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 (H2L), 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 Mn2+, Co2+ and Zn2+ were extracted as 1:1 neutral complexes ([ML]), while Ni2+ and Cu2+ as ion-pairs of 1:1 cationic complex ([MHL]+) with anion in SPE with H2L. 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

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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 \( \text{H}_2\text{L} \) (\( C_{\text{H}_2\text{L}} = 0.001 - 0.03 \) mol L\(^{-1}\)) in a centrifuge tube. The concentration of the reagent present in toluene, \( [\text{H}_2\text{L}]_t \), was determined by UV-vis spectroscopy. The concentration of the reagent in ODS, \( [\text{H}_2\text{L}]_\text{s,obsd} \), was calculated by Eq. (1) and was expressed in terms of mol kg\(^{-1}\):

\[
[\text{H}_2\text{L}]_\text{s,obsd} = \frac{V \times (C_{\text{H}_2\text{L}} - [\text{H}_2\text{L}])}{m},
\]  

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

The NEC-ODS retaining \( \text{H}_2\text{L} \) for SPE of metal ions was prepared using a toluene solution of 0.02 mol L\(^{-1}\) \( \text{H}_2\text{L} \). The concentration of \( \text{H}_2\text{L} \) 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 \( \text{H}_2\text{L} \)

An aliquot (0.4 g) of NEC-ODS retaining \( \text{H}_2\text{L} \) was shaken with 20 mL of an aqueous phase containing \( 10^{-4} \) mol L\(^{-1}\) of each divalent transition metal ion (\( \text{M}^{2+}: \text{Mn}^{2+}, \text{Co}^{2+}, \text{Ni}^{2+}, \text{Cu}^{2+} \) or \( \text{Zn}^{2+} \)), a 0.01 mol L\(^{-1}\) buffer (\( \text{ClCH}_2\text{COOH} \) or good’s buffer) and 0.05 mol L\(^{-1}\) \( \text{Na}_2\text{SO}_4 \). The concentration of the metal ion in the aqueous phase was determined by atomic absorption spectrometry. The equilibration time was assessed for extraction of \( \text{Zn}^{2+} \) at pH 4.1; the percent extraction (%\( E \)) was 90 after 18 h and 100 after 65 h.

Results and Discussion

Retention behavior of \( \text{H}_2\text{L} \) in ODS from toluene

As expected from the distribution constant of \( \text{H}_2\text{L} \) between \( \text{H}_2\text{O} \) and \( \text{CHCl}_3 \) described in the Introduction, dissolution of \( \text{H}_2\text{L} \) in neutral water was an undetectable level. This is advantageous in that loss of \( \text{H}_2\text{L} \) from ODS exposed to aqueous solutions is negligible. At the same time, this suggests that an extremely large volume of an aqueous solution of \( \text{H}_2\text{L} \), 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 \( \text{H}_2\text{L} \) 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 \( \text{H}_2\text{L} \).

Two different ODSs were exposed to a toluene solution of the reagent, and a change in concentration of \( \text{H}_2\text{L} \) in toluene was monitored. With regard to NEC-ODS, the concentration of \( \text{H}_2\text{L} \) 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 \( \text{H}_2\text{L} \) and silanol groups play an important role for retention of \( \text{H}_2\text{L} \) in NEC-ODS.

The concentration of \( \text{H}_2\text{L} \) in NEC-ODS, \( [\text{H}_2\text{L}]_\text{s} \), was calculated by Eq. (1) and was plotted against the initial or total concentration of \( \text{H}_2\text{L} \) in toluene in Fig. 1(a). The larger slope at \( [C_{\text{H}_2\text{L}}] < 0.01 \) mol L\(^{-1}\) indicates the higher and thereby more effective retention ratio of the reagent than at \( [C_{\text{H}_2\text{L}}] > 0.01 \) mol L\(^{-1}\) (3.6 times). The adsorption isotherm in Fig. 1(b) indicates a steep increase at \( [\text{H}_2\text{L}] < 0.005 \) mol L\(^{-1}\) and a gradual increase at \( [\text{H}_2\text{L}] > 0.005 \) mol L\(^{-1}\). The retention of \( \text{H}_2\text{L} \) is attributed to the Langmuir adsorption and the simple distribution into hydrophobic space, contributing independently as given by Eq. (2):

\[
[\text{H}_2\text{L}]_\text{s,cald} = A_{\text{max}} \times K_{\text{ad}} [\text{H}_2\text{L}] / (1 + K_{\text{ad}} [\text{H}_2\text{L}]) + K_{\text{d}} [\text{H}_2\text{L}],
\]  

where \( K_{\text{ad}} \) denotes an adsorption constant (mol\(^{-1}\) L), \( A_{\text{max}} \) a saturated adsorption amount (mol kg\(^{-1}\)) and, \( K_{\text{d}} \) a distribution constant (kg\(^{-1}\) L). These parameters were optimized to give a minimum error square sum on \( [\text{H}_2\text{L}]_\text{s} \), \( U_1 \), as given by Eq. (3):
$U_i = \sum (\text{[H}_2\text{L}]_{\text{obsd}} - \text{[H}_2\text{L}]_{\text{cald}})^2$ (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$_2$L] = 0.005 mol L$^{-1}$ (corresponding to C$_{\text{H2L}}$ = 0.01 mol L$^{-1}$), while simple distribution continuously increases at [H$_2$L] > 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 $K_{\text{ad}}$ 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 $A_{\text{max}}$ value had a tendency to decrease with an increase in structural complexity. For example, the $A_{\text{max}}$ value of qu ($n = 1$) was about half the $A_{\text{max}}$ 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 $K_{\text{ad}}$ of H$_2$L 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$_2$L 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 $A_{\text{max}}$ 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$_2$L

Figure 3 shows extraction curves of divalent transition metal ions in SPE with NEC-ODS retaining H$_2$L. 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.$^{16}$

$$\text{M}^{2+} + (\text{H}_2\text{L}) \rightleftharpoons (\text{ML}) + 2\text{H}^+,$$ (4)

The extraction constant $K_{\text{ex}}$ corresponding to Eq. (4) is expressed by Eq. (5):

![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.](image-url)
Figure 3  Solid-phase extraction behaviors of divalent transition metal ions with NEC-ODS retaining H₂L. Metal ion: Mn²⁺ (●), Co²⁺ (○), Ni²⁺(△), Cu²⁺ (■), Zn²⁺ (◆). Dotted line: calculated by Eq. (8).

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

Equations (6) and (7) show the mass balances of M²⁺ and H₂L when V (mL) of an aqueous solution containing C₅ mol L⁻¹ divalent transition metal ion is reacted with m (g) of ODS containing C₅₅ mol kg⁻¹ H₂L; the dissolution of H₂L from ODS to water is negligible as described previously.

\[ C₅ = \frac{[M^2+]}{V} + m[ML] \]

\[ C₅₅ = [H₂L] + [ML] \]  
The total amount of H₂L (32 µmol) was significantly larger than that of the metal ion (2 µmol), so that [H₂L] is approximated as C₅₅ and the %E is expressed by Eq. (8).

\[ \%E = \frac{K_{ex}C₅₅}{K_{ex}C₅₅ + \frac{1}{m}[H^+]^2} \times 100 \]  
The Kₐ values for Mn²⁺, Co²⁺ and Zn²⁺ were optimized to give a minimum error square sum on %E, U₂ as given by Eq. (9).

\[ U₂ = \sum (%E_{obs} - %E_{calc})^2 \]  

The calculated curves using the optimized values (log Kₐ: -2.64 for Co²⁺, -3.74 for Zn²⁺, -9.52 for Mn²⁺) 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 H₂L in SPE (0.08 mol kg⁻¹) was 8 times higher than that in LLE (0.01 mol L⁻¹). The actual difference in pH₅₀ was 0.9 - 1.1 (pH₅₀ of 3.3 compared with 4.4 for Zn²⁺, 6.1 compared with 7.0 for Mn²⁺). The practical concentration H₂L 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 pH₅₀ 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 pH₅₀ of Zn²⁺ and Mn²⁺ was similar in the respective extraction systems (2.8 in SPE, 2.6 in LLE). The selectivity in LLE was also quantitatively kept in the SPE.

Gradual increases in the extraction curves of the second group, Cu²⁺ and Ni²⁺ are, in contrast, attributed to formation of the cationic complex, [MHL⁺], by releasing one proton as in the case of LLE. 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):

\[ M^{2+} + (H₂L) + A^- \rightleftharpoons (MHL^+, A^-) + H^+ \]  
The extractability of this type of species is strongly dependent on the type of anion present in the supporting electrolyte. Although HSO₄⁻, ClCH₂COO⁻ 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, 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 H₂L 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.

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References

1. B. A Moyer, “Ion Exchange and Solvent Extraction”, 2013, Vol. 21, CRC Press, New York.
2. N. Hirayama, M. Deguchi, and T. Honjo, Solv. Extr. Res. Dev. Jpn., 2006, 13, 83.
3. K. Shimojo, H. Okamura, N. Hirayama, S. Umetani, H. Imura, and H. Nagana, Dalton Trans., 2009, 25, 4850.
4. H. Okamura, A. Ikeda-Olino, T. Saito, N. Aoyagi, H. Naganawa, N. Hirayama, S. Umetani, H. Imura, and K. Shimojo, Anal. Chem., 2012, 81, 9332.
5. M. Sakato and N. Hirayama, Anal. Sci., 2014, 30, 783.
6. R. Sepúlveda, J. Romero, and J. Sánchez, J. Chem. Technol. Biotechnol., 2014, 89, 899.
7. B. Ya. Spivakov, G. I. Malofeeva, and O. M. Petrukhin, Anal. Sci., 2006, 22, 503.
8. M. Kato, Bull. Chem. Soc. Jpn., 1985, 58, 2056.
9. M. Kato and H. Shimofuruya, Bull. Chem. Soc. Jpn., 1990.
10. M. Kato, T. Hattori, T. Suzuki, and K. Tsutsumi, *Bull. Chem. Soc. Jpn.*, **1994**, 67, 2712.
11. M. Kato, T. Nakano, and T. Hattori, *Bull. Chem. Soc. Jpn.*, **1994**, 67, 3231.
12. M. Kato, S. Kudo, and T. Hattori, *Bull. Chem. Soc. Jpn.*, **1998**, 71, 149.
13. M. Iiyama, S. Oshima, H. Kokusen, M. Sekita, S. Tsurubou, and Y. Komatsu, *Anal. Sci.*, **2004**, 20, 1463.
14. M. Iiyama, H. Kokusen, S. Tsurubou, and Y. Komatsu, *J. Ion Exch.*, **2007**, 18, 440.
15. K. Kubono, N. Hirayama, Y. Matsuoka, and H. Kokusen, *Anal. Sci.*, **1996**, 12, 133.
16. N. Hirayama, N. Ichitani, K. Kubono, Y. Matsuoka, H. Kokusen, and T. Honjo, *Talanta*, **1997**, 44, 2019.
17. H. Kokusen, K. Kubono, N. Hirayama, and Y. Komatsu, *J. Ion Exch.*, **2003**, 14, 377.
18. S. Oshima, N. Hirayama, K. Kubono, and H. Kokusen, *J. Ion Exch.*, **2007**, 18, 360.
19. A. Walcarius and L. Mercier, *J. Mater. Chem.*, **2010**, 20, 4478.
20. A. Neves, S. M. D. Erthal, I. Vencato, A. S. Ceccato, Y. P. Mascarenhas, O. R. Nascimento, M. Hörner, and A. A. Batista, *Inorg. Chem.*, **1992**, 31, 4749.
21. D. V. McCalley, *J. Chromatogr. A*, **2010**, 1217, 858.