Enhanced Retention of Chelating Reagents in Octadecylsilyl Silica Phase by Interaction with Residual Silanol Groups in Solid Phase Extraction of Divalent Metal Ions

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Solid-phase extraction (SPE) of divalent metal ions with a lipophilic and potentially divalent hexadentate chelating reagent (H_2L), with which octadecylsilyl silica (ODS) was impregnated, was studied to gain more insight into and develop the potential of this methodology. This is the first time to demonstrate that this reagent as well as other common nitrogen-containing reagents were retained both by adsorption due to hydrogen bonding between nitrogen atoms of the reagent and residual silanol groups in the ODS phase and by simple distribution into the hydrophobic space. An appreciably large amount of this reagent could be retained by the adsorption mechanism even with a relatively thin loading solution. The divalent metal ions of Mn^{2+}, Co^{2+} and Zn^{2+} were extracted as 1:1 neutral complexes ([ML]), while Ni^{2+} and Cu^{2+} as ion-pairs of 1:1 cationic complex ($[MHL]^+$) with anion in SPE with H_2L. The extractability and selectivity were substantially the same as that in liquid–liquid extraction.

Keywords ODS, extraction, nitrogen-containing reagents, Langmuir adsorption, distribution, divalent transition metal ions

Introduction

Liquid–liquid extraction (LLE) is widely used for separation and concentration of metal ions.[1] The performances of a variety of extraction systems, each consisting of an extracting reagent and an extraction solvent, have been studied, so that a suitable extraction system is selectable for each general application. Extracting reagents with novel selectivities have been extensively developed, while alternative media for organic solvents such as ionic liquids[2-5] and supercritical fluids[6] have been lately studied by taking into account their harmful effects on the environment. Solid-phase extraction (SPE) of metal ions using octadecylsilyl silica (ODS) has also been developed in this respect. Although SPE is practically employed as pretreatment for instrumental analysis of metal ions,[7] several issues still remain to be addressed from a scientific point of view. The first is the difference in retention mechanism between extracting reagents. For example, simple distribution was proposed for β-diketone derivatives,[8-11] while Langmuir adsorption for phenanthroline.[12] The second is the difference in composition between extracted species. For example, 1:1 cationic complex was proposed for SPE with monovalent bidentate β-diketone derivatives added in an aqueous divalent metal solution,[8-11] while 1:2 neutral complex for SPE with ODS impregnated with the same reagent prior to the extraction.[13,14]

In order to gain more insight into and develop the potential of

this methodology, we have examined SPE of divalent metal ions with a potentially divalent hexadentate and more lipophilic chelating reagent, *N,N′*-di(4-chlorophenol-2-ylmethyl)-*N,N′*-di(pyridin-2-ylmethyl)ethane-1,2-diamine (H_2L, distribution constant between H_2O and $CHCl_3$: $10^{5.12}$) and have compared its performance with that in LLE already reported elsewhere.[15-18] This is the first time to demonstrate that the residual silanol group in the ODS phase plays an important role in retention of the reagent for SPE.

Experimental

Materials

Two types of ODS having different amounts of residual silanol group were evaluated. A commercially available ODS (Chromatorex C18 MB100-75/20, C: 17.3 wt%, particle size: 100 μm, Fuji Silysia Chemical Co., Ltd.) was used as a highly end-capped ODS (EC-ODS), while a non-end-capped ODS (NEC-ODS) was prepared from silica gel 60N (particle size: 40 – 50 μm, specific surface area: 680 ± 50 m^2 g^{-1}, pore diameter: 5.4 ± 1.0 nm, Kanto Chemical Co., Inc.) as described previously.[19] The chemical amount of the octadecylsilyl group was calculated to be 0.66 mol kg^{-1} from the result of elemental analysis (C: 14.3 wt%).

Then, H_2L was synthesized by the Neves's method.[20] Other neutral nitrogen-containing compounds (NC), 2,2′: 6,2″-terpyridine (tpy), 2,2′-bipyridine (bpy), pyridine (py) and quinoline (qu), were reagent grade and were used without any further purification. A series of divalent transition metal ion

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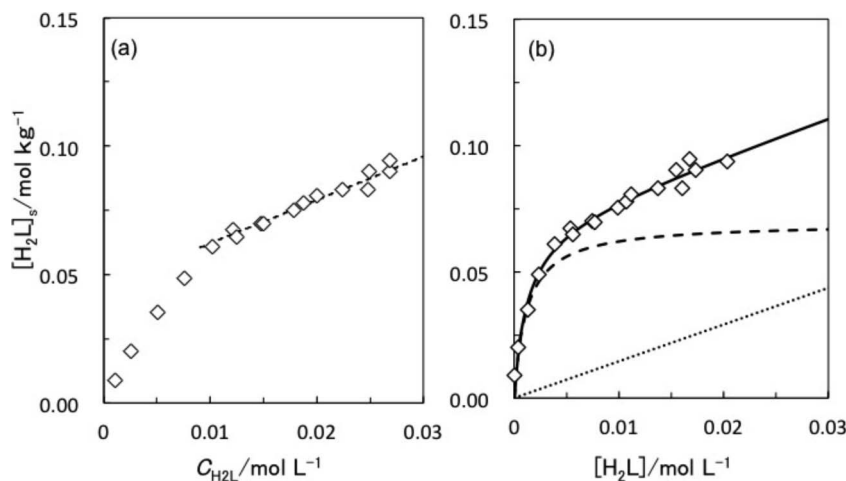E-mail: s.ohmuro.727@nitech.jp

Fig. 1 Retention of H_2L from toluene in NEC-ODS. (a) Plot of $[H_2L]_s$ vs. C_{H2L}. (b) Adsorption isotherm of H_2L. Solid line: calculated by Eq. (2); broken line: Langmuir adsorption term; dotted line: distribution term.

solutions were made of sulfates to minimize the contribution of ion-pair extraction.

Retention of reagent

An aliquot of ODS (typically $m = 0.5$ g) was shaken with toluene solutions (typically $V = 5$ mL) of various concentrations of H_2L ($C_{H2L} = 0.001 – 0.03$ mol L^{-1}) in a centrifuge tube. The concentration of the reagent present in toluene, $[H_2L]$, was determined by UV-vis spectroscopy. The concentration of the reagent in ODS, $[H_2L]_{s,obsd}$, was calculated by Eq. (1) and was expressed in terms of mol kg^{-1}:

$$[H_2L]_{s,obsd} = V \times (C_{H2L} - [H_2L])/m, \qquad (1)$$

where the subscript "s" denotes a chemical species in an ODS phase. Retention of NCs was studied at higher concentrations ($C_{NC} = 0.001 – 0.2$ mol L^{-1}).

The NEC-ODS retaining H_2L for SPE of metal ions was prepared using a toluene solution of 0.02 mol L^{-1} H_2L. The concentration of H_2L in the NEC-ODS calculated from the result of elemental analysis of nitrogen, 0.081 mol kg^{-1}, was in good agreement with that given by Eq. (1).

Solid phase extraction of divalent transition metal ions by NEC-ODS retaining H_2L

An aliquot (0.4 g) of NEC-ODS retaining H_2L was shaken with 20 mL of an aqueous phase containing 10^{-4} mol L^{-1} of each divalent transition metal ion (M^{2+}: Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} or Zn^{2+}), a 0.01 mol L^{-1} buffer ($ClCH_2COOH$ or good's buffer) and 0.05 mol L^{-1} Na_2SO_4. The concentration of the metal ion in the aqueous phase was determined by atomic absorption spectrometry. The equilibration time was assessed for extraction of Zn^{2+} at pH 4.1; the percent extraction (%E) was 90 after 18 h and 100 after 65 h.

Results and Discussion

Retention behavior of H_2L in ODS from toluene

As expected from the distribution constant of H_2L between H_2O and $CHCl_3$ described in the Introduction, dissolution of H_2L in neutral water was an undetectable level. This is advantageous in that loss of H_2L from ODS exposed to aqueous solutions is negligible. At the same time, this suggests that an extremely large volume of an aqueous solution of H_2L, if saturated, would be required for retention of the reagent in ODS. Thus a toluene solution (solubility of about 0.05 mol L^{-1}) was used instead to retain H_2L in ODS as described previously.[13,14] In this case, toluene present in large excess may be competitively distributed into ODS to interfere with the distribution of H_2L.

Two different ODSs were exposed to a toluene solution of the reagent, and a change in concentration of H_2L in toluene was monitored. With regard to NEC-ODS, the concentration of H_2L was considerably reduced within 1 h and was kept constant after 1 h. With regard to EC-ODS, on the other hand, the concentration was not changed within an experimental error. It is known that in reversed-phase HPLC using ODS, nitrogen-containing compounds are irreversibly adsorbed or suffer from peak tailing due to hydrogen bonding between nitrogen atoms and residual silanol groups.[21] Thus, most ODSs for HPLC are nowadays treated to be end-capped by trimethylsilyl groups. These suggest that hydrogen bonding between nitrogen atoms in H_2L and silanol groups play an important role for retention of H_2L in NEC-ODS.

The concentration of H_2L in NEC-ODS, $[H_2L]_s$, was calculated by Eq. (1) and was plotted against the initial or total concentration of H_2L in toluene in Fig. 1(a). The larger slope at $C_{H2L} < 0.01$ mol L^{-1} indicates the higher and thereby more effective retention ratio of the reagent than at $C_{H2L} > 0.01$ mol L^{-1} (3.6 times). The adsorption isotherm in Fig. 1(b) indicates a steep increase at $[H_2L] < 0.005$ mol L^{-1} and a gradual increase at $[H_2L] > 0.005$ mol L^{-1}. The retention of H_2L is attributed to the Langmuir adsorption and the simple distribution into hydrophobic space, contributing independently as given by Eq. (2):

$$[H_2L]_{s,cald} = A_{max} \times K_{ad}[H_2L]/(1 + K_{ad}[H_2L]) + K_d[H_2L], \qquad (2)$$

where K_{ad} denotes an adsorption constant (mol^{-1} L), A_{max} a saturated adsorption amount (mol kg^{-1}) and, K_d a distribution constant (kg^{-1} L). These parameters were optimized to give a minimum error square sum on $[H_2L]_s$, U_1, as given by Eq. (3):

$$U_1 = \sum([H_2L]_{s,obsd} - [H_2L]_{s,cald})^2 \qquad (3)$$

Table 1 shows optimized parameters. A calculated curve using these parameters well reproduces the experimental points and indicates the validity of Eq. (2). Figure 1(b) also includes the contribution of two terms in Eq. (2): Langmuir adsorption given by a broken line and simple distribution given by a dotted line. Adsorption is almost saturated at $[H_2L] = 0.005$ mol L^{-1} (corresponding to $C_{H2L} = 0.01$ mol L^{-1}), while simple distribution continuously increases at $[H_2L] > 0.005$ mol L^{-1}. If only the simple distribution mechanism worked, a toluene solution of as high as 0.05 mol L^{-1} would be necessary to retain the reagent, for example, at the saturated adsorption amount of 0.07 mol kg^{-1}. The results accordingly show that the reagent is effectively retained by the adsorption mechanism.

Retention behavior of other nitrogen compounds in ODS from toluene

In order to confirm the involvement of adsorption due to hydrogen bonding between silanol groups and nitrogen atoms, a series of NCs with the number of nitrogen atoms $n = 1 - 3$ were subjected to measurement of adsorption isotherms. The adsorption isotherms of all the compounds on NEC-ODS (Figs. 2(a) – 2(d)) indicated contribution of both distribution and adsorption; the parameters similarly evaluated are included in Table 1. The logarithmic values of K_d of these four compounds were as low as around 0; this is attributed to competitive distribution of toluene in ODS phases. The logarithmic values of K_{ad} were in a range of 1.9 – 2.1, regardless

of n. This suggests that only one nitrogen atom is involved in the adsorption, irrespective of n. The A_{max} value had a tendency to decrease with an increase in structural complexity. For example, the A_{max} value of qu ($n = 1$) was about half the A_{max} value of py ($n = 1$). It suggests that the interaction of qu with silanol is suppressed by the structural restriction of additional benzo group on qu, compared with that of py. Only one nitrogen atom is also involved with regard to the reagents of $n = 2$ and 3, and the other parts rather interfere with the interaction of adjacent silanol groups with another reagent.

In contrast, $\log K_{ad}$ of H_2L is about 10 times as large as those of NCs. Since phenol in toluene was not retained to NEC-ODS, the high affinity is attributed to that H_2L contains aliphatic nitrogen atoms of the higher basicity as well as aromatic nitrogen atoms and that more than two nitrogen atoms are involved in the adsorption. The decrease in A_{max} may be attributed to the multiple interactions and steric restriction.

In contrast, substantially no retention was observed for any compound on EC-ODS. It is understandable that the adsorption term becomes negligible due to end-capping. The reason for reduction of the distribution term is, however, not clear at this stage.

Solid-phase extraction of divalent transition metal ions with NEC-ODS retaining H_2L

Figure 3 shows extraction curves of divalent transition metal ions in SPE with NEC-ODS retaining H_2L. All the metal ions were completely extracted at pH values higher than the respective critical values. The extraction curve had steep increases for Mn^{2+}, Co^{2+} and Zn^{2+}, but had gradual increases for Ni^{2+} and Cu^{2+} as in LLE using the same reagent and chloroform.[16] Thus, NEC-ODS may be an alternative to the organic solvent in the extraction using this reagent.

Extraction of the first group is attributed to formation of the 1:1 neutral complex given by Eq. (4) as described previously.[16]

$$M^{2+} + (H_2L)_s \rightleftharpoons (ML)_s + 2H^+, \qquad (4)$$
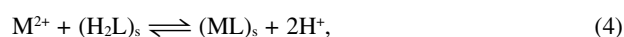
The extraction constant K_{ex} corresponding to Eq. (4) is expressed by Eq. (5):

Table 1   Parameters in retention of reagents from toluene in NEC-ODS

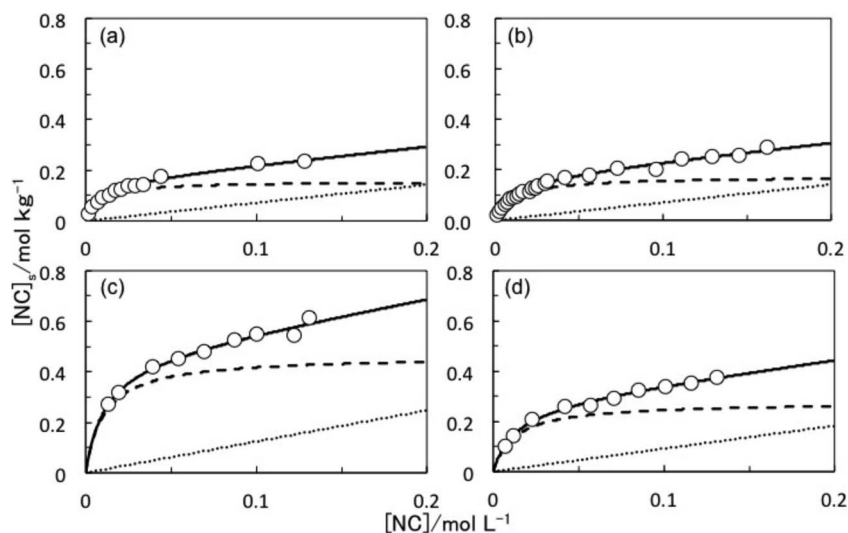| Reagent	n	$\log K_{ad}$	A_{max}	$\log K_d$
H_2L	4	3.0 ± 0.1	0.07 ± 0.01	0.18 ± 0.01
tpy	3	2.08 ± 0.05	0.16 ± 0.01	-0.15 ± 0.04
bpy	2	1.9 ± 0.1	0.17 ± 0.01	-0.15 ± 0.05
py	1	1.97 ± 0.05	0.45 ± 0.01	0.09 ± 0.05
qu	1	1.9 ± 0.1	0.28 ± 0.01	-0.04 ± 0.05

Fig. 2   Adsorption isotherms of NCs from toluene to ODS. NC: tpy (a), bpy (b), py (c), qu (d). Solid line: calculated by Eq. (2); broken line: Langmuir adsorption term; dotted line: distribution term.
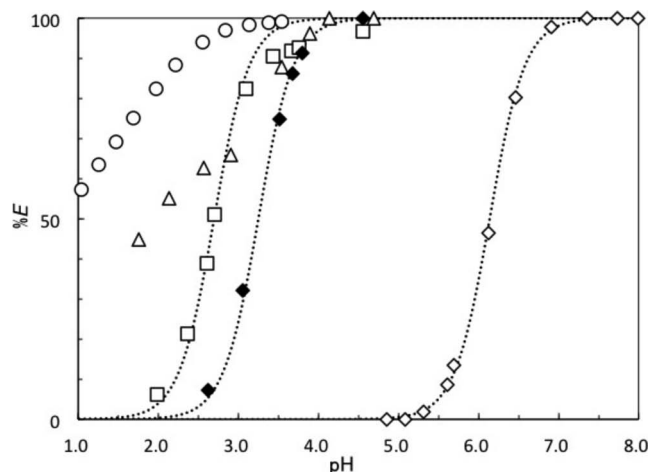
Fig. 3   Solid-phase extraction behaviors of divalent transition metal ions with NEC-ODS retaining H_2L. Metal ion: Mn^{2+} ($\Diamond$), Co^{2+} ($\Box$), Ni^{2+}($\triangle$), Cu^{2+} ($\bigcirc$), Zn^{2+} ($\blacklozenge$). Dotted line: calculated by Eq. (8).

$$K_{ex} = \frac{[ML]_s[H^+]^2}{[M^{2+}][H_2L]_s} \tag{5}$$

Equations (6) and (7) show the mass balances of M^{2+} and H_2L when V (mL) of an aqueous solution containing C_M mol L^{-1} divalent transition metal ion is reacted with m (g) of ODS containing C'_{H2L} mol kg^{-1} H_2L; the dissolution of H_2L from ODS to water is negligible as described previously.

$$C_M = [M^{2+}] + m[ML]_s/V \tag{6}$$

$$C'_{H2L} = [H_2L]_s + [ML]_s \tag{7}$$

The total amount of H_2L (32 μmol) was significantly larger than that of the metal ion (2 μmol), so that $[H_2L]_s$ is approximated as C'_{H2L} and the $\%E$ is expressed by Eq. (8).

$$\%E = \frac{K_{ex}C'_{H2L}}{K_{ex}C'_{H2L} + \dfrac{V}{m}[H^+]^2} \times 100 \tag{8}$$

The K_{ex} values for Mn^{2+}, Co^{2+} and Zn^{2+} were optimized to give a minimum error square sum on $\%E$, U_2 as given by Eq. (9).

$$U_2 = \sum(\%E_{obsd} - \%E_{cald})^2 \tag{9}$$

The calculated curves using the optimized values (log K_{ex}: –2.64 for Co^{2+}, –3.74 for Zn^{2+}, –9.52 for Mn^{2+}) well reproduced the experimental points (Fig. 3).

If the extraction constants of SPE and LLE were the same for the respective metal ions, the extraction curves would shift to the lower pH region by 0.45 because the concentration of H_2L in SPE (0.08 mol kg^{-1}) was 8 times higher than that in LLE (0.01 mol L^{-1}). The actual difference in $pH_{1/2}$ was 0.9 – 1.1 ($pH_{1/2}$ of 3.3 compared with 4.4^{16} for Zn^{2+}, 6.1 compared with 7.0^{16} for Mn^{2+}). The practical concentration H_2L in the ODS phase except silica body (14.3 wt%) was, however, 0.56 mol kg^{-1}, while the concentration in chloroform was 0.0068 mol kg^{-1}. The shift in $pH_{1/2}$ expected between these concentrations, 0.96, agreed with the difference observed. Thus, the extracting ability of NEC-ODS is comparable to chloroform.   The difference in $pH_{1/2}$ of Zn^{2+} and Mn^{2+} was similar in the respective extraction

systems (2.8 in SPE, 2.6 in LLE).[16] The selectivity in LLE was also quantitatively kept in the SPE.

Gradual increases in the extraction curves of the second group, Cu^{2+} and Ni^{2+} are, in contrast, attributed to formation of the cationic complex, $[MHL]^+$, by releasing one proton as in the case of LLE.[16] Strong coordination of nitrogen atoms of this reagent to these soft metal ions may interfere with coordination of one of two phenol groups, so as to give a protonated complex. This complex is extracted into an organic solvent or the ODS phase as an ion-pair with some anion, A^-, as given by Eq. (10):

$$M^{2+} + (H_2L)_s + A^- \rightleftharpoons (MHL^+, A^-)_s + H^+ \tag{10}$$
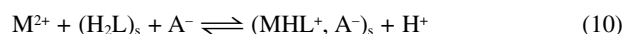
The extractability of this type of species is strongly dependent on the type of anion present in the supporting electrolyte.[16] Although HSO_4^-, $ClCH_2COO^-$ or deprotonated silanol group is expected as the counter anion in this extraction system, further equilibrium analysis is beyond the scope of this study.

Conclusions

The adsorption to residual silanol group guarantees effective retention of the nitrogen-containing reagent from the organic solvent such as toluene even at a relatively low concentration. Although disadvantages of such interaction have been pointed out in the reversed phase HPLC,[21] this can be utilized rather positively in SPE. In extraction of the divalent transition metal ion by the potentially divalent hexadentate chelating reagent, ODS may serve as an alternative to the organic solvent while maintaining the original extractability and selectivity. Since all the nitrogen atoms of H_2L are supposed to be used in the resulting complexes, the retention is attributable only to the simple distribution. This could not, however, be experimentally verified due to the low solubilities of metal complexes in toluene and awaits further studies.

Acknowledgements

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