Roles of Residual Silanol in Solid Phase Extraction of Copper to Octadecylsilyl Silica in the Presence of Acetylacetone

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Abstract

Batchwise studies have demonstrated that the retention of acetylacetone (Haa) from an aqueous phase in non-endcapped octadecylsilyl (ODS) silica with silanol intentionally left (NEC) is stronger than the retention in endcapped ODS silica under ambient pressure, due to the enhanced wettability and the contribution of adsorption to silanol (-SiOH), as well as the distribution into the ODS phase. Equilibrium analysis on solid phase extraction (SPE) of copper ion with Haa to NEC has indicated the adsorption of 1:1 species by the proton replacement reaction with silanol to give [-SiOCu(aa)] at relatively low Haa concentrations and the adsorption of [Cu(aa)₂] to silanol, as well as the distribution of [Cu(aa)₂] into the ODS phase. These adsorbed- and distributed-species of the same composition could be differentiated by ESR spectroscopy. The advantages of residual silanol in SPE of metal ions are discussed.

Keywords: Solid phase extraction, octadecylsilyl silica, residual silanol, copper, acetylacetone, ESR.
Introduction

Phase transfer has been effectively used for separation and purification of chemical substances. The transfer from an aqueous phase to a solid phase, which is used as a separating medium alternative to organic solvents, is especially promising with a view to reducing the environmental load. In this context, octadecylsilyl (ODS) silica has been successfully developed as a stationary phase for reversed phase liquid chromatography (RPLC) by jumping over two hurdles. The first difficulty, severe tailing of certain compound's peak due to interaction of their basic functional groups with residual silanol, was overcome by endcapping treatment with trimethylsilyl (TMS) group or by thermal treatment of base silica. The second difficulty, reduction in retention or in reproducibility of the retention time due to dewetting of micropores in the case of using a highly aqueous mobile phase, was overcome by increasing the backpressure, increasing the pore size of silica gel, or embedding a hydrophilic anchor.

The ODS silica thus developed has also been utilized as an extracting medium in solid phase extraction (SPE) for the preconcentration of organic analytes and for the removal of foreign substances. Because SPE is occasionally performed under ambient pressure, conditioning the ODS silica by using some water-miscible organic solvents, such as methanol and acetonitrile, prior to introduction of an aqueous sample solution is inevitable, in order to enhance the wettability of the ODS silica and thereby improve the mass transfer at the interface. In a previous work, we have studied the retention of a certain nitrogen-containing compound in an ODS silica subjected to sufficient endcapping treatment and an ODS silica with silanol intentionally left, under ambient pressure. This study has revealed that residual silanol enhances the wettability of the ODS silica even in the absence of any water-miscible organic solvent, that the retention of the compound may be attributed to the sum of the
Langmuir adsorption term and the simple distribution term, and that a high retention ratio may be obtained even at a low total concentration by virtue of the Langmuir adsorption term.

SPE has also been utilized for separation and preconcentration of metal ions in the form of complexes with some chelating reagents in ODS silica. Since endcapping treatment was inevitably insufficient in the initial stage of development of ODS silica, it was reported that the residual silanol was involved in the retention of metal ions, in addition to the simple distribution of the neutral complex. More specifically, a positively-charged, coordinatively-unsaturated complex was suggested to interact with a deprotonated silanol group (ion-pair formation or coordination) in retention of divalent and trivalent metal ions using β-diketones. In the first place, on silica gel, a positively-charged, coordinatively-saturated complex was ion-exchanged, whereas a neutral, coordinatively-saturated complex was retained by hydrogen bonding between coordinating oxygen atoms and silanol hydrogen. These reactions are also expected to contribute to the retention of metal ions in SPE to ODS silica. With development of the endcapping technique, however, such contributions have become relatively insignificant and have not been viewed. Inspired by the recent findings of the positive effects of residual silanol on retention of organic compounds, SPE of divalent copper ion with acetylacetone (Haa) as a chelating reagent to ODS silica with residual silanol is extensively explored. Two species (Cu:Haa = 1:0 and 1:1) are identified in the absence of or in the presence of a substoichiometric amount of Haa, whereas two 1:2 species which may be differentiated by the ESR spectra are identified in the presence of an excess Haa.

**Experimental**

*Materials*
Silica gel (SG, pour size of 50 Å; specific surface area of 680 ± 50 m² g⁻¹) was reacted with trichlorooctadecylsilane to give non-endcapped ODS silica (NEC) according to the literature.¹²,²² A portion of NEC was thoroughly washed and then endcapped by trimethylchlorosilane to give endcapped ODS silica (EC). After equilibration at 25 °C and at a relative humidity of 50%, both NEC and EC were subjected to the determination of the carbon content (CC) by elemental analysis and of the water content (WC) by Karl-Fischer coulometry. The chemical amounts of X in a unit mass (MCₓ/mol kg⁻¹; X: ODS, TMS (trimethylsilyl) and W (adsorbed water)) calculated from these parameters are summarized in Table 1.

The MCODS of NEC is lower than the typically reported values.²³ This is because both the reaction of trichlorooctadecylsilane with surface silanol and the polymerization of ODS group were interfered due to the smaller pore size of SG used in this study than those commonly used (100 Å). This is supported by the fact that more than 1.5 times the chemical amount of TMS was introduced into NEC by endcapping. The MCW value of SG suggests that one water molecule or partly two water molecules remain on each silanol group (usually, 5.4 mmol g⁻¹) under the present experimental condition of the relative humidity of 50%. Nearly the same ΣMCₓ values of NEC and EC, which are appreciably smaller than that of SG, suggest that one water molecule interacts with each silanol with respect to both NEC and EC and that introduction of one TMS group reduces one hydratable residual silanol.

Retention of Haa and [Co(aa)₃] in ODS silicas

Aqueous solutions containing a compound (R) at varying concentrations (Ce/mol L⁻¹, volume (V) of 5 mL) and 0.1 mol L⁻¹ KNO₃ were shaken with an aliquot of ODS silica or SG (mass (m) of 0.5 g for R: Haa and 0.02 g for R: [Co(aa)₃], Co complex with Haa) for 24 hours at 25 °C. After centrifugation, the UV spectrum of the supernatant was recorded for measurement of the
concentration of R in the aqueous phase, \([R]/\text{mol L}^{-1}\). The retention of R in the solid phase, \([R]_{S,\text{obsd}}/\text{mol kg}^{-1}\) (hereinafter, the subscript S denotes that the species is in the solid phase) was calculated by Eq. (1).

\[
[R]_{S,\text{obsd}} = (C_R - [R]) \times V/m
\]  

(1)

Retention of copper in ODS silicas in the presence of and in the absence of Haa

Suspensions of an aliquot ODS silica or SG (\(m = 0.5\) g) in aqueous solutions containing \(\text{Cu}^{2+}\) (\(C_{\text{Cu}} = 10^{-4.0}, 10^{-3.0}, \text{and } 10^{-2.5} \text{ mol L}^{-1}, V = 20\) mL), Haa (\(C_{\text{Haa}} = 0, 10^{-4.0}, 10^{-3.7}, 10^{-3.5}, 10^{-3.0}, 10^{-2.5}, 10^{-2.0}, 10^{-1.5}, 10^{-1.0} \text{ mol L}^{-1}\)) and 0.1 mol L\(^{-1}\) KNO\(_3\) (pH was adjusted by HNO\(_3\) or KOH) were shaken for 24 hours at 25 °C. After centrifugation, the supernatant was subjected to pH measurement and determination of the total concentration of copper in an aqueous phase, \(C_{\text{Cu,w}} = [\text{Cu}^{2+}] + [\text{Cu(aa)}]^+ + [\text{Cu(aa)}_2]\), by atomic absorption spectrometry. The fractional retention of copper, \(FR_{\text{Cu,obsd}}\), given by Eq. (2) was used for equilibrium analysis, so that the experiments at the different total concentrations of \(\text{Cu}^{2+}\) were treated evenly.

\[
FR_{\text{Cu,obsd}} = (C_{\text{Cu}} - C_{\text{Cu,w}})/C_{\text{Cu}}
\]  

(2)

The NEC and EC which were used for SPE of \(\text{Cu}^{2+}\) (\(C_{\text{Cu}} = 10^{-4.0} \text{ mol L}^{-1}\)) with Haa (\(C_{\text{Haa}} = 10^{-2.0} \text{ mol L}^{-1}\)) at pH 4 (\(FR_{\text{Cu}} = 0.92\) and 0.27, respectively) were subjected to the ESR measurement (JEOL, JES-FA200) after removal of the remaining supernatant on the surface by filter paper.
Results and Discussion

Retention of Haa and [Co(aa)₃] in ODS silicas

The retention isotherms of acetylacetone (R: Haa) to NEC and EC are shown in Fig. 1. The silica gel SG showed negligibly small retention. Both the isotherms suggested substantially the same characteristics as those of nitrogen-containing compounds, and were thus fitted by Eq. (3) as the sum of a simple distribution term and a Langmuir adsorption term by hydrogen bonding between oxygen atom of R and silanol hydrogen:

\[
[R]_{S,\text{cald}} = K_{D,R}[R] + \frac{A_R 	imes K_{ad,R}[R]}{1 + K_{ad,R}[R]}
\]  (3)

where \(K_{D,R}\) is the distribution constant of R given in terms of L kg\(^{-1}\); \(K_{ad,R}\) is the adsorption constant of R given in terms of mol\(^{-1}\) L; and \(A_R\) is the saturated adsorption capacity of R given in terms of mol kg\(^{-1}\). These three parameters were respectively optimized to give a minimum error square sum on retention given by Eq. (4) and are summarized in Table 2.

\[
U = \sum ([R]_{S,\text{obsd}} - [R]_{S,\text{cald}})^2
\]  (4)

The calculated retention was in good agreement with the experimental points in both systems. The contributions of adsorption and distribution are also shown in Fig. 1.

In the retention to NEC, the superiority between these contributions is reversed at the Haa concentration of about 0.15 mol L\(^{-1}\). In the retention to EC, on the other hand, the contribution of adsorption is negligibly small over the Haa concentration range in this study. The \(K_{D,R}\) value decreases to be less than half by endcapping. This is attributed to a decrease in the fraction of the ODS phase that actually functions, due to dewetting at an ambient pressure.\(^5\)\(^-\)\(^8\)
With regard to the adsorption term, on the other hand, the $A_R$ value decreases to be less than one tenth by endcapping, due to reduction in the chemical amount of residual silanol group serving as a hydrogen-bond donor. In contrast, the $K_{ad,R}$ value increases by about 5 times. Although the adsorption is attributed to the hydrogen bonding in the first place, the concurrent lipophilic interaction between the organic moiety of R and the ODS groups may become more favorable by the endcapping to enhance the adsorption.

The retention isotherm of [Co(aa)$_3$], which is inert and may be regarded as one compound, in NEC is shown in Fig. S1 (Supporting Information). Although the solubility of the complex limited the experimental conditions ([Co(aa)$_3$] after equilibration up to 0.002 mol L$^{-1}$), the experimental data were similarly reproducible by Eq. (3) using the constants given in Table 2. The logarithmic $K_{D,R}$ value of [Co(aa)$_3$] was about three times that of Haa, as usually observed in the liquid-liquid system. The adsorption term may be attributed to the hydrogen bonding with residual silanol proton, as found for thin-layer chromatography of inert trivalent metal complexes with Haa on unmodified silica gel. The $A_R$ value of [Co(aa)$_3$] is appreciably smaller than that of Haa, whereas the $K_{ad,R}$ value is larger than that of Haa by more than two orders of magnitude. Such enhancement of the interaction may be attributed to the interactions of silanol with a plurality of coordinating oxygen atoms, which are located in the $fac$-plane of an octahedron of the metal complex. This type of interactions was characterized by various spectroscopic techniques in the synergistic extraction of metal ions with Haa and dichlorophenol in the liquid-liquid extraction system.

**Overall characteristics of copper retention in ODS silicas**

The effects of pH on FR$_{Cu}$ in the retention of a fixed total concentration of Cu$^{2+}$ ($C_{Cu} = 10^{-4.0}$ mol L$^{-1}$) with varying total concentrations of Haa ($C_{Haa} = 0 - 10^{-1}$ mol L$^{-1}$) in NEC are shown in Fig. 2. Retention of Cu$^{2+}$ was observed even in the absence of Haa. This is
attributed to ion exchange at residual silanol groups to give a species such as \([(-\text{SiO})_2\text{Cu}]_s\) given by Eq. (5), as found for alkali metal ions on ODS silica\(^{27}\) and for divalent metal ions including \(\text{Cu}^{2+}\) on silica gel.\(^{28}\)

\[
\text{Cu}^{2+} + 2[\text{SiOH}]_s \rightleftharpoons [(-\text{SiO})_2\text{Cu}]_s + 2 \text{H}^+ \quad (5)
\]

Since the chemical amount of residual silanol (1 mmol in 0.5 g ODS silica) is much larger than the total amount of \(\text{Cu}^{2+}\) (0.002 to 0.06 mmol in 20 mL) under the present experimental conditions, the equilibrium constant \(K_{\text{Cu}}\), which includes the chemical amount of silanol, is expressed as follows:

\[
K_{\text{Cu}} = \frac{[(-\text{SiO})_2\text{Cu}]_s\text{[H}^+]^2}{[\text{Cu}^{2+}]}
\]

This constant was determined to be \(K_{\text{Cu}} = 10^{-11.7}\), which reproduces the experimental points as shown in Fig. 2.

In the presence of the same total concentration (substoichiometric concentration as \([\text{Cu(aa)}_2]\)) of Haa as that of \(\text{Cu}^{2+}\), the retention curve was appreciably shifted to a more acidic region, compared with the retention curve in the absence of Haa. This finding indicates a species such as \([(-\text{SiO})\text{Cu(aa)}]_s\). Interaction of deprotonated silanol with charged species such as \([(-\text{SiO})\text{M}^{II}(\text{mb})]_s\) and \([(-\text{SiO})\text{M}^{III}(\text{mb})_2]_s\) (mb: monoanionic bidentate ligand) was previously suggested.\(^{15-19}\) A further increase in \(C_{\text{Cu}}\) made the retention curve shift to a further acidic side as usually observed in the ordinary liquid-liquid extraction system. It is, however, unusual that the shift and even the saturated \(\text{FR}_{\text{Cu}}\) became smaller at \(C_{\text{Haa}} \geq 10^{-1.5}\ \text{mol L}^{-1}\). These suggest the competition in adsorption between Haa and \([\text{Cu(aa)}_2]\). The effects of pH on \(\text{FR}_{\text{Cu}}\) at higher \(\text{Cu}^{2+}\) concentrations (\(C_{\text{Cu}} = 10^{-3.0}, 10^{-2.5}\ \text{mol L}^{-1}\)) at a fixed \(C_{\text{Cu}}:C_{\text{Haa}}\) ratio of 100 are shown in Fig.
S2 (Supporting Information). A further decrease in the saturated FR$_{Cu}$ supports such competition. With regard to EC, in contrast, Cu$^{2+}$ was not retained enough for the equilibrium analysis.

**Equilibrium Analysis**

Scheme 1 shows all the species relevant to the retention of Cu$^{2+}$ in NEC in the presence of Haa. The equilibria in an aqueous phase have been sufficiently elucidated, so that the literature values are used.

\[
\text{Haa} \rightleftharpoons H^+ + \text{aa}^- \quad K_a = 10^{-8.80} \quad (6)
\]

\[
\text{Cu}^{2+} + \text{Haa} \rightleftharpoons [\text{Cu(aa)}]^+ + H^+ \quad K_1 = 10^{-0.64} \quad (7)
\]

\[
[\text{Cu(aa)}]^+ + \text{Haa} \rightleftharpoons [\text{Cu(aa)}_2]^+ + H^+ \quad K_2 = 10^{-2.20} \quad (8)
\]

In the solid phase, four species including [(-SiO)$_2$Cu]$_s$ are expected based on the findings described above. One of them is formed by the chemical reaction given by Eq. (9):

\[
\text{Cu}^{2+} + \text{Haa} + [-\text{SiOH}]_s \rightleftharpoons [-\text{SiOCu(aa)}]_s + 2 H^+ \quad (9)
\]

As in the case of [(-SiO)$_2$Cu]$_s$, the following constant may be defined:

\[
K_{Cu(aa)} = [-\text{SiOCu(aa)}]_s[H^+]^2/([\text{Cu}^{2+}][\text{Haa}])
\]

The 1:2 species [Cu(aa)$_2$] is expected to be involved in both the distribution ($K_{D,Cu(aa)_2}$) and the adsorption ($A_{Cu(aa)_2}$, $K_{ad,Cu(aa)_2}$) as found for [Co(aa)$_3$]. The competitive adsorption of [Cu(aa)$_2$] and Haa to silanol may be expressed as described previously.\(^{30}\)
\[ [\text{Cu}(\text{aa})_2]_{\text{S,ad}} = \frac{A_{\text{Cu}(\text{aa})_2} \times K_{\text{ad,Cu}(\text{aa})_2} [\text{Cu}(\text{aa})_2]}{1 + K_{\text{ad,Haa}} [\text{Haa}] + K_{\text{ad,Cu}(\text{aa})_2} [\text{Cu}(\text{aa})_2]} \] (10)

Since the formation of [aa'] is negligible under the present experimental conditions, the mass balances on Cu\(^{2+}\) and Haa are expressed by Eqs. (11) and (12).

\[ C_{\text{Cu}} = [\text{Cu}^{2+}] + [\text{Cu}(\text{aa})'] + [\text{Cu}(\text{aa})_2] + m/V \times ([(-\text{SiO})_2\text{Cu}]_S + [-\text{SiOCu}(\text{aa})]_S + [\text{Cu}(\text{aa})_2]_{S,D} + [\text{Cu}(\text{aa})_2]_{S,ad}) \] (11)

\[ C_{\text{Haa}} = [\text{Haa}] + [\text{Cu}(\text{aa})'] + 2 \times [\text{Cu}(\text{aa})_2] + m/V \times ([\text{Haa}]_D + [\text{Haa}]_{ad} + [-\text{SiOCu}(\text{aa})]_S + 2 \times [\text{Cu}(\text{aa})_2]_{S,D} + 2 \times [\text{Cu}(\text{aa})_2]_{S,ad}) \] (12)

The calculated fractional retention of Cu\(^{2+}\), \(F_{\text{Cu,obsd}}\), is obtained by Eq. (13) with use of \([\text{Cu}^{2+}]\) and [HL] which simultaneously satisfy Eqs. (5 - 12).

\[ F_{\text{Cu,obsd}} = ([(-\text{SiO})_2\text{Cu}]_S + [-\text{SiOCu}(\text{aa})]_S + [\text{Cu}(\text{aa})_2]_{S,D} + [\text{Cu}(\text{aa})_2]_{S,ad}) \times m/(C_{\text{Cu}} \times V) \] (13)

Four unknown constants relevant to three of the four species contributing to the retention are optimized to give minimum errors on FR:

\[ \Delta F_{\text{R}} = \sqrt{\sum (F_{\text{Cu,obsd}} - F_{\text{Cu,cald}})^2/\text{ND}} \] (14)

where ND is the total number of data. Table S1 (Supporting Information) shows the mean
errors in relative retention after optimization of seven combinations based on the presence and the absence of three species. The ΔFR value was large on the assumption of the presence of any one of the species. Only a combination of [(−OSi)Cu(aa)]₈ and [Cu(aa)₂]₈,ad among the respective combinations of two species showed satisfactory agreement. Although inclusion of [Cu(aa)₂]₈,D as the third species did not sufficiently improve the error to such a level that indicates its presence, it was tentatively adopted here.

The optimized $K_{Cu(aa)}$ was $10^{-4.18}$; the constants relevant to [Cu(aa)₂]₈,D and [Cu(aa)₂]₈,ad are included in Table 2. The contributions of the respective species are shown in Figs. S2 and S3 (Supporting Information). At $C_{Cu} = 10^{-4.0}$ mol L⁻¹ and at $C_{Haa} = 10^{-4.0}$ mol L⁻¹, [-SiO(Cu(aa))]₈ is mainly responsible for the retention; the adsorption of [Cu(aa)₂]₈,ad, which inevitably leaves Cu²⁺ in the aqueous phase, rather interferes with the retention of Cu²⁺ at pH of around 5 to give a more gradual retention curve. The contribution of [Cu(aa)₂]₈,ad is comparable to that of [-SiO(Cu(aa))]₈ even in the presence of the stoichiometric amount of Haa but becomes major at $C_{Haa} \geq 10^{-3.0}$ mol L⁻¹. The retention curve of Cu²⁺ is shifted to a lower pH region due to the enhanced formation of [Cu(aa)₂] in the aqueous phase by an increase in $C_{Haa}$. At $C_{Haa} \geq 10^{-1.5}$ mol L⁻¹, however, the competitive adsorption of Haa interferes with adsorption of [Cu(aa)₂] and reduces FR. The contribution of [Cu(aa)₂]₈,D, which is negligible at $C_{Cu} = 10^{-4}$ mol L⁻¹, increases with an increase in $C_{Cu}$ to $10^{-3.0}$ and $10^{-2.5}$ mol L⁻¹ (Fig. S2). The logarithmic value of $K_{D,Cu(aa)²}$ is around twice that of Haa, as usually observed in the liquid-liquid system; this supports the presence of this species. The $K_{ad,Cu(aa)²}$ is rather larger than that of [Co(aa)₃]₈,ad, because [Cu(aa)₂]₈,ad is coordination-unsaturated and may further interact with residual silanol, such as coordination of silanol oxygen, as well as hydrogen bonding of coordinating oxygen atoms with silanol hydrogen. The much less retention to EC may, on the other hand, be attributed to the absence of [Haa]₈,ad and [Cu(aa)₂]₈,ad terms and to the less wetting of ODS silica.
ESR Spectra

With a view to obtaining the independent evidence for the presence of two different species, [Cu(aa)₂]₅,D and [Cu(aa)₂]₅,ad, having the same chemical compositions, the ESR spectra of NEC and EC after SPE of Cu²⁺ in the presence of Haa are shown in Fig. 3; SPE to NEC was conducted such that [-SiOCu(aa)]₅ was not formed, as indicated in Fig. S3. The spectrum of EC was shown with the enhanced intensity for comparison. Both the spectrum of NEC and the spectrum of EC are characteristic of a square planar or an axially elongated octahedral complex of copper(II). The spectrum of EC is sharp and may be attributed to [Cu(aa)₂]₅,D, based on the findings described above. In contrast, the spectrum of NEC suggests the presence of more than two species; peaks of another set were observed respectively in the slightly lower fields with shoulders at the same positions as the peaks of EC. This indicates the presence of [Cu(aa)₂]₅,D as a minor species and [Cu(aa)₂]₅,ad as a major species in accordance with the equilibrium analysis. These species may be differentiated due to the slow mutual exchange.

Conclusions

In the retention of Haa, residual silanol enhances wetting of ODS and increases the fraction of the actually functioning ODS phase to give a larger distribution constant to NEC than a distribution constant to EC. The residual silanol also functions as a hydrogen bond donor, such as to add the adsorption term as well as the distribution term in the retention and allows for the higher retention at the lower concentration of the compound. In the retention of Cu²⁺ to NEC in the presence of Haa, the adsorption of [Cu(aa)₂] to silanol plays a major role on the basis of high retention of Haa, although the adsorption of Haa competes at the higher Haa concentration.
ODS with residual silanol is worthwhile to be used as a solid phase in SPE.

Acknowledgements

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Supporting Information

Additional table and figures about the retention of \([\text{Co(aa)}_3]\) and the retention of \(\text{Cu}^{2+}\) in the presence of Haa to NEC. This material is available free of charge on the Web at http://www.jsac.or.jp/analsci/.

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### Table 1  Properties of SG and ODS-silicas\textsuperscript{a}

| Solid phase | CC    | WC    | MC\textsubscript{ODS} | MC\textsubscript{TMS} | MC\textsubscript{W} | \(\Sigma\) MC\textsubscript{X} |
|-------------|-------|-------|-----------------------|-----------------------|---------------------|--------------------------|
| SG          | 0     | 0.130 | 0                     | 0                     | 7.21                | 7.21                     |
| NEC         | 0.143 | 0.034 | 0.84                  | 0                     | 1.89                | 2.73                     |
| EC          | 0.168 | 0.010 | 0.84                  | 1.32                  | 0.55                | 2.71                     |

\textsuperscript{a} Relative error of 5\%. 
Table 2  Parameters relevant to retention of acetylacetone and its metal complexes from aqueous phase to ODS silicas

| Compound        | ODS silica | log $K_{D,R}$ L kg$^{-1}$ | log $K_{ad,R}$ mol$^{-1}$ L | $A_R$ mol kg$^{-1}$ |
|-----------------|------------|---------------------------|----------------------------|---------------------|
| Acetylacetone   | NEC        | 0.44(1)                   | 1.93(2)                    | 0.42(3)             |
| Acetylacetone   | EC         | 0.07(1)                   | 2.6(1)                     | 0.03(1)             |
| [Co(aa)$_3$]    | NEC        | 1.52(3)                   | 4.25(3)                    | 0.25(4)             |
| [Cu(aa)$_2$]    | NEC        | 1.0(1)                    | 4.83(5)                    | 0.042(5)            |

a. Number in parenthesis denotes error in the last digit.
**Figure Captions**

Scheme 1  Relation between species involved in retention of Cu$^{2+}$ from aqueous phase to NEC in the presence of Haa and relevant constants.

Fig. 1  Retention isotherms of Haa from aqueous phase to NEC (a) and EC (b). Ionic strength: 0.1 mol L$^{-1}$ KNO$_3$. Red: calculated curves according to Eq. (3); green broken: distribution term; blue dotted: Langmuir adsorption term.

Fig. 2  Effects of pH and $C_{\text{Haa}}$ on fractional retention of Cu$^{2+}$ from aqueous phase to NEC in the presence and in the absence of Haa. $C_{\text{Cu}} = 10^{-4}$ mol L$^{-1}$. Ionic strength: 0.1 mol L$^{-1}$ KNO$_3$. $C_{\text{Haa}}$/mol L$^{-1}$: (●) 0, (◇) $10^{-4}$, (□) $10^{-3.7}$, (△) $10^{-3.5}$, (●) $10^{-3.0}$, (◇) $10^{-2.5}$, (■) $10^{-2.0}$, (▲) $10^{-1.5}$, (●) $10^{-1.0}$. Solid curves of the corresponding colors are calculated using the constants obtained.

Fig. 3  ESR spectra of NEC and EC after SPE of Cu$^{2+}$ in the presence of Haa. ODS: NEC, black; EC, red.
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C_{Haa}/mol L^{-1}: (●) 0, (◇) \( 10^{-4} \), (□) \( 10^{-3.7} \), (△) \( 10^{-3.5} \), (●) \( 10^{-3.0} \), (●) \( 10^{-2.5} \), (■) \( 10^{-2.0} \), (▲) \( 10^{-1.5} \), (●) \( 10^{-1.0} \).  Solid curves of the corresponding colors are calculated using the constants obtained.
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aqueous phase

\[
\begin{align*}
[Cu^{2+}] & \rightleftharpoons [Cu(aa)]^+ \rightleftharpoons [Cu(aa)]_2 \vspace{0.5cm} \\
(Haa)_3 & \quad (Haa)_{3,ad} \quad [(-SiO)Cu]_3 \quad [-SiOCu(aa)]_3 \quad [Cu(aa)]_{3,D} \quad [Cu(aa)]_{3,ad}
\end{align*}
\]

solid phase

\(\rho\): distributed; \(\text{ad}\): adsorbed

differentiated by ESR