Formaldehyde Removal by Using Solid Phase Extraction with an Imination Reaction on an Amine Type Trident Molecule-Impregnated Resin

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Solid phase extractive removal of harmful formaldehyde with an imination reaction on a resin impregnated with a trident amine derivative has been investigated to compare the removal behavior with extractive removal with the trident amine derivative reported in the previous work. The impregnated resin also effectively removed formaldehyde while maintaining the extractive removal performance of the impregnated triamine. In particular, the leakage of the impregnated amine was significantly suppressed in the solid phase extraction with the impregnated resin compared with that in the extraction system.

1. Introduction

So-called “trident molecules” [1], tripodal alkyl trimethylol derivatives, have been prepared to investigate extraction behavior in our laboratory [1-3]. The trident molecules provide the following characteristics, that is, easy availability of the alkyltrimethylols from the corresponding aldehydes and formaldehyde, the possession of three alcoholic hydroxyl groups for modification to a tridentate ligand with $C_3$ symmetry, a relatively narrow coordination site for size discrimination, and a high coordination ability due to the chelating effect and converging effects of multifunctionality [4], in a similar fashion with macrocyclic calixarene derivatives with certain size cavities [5,6], although they do not possess a macrocyclic framework.

In our previous work, the trident amine molecule exhibited excellent extractive removal of harmful aldehyde and ketone derivatives due to its specific plural functionality structure [7]. However, the prepared trident amine compound was eluted in acidic aqueous solution, because the single molecule possesses three amino groups. The $pK_a$ values of the less lipophilic tris(aminomethyl)ethane were reported to be 10.4, 8.6, and 5.8 [8]. The alkyl branch of the more lipophilic tris(aminomethyl)nonene does not significantly affect the $pK_a$ values. To use such compounds as an impregnated resin [9-12] is another approach in keeping functionality in formaldehyde removal.

In the present study, the preparation of the impregnated resin containing an amine type trident molecule for removal of harmful formaldehyde is investigated with regard to suppressed elution of the trident amino compound into the aqueous phase. Further experiments for formaldehyde removal on the resin were carried out to investigate each parameter, removal rate, pH dependency, maximum loading (reaction) amount, and the reverse (recovered) reaction.
2. Experimental

2.1 Reagents

The trident molecule, 1,1,1-tris(aminomethyl)-9-decene ($^8$None{$\equiv$}CH$_2$NH$_2$) was prepared in a similar manner to that described previously [7]. The chemical structures of the trident molecule, together with the compounds for the impregnated resin employed in the present work are shown in Figure 1.

Amberlite XAD-7HP was purchased from Organo Co. Ltd. The average pore size, porosity and specific surface area were 200Å, 55%, 350-550 m$^2$ g$^{-1}$, respectively. Other chemicals were purchased and used without further purification.

![Chemical structures](image)

Figure 1. Chemical structures of the compounds employed in the present work.

2.2 Preparation of the impregnated resin

The $^8$None{$\equiv$}CH$_2$NH$_2$-impregnated resin was prepared in a similar manner to that described previously [9,10]. The trident molecule, $^8$None{$\equiv$}CH$_2$NH$_2$ (1.0 g), was dissolved in analytical grade chloroform (50 cm$^3$). The macroporous resin, Amberlite XAD-7, was washed with methanol for preconditioning and dried in vacuo. The dried Amberlite XAD-7 (2.0 g) was immersed in the chloroform solution overnight. The chloroform was removed in vacuo. The percentage impregnation was 33% (1.4 mol kg$^{-1}$).

2.3 Leakage of the trident molecule to the aqueous phase

The aqueous solution was prepared by mixing 0.1 M (M = mol dm$^{-3}$) hydrochloric acid, 0.1 M HEPES (2-[4-(2-hydroxyethyl)-1-piperazinyl]ethanesulfonic acid) as a buffer solution, and 0.1 M sodium hydroxide solution. The solutions were arbitrarily mixed to adjust the pH. The resin (20 mg) was added to the aqueous solution (10 cm$^3$) and the mixture was shaken at 150 rpm at 303 K for more than 10 h. After filtration, the $^8$None{$\equiv$}CH$_2$NH$_2$ concentration in the aqueous phase was measured by means of an ultraviolet-visible spectrophotometer (Hitachi, UV-VIS U-3310) at 240 nm, the wavelength of the $\pi - \pi^*$ transfer of the unsaturated bond in $^8$None{$\equiv$}CH$_2$NH$_2$.

2.4 Adsorptive removal of formaldehyde

Aqueous solutions were prepared by diluting a formaldehyde standard solution (1,000 ppm) in 0.1 M hydrochloric acid, 0.1 M HEPES, and 0.1 M sodium hydroxide solutions to the desired concentrations. Three stock solutions were mixed to adjust the pH. The resin (20 mg) was added to the aqueous solution (10 cm$^3$) and the mixture was shaken at 150 rpm at 303 K for more than 10 h. After filtration, the formaldehyde concentration in the aqueous phase was measured by colorimetry for acetic acetone determination (JIS K0102, 29.1) using an ultraviolet-visible spectrophotometer (Hitachi, UV-VIS U-3310) at 413 nm. The pH value of the aqueous phase was measured using a pH meter (TOA-DKK HM-30R).
3. Results and Discussion

3.1 Leakage of the trident molecule to the aqueous phase

The effect of pH on the percentage leakage of $^8$None{3}CH$_2$NH$_2$ into the aqueous phase is shown in Figure 2, together with the effect of pH on the percentage elution. The percentage leakage of $^8$None{3}CH$_2$NH$_2$ was calculated by equation (1),

$$\% \text{Leakage} = \frac{n_{\text{aq},^8\text{None}{3}\text{CH}_2\text{NH}_2}}{n_{\text{imp},^8\text{None}{3}\text{CH}_2\text{NH}_2}} \times 100$$  \hspace{1cm} (1),

where $n_{\text{imp},^8\text{None}{3}\text{CH}_2\text{NH}_2}$ and $n_{\text{aq},^8\text{None}{3}\text{CH}_2\text{NH}_2}$ are the mole amounts of $^8$None{3}CH$_2$NH$_2$ impregnated in the resin and that leaked into the aqueous solution. Since $^8$None{3}CH$_2$NH$_2$ possesses three primary amino groups and one lipophilic nonenyl branch, it is easily protonated under acidic conditions and eluted into the aqueous phase. In contrast, the leakage of $^8$None{3}CH$_2$NH$_2$ into the aqueous phase was drastically suppressed by using the reagent in the form of an impregnated resin. The percentage elution was 56% to 20%, whereas the percentage leakage was reduced to 8.9% to 5.4%. The low leakage may be attributed to hydrophobic interaction between the lipophilic moiety in XAD-7 and the lipophilic alkenyl chain. It is readily expected that such suppressed leakage is further suppressed after the imination reaction, because of the interaction between the lipophilic moiety in XAD-7 and the imino groups which forms the polarity of the amino groups and protonated amino groups.

3.2 Adsorptive removal of formaldehyde

The effect of the shaking time on the percentage removal of formaldehyde on the $^8$None{3}CH$_2$NH$_2$-impregnated resin is shown in Figure 3, together with the effect of the shaking time on the percentage removal. The % Removal is defined by equation (2),

$$\% \text{Removal} = \frac{[\text{HCHO}]_i - [\text{HCHO}]_e}{[\text{HCHO}]_i} \times 100$$  \hspace{1cm} (2),

where $[\text{HCHO}]_i$ and $[\text{HCHO}]_e$ are the formaldehyde concentrations in the aqueous phase before and after the imination reaction. The percentage removal became constant, at 63%, within a reaction time of 6 h under the present conditions. The shaking rate was moderate and adjusted to 150rpm. In comparison with the extraction data for 2 h, a longer time was required for complete reaction. The slow removal is attributed to the hydrophobicity of the resin surface. The result of slow removal is similar to that for slow lead (II) removal on calixarene-impregnated resins [9,10]. The percentage removal of 63% very roughly corresponds to the ratio of the amino groups in $^8$None{3}CH$_2$NH$_2$ to formaldehyde, i.e. 84%. This means the reaction is roughly quantitative by using $^8$None{3}CH$_2$NH$_2$ in the impregnated resin. Strictly speaking, the removal percentage and the ratio of amino groups in $^8$None{3}CH$_2$NH$_2$ to formaldehyde in the case of the extraction obviously correspond to each other. The three amino groups of $^8$None{3}CH$_2$NH$_2$ in the impregnated resin may form hydrogen bonds with the ester carbonyl oxygen atoms in XAD-7, consequently the percentage removal was slightly low. However, slow removal may contribute to less leakage of $^8$None{3}CH$_2$NH$_2$ to the aqueous phase.

The effect of pH on the percentage removal of formaldehyde on $^8$None{3}CH$_2$NH$_2$-impregnated resin and the macroporous matrix XAD-7 itself is shown in Figure 4, together with the effect of pH on the
percentage removal. In this experiment, the formaldehyde concentration was adjusted to 2.5 mM. Since the amount of $\text{CH}_2\text{NH}_2$ was sufficiently higher than that of formaldehyde, the percentage removal of formaldehyde was almost quantitative in the pH region from 1 to 9. In contrast, XAD-7 hardly removed any formaldehyde in the same pH region. The result supports that $\text{CH}_2\text{NH}_2$ impregnated into XAD-7 is effective in the imination reaction.

The effect of the initial formaldehyde concentration on the amount of formaldehyde removed on the $\text{CH}_2\text{NH}_2$-impregnated resin is shown in Figure 5. The amount of formaldehyde removed on the $\text{CH}_2\text{NH}_2$-impregnated resin is estimated using equation (3),

$$q = \frac{[\text{HCHO}]_i - [\text{HCHO}]_e}{w} \times V \tag{3}$$

where $[\text{HCHO}]_i$ and $[\text{HCHO}]_e$ are the initial and final concentrations [mol dm$^{-3}$] of $\text{CH}_2\text{NH}_2$ in the aqueous phase before and after the reaction, $w$ [kg] and $V$ [dm$^3$] represent the resin amount and the volume of the aqueous phase, respectively. Although the value did not become constant, it was about 3.5 mol kg$^{-1}$. The amount of the amino groups in the $\text{CH}_2\text{NH}_2$-impregnated resin is 4.2 mol kg$^{-1}$ which is high enough and the stoichiometry of the imination reaction can be estimated to be 1 : 1 (amino group to formaldehyde). The slight discrepancy may be caused by formation of hydrogen bonds between the amino groups with the ester carbonyl oxygen atoms in XAD-7 and the steric hindrance of the imino groups so formed.

The effect of hydrochloric acid concentration on the percentage recovery of formaldehyde from formaldehyde-loaded $\text{CH}_2\text{NH}_2$ is shown in Figure 6. The percentage recovered of formaldehyde is calculated by equation (4),

$$\%\text{Recovered} = \frac{\text{HCHO}_n,\text{recovered}}{\text{HCHO}_n,\text{loaded}} \times 100 \tag{4}$$

where $\text{HCHO}_n,\text{loaded}$ and $\text{HCHO}_n,\text{recovered}$ are the amount of formaldehyde loaded on $\text{CH}_2\text{NH}_2$ in the resin and that recovered from the loaded resin, respectively. The amount of formaldehyde loaded on $\text{CH}_2\text{NH}_2$ in the resin by forward adsorption was 23.75 $\mu$mol (2.5 mM, 10 cm$^3$, 95.0% adsorption). The percentage recovery of formaldehyde from the formaldehyde-loaded $\text{CH}_2\text{NH}_2$ resin was significantly lower compared with that in the case of the extraction and was only 21% due to the chemical stability of the aldmino compound.

4. Conclusion

Adsorptive removal of harmful formaldehyde using an imination reaction on a resin impregnating with a trident amine derivative has been investigated to compare the removal behavior with extractive removal with the trident amine derivative reported in the previous work. The impregnated resin performance for formaldehyde removed was similar to that for the extraction system and the quantitative imination reaction took place over a wide pH range and was consistent with the amount of amino groups in the trident molecule. The removal rate was slightly slow due to the hydrophobicity of the resin surface. The leakage of the impregnated amino compound to the aqueous phase was significantly reduced compared with that in the extraction system.
Figure 2. Effect of pH on the percentage leakage of $^8$None{3}CH$_2$NH$_2$ to the aqueous solution in the adsorption and the percentage elution to the aqueous phase in the extraction. ○: Extraction ($[^8\text{None}\{3\}\text{CH}_2\text{NH}_2] = 5 \text{ mM}, 10 \text{ cm}^3$, data from [7]), ●: adsorption (Resin = 20 mg, 33wt%), [formaldehyde] = 10 mM in 10 cm$^3$, pH = 9.0 (0.1 M HEPES solution - 0.1 M NaOH solution).

Figure 3. Effect of the reaction time on the percentage removal of formaldehyde with $^8$None{3}CH$_2$NH$_2$. ○: Extraction ($[^8\text{None}\{3\}\text{CH}_2\text{NH}_2] = 5 \text{ mM}, 10 \text{ cm}^3$, data from [7]), ●: adsorption (Resin = 20 mg, 33wt%), [formaldehyde] = 10 mM in 10 cm$^3$, pH = 9.0 (0.1 M HEPES solution - 0.1 M NaOH solution).

Figure 4. Effect of pH on percentage removal of formaldehyde with $^8$None{3}CH$_2$NH$_2$. ○: Extraction ($[^8\text{None}\{3\}\text{CH}_2\text{NH}_2] = 5 \text{ mM}, 10 \text{ cm}^3$, data from [7]), ●: adsorption (Impregnated resin = 20 mg, 33.3wt%), □: adsorption (XAD-7 itself = 20 mg), [formaldehyde] = 2.5 mM, 0.1 M HCl - 0.1 M HEPES solution - 0.1 M NaOH solution.

Figure 5. Effect of the initial formaldehyde concentration on the amount of formaldehyde removal on $^8$None{3}CH$_2$NH$_2$-impregnated resin. Resin amount = 20 mg, pH = 9.0 (0.1 M HEPES solution - 0.1 M NaOH solution).
Figure 6. Effect of hydrochloric acid concentration on the percentage recovery of formaldehyde from formaldehyde-loaded 
$^8$None{3}$\text{CH}_2\text{NH}_2$. ○: Extraction (data from [7]), ●: adsorption, 
$[\text{HCl}] = 0.25 – 5.0 \text{ M}$, volume of HCl solution = 10 cm$^3$, shaking time 24 h.

References

1) R. Yamaguma, A. Yamashita, H. Kawakita, T. Miyajima, C. Takemura, K. Ohto, N. Iwachido, Sep. Sci. Technol., 47, 1303-1309 (2012).
2) H. Furugou, K. Ohto, H. Kawakita, H. Harada, K. Inoue, Ars Separatoria Acta, 5, 68-75 (2007).
3) Y. Ueda, S. Morisada, H. Kawakita, K. Ohto, Solvent Extr. Res. Dev. Jpn., 21, 9-19 (2014).
4) K. Ohto, H. Nakagawa, H. Furutsuka, T. Shinozaki, T. Nakamura, T. Oshima, K. Inoue, Solvent Extr. Res. Dev. Jpn., 11, 121-134 (2004).
5) K. Ohto, Solvent Extr. Res. Dev. Jpn., 17, 1-18 (2010).
6) K. Ohto, Ion Exch. Solv. Extr., 21, 81-127 (2014).
7) K. Ohto, A. Yamashita, Y. Ueda, R. Yamaguma, S. Morisada, H. Kawakita, Solvent Extr. Res. Dev. Jpn., 21, 173-180 (2014).
8) T. G. Sprigings and C. D. Hall, J. Chem. Soc., Perkin Trans. 2, 2063-2067 (2001).
9) K. Ohto, Y. Senba, N. Eguchi, T. Shinozaki, K. Inoue, Solvent Extr. Res. Dev. Jpn., 6, 101-112 (1999).
10) K. Ohto, S. Inoue, N. Eguchi, T. Shinozaki, K. Inoue, Sep. Sci. Technol., 37, 1943-1958 (2002).
11) N. Hashiguchi, M. Tanaka, K. Ohto, H. Kawakita, K. Inoue, Solvent Extr. Res. Dev. Jpn., 15, 99-110, (2008).
12) H. Li, J. Liu, L. Zhu, X. Gao, S. Wei, L. Guo, S. Zhang, X. Liu, Solvent Extr. Res. Dev. Jpn., 21, 147-161 (2014).