II) ions adsorbed on the resin phase show anisotropic spectra and ESR parameters for VO(II) ions on Dowex A-1 and Unicellex UR-50 are virtually unchanged. In the resin phase infrared spectra of VO(II) ions adsorbed on Dowex A-1 and Unicellex UR-50 in the media of pH 9, V–O stretching bands were observed at 970 and 1010 cm$^{-1}$, respectively. This fact may reflect the coordination of the phenolic hydroxyl group in Unicellex UR-50. VO(II) ions adsorbed on Dowex A-1 and Unicellex UR-50 are considered to be of distorted tetragonal symmetry completed by water molecules.

In the resin phase ESR spectra of Cr(III) ions adsorbed on Dowex A-1 in the media of pH 4, signals with $g \cong 5$ and $g = 1.97$ resulting from the zero-field splitting were observed. In the resin phase ESR spectra of Cr(III) ions adsorbed on Unicellex UR-50 in alkaline media, the $g \cong 5$ signal splitted into $g = 5.28$ and $g = 4.93$ and the $g \cong 2.5$ signal appeared. This fact may reflect the coordination of the phenolic hydroxyl group in Unicellex UR-50.

Gd(III) ions adsorbed on Dowex A-1 and Unicellex UR-50 also show signals resulting from the zero-field splitting. The difference in $(Gd)_R$ values and resin phase ESR spectral patterns between Dowex A-1 and Unicellex UR-50 also may reflect the coordination of the phenolic hydroxyl group in Unicellex UR-50.

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