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Efficient Hg(II) Ion Transport through Liquid Membranes by Diamide Derivatives of Methionine with a 8-Quinolyl Group

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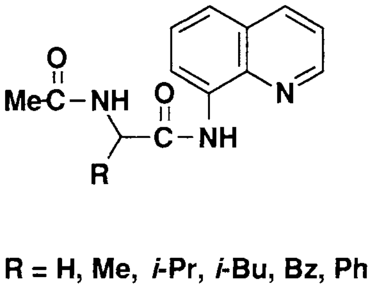
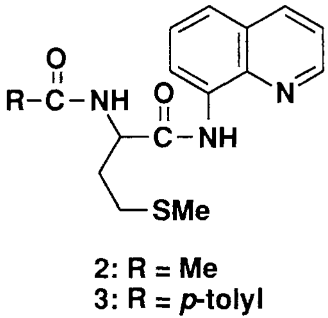
Several new diamide compounds with a 8-quinolyl group were synthesized from methionine and their metal ion transport abilities as carriers through liquid membranes were investigated. Hg(II) ion was transported most effectively by these carriers . The selectivity for Hg(II) over Cu(II) was improved by the introduction of a bulky *p*-toluoyl group as the acyl group on the 2-acylamino substituent.

Considerable attention has been focused on the extraction and transport of heavy metal ions through liquid membranes by synthetic ionophores.1) Some of heavy metals are invaluable as so-called noble metals, while some are harmful to ecosystems and cause serious environmental problems. Therefore, besides industrial significance, effective separation and recovery of these metals by ionophores are regarded as the key technologies which can resolve these problems. From this aspect, development of new ionophores is required, which are easy to prepare and exhibit high efficiency toward heavy metal ions.

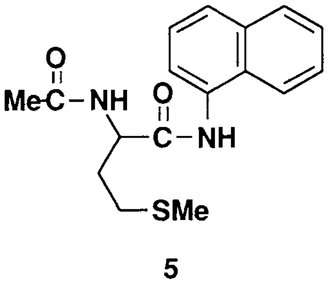
In the previous study,2) we found that diamide compounds **1** prepared from α-amino acids are effective for Cu(II)-selective transport through liquid membranes. The alanine and phenylalanine derivatives **1** (R = Me, Bz, respectively) have good Cu(II) transport abilities. In this paper, we report the properties of sulfur-containing diamide compounds **2**, **3**, and **4** derived from methionine as metal ionophores. As reported already, sulfur-containing ionophores like thiocrown ethers,3-5) thiolariat ethers,6) and acyclic thioethers7) show high affinity toward soft heavy metal ions such as Ag(I), Hg(II), and Cd(II) ions. Consequently, compounds **2**, **3**, and **4** might be expected to have the same property as above.



1: R = H, Me, *i*-Pr, *i*-Bu, Bz, Ph



2: R = Me
3: R = *p*-tolyl
4: R = 2-thienyl



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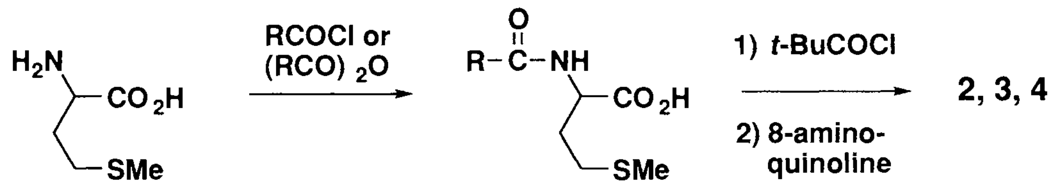

Compounds **2**, **3**, and **4** were prepared from DL-methionine in two steps as shown in above scheme.[8] Reactions of DL-methionine with appropriate acid chlorides or acid anhydrides furnished *N*-acyl-DL-methionines, which were converted to the desired diamides **2**, **3**, and **4** by a reaction of corresponding mixed acid anhydrides with 8-aminoquinoline. For comparison, compound **5** was also prepared with 1-aminonaphathalene instead of 8-aminoquinoline.

The transport experiments were done with a U-type glass cell across a chloroform liquid membrane from a buffered aqueous source phase (pH 6.2) containing one or several kinds of heavy metal ions into a receiving phase containing 0.05 M(= mol dm^{-3}) sulfuric acid.[9] The cell was kept at 25 °C and each phase was mechanically agitated at 200 rpm. Other transport conditions are described in Table 1. At regular intervals, the aqueous phase was sampled. The sample was suitably diluted, and the concentration of metal ion was assayed with an atomic absorption spectrophotometer.[10]

Table 1 shows the results of single ion transport experiments for Hg(II) and Cu(II) ions by compounds **2** - **5**. Compound **2** transported Hg(II) faster than Cu(II). The transport of Hg(II) by **2** was almost completed by 36 h. With excess Hg(II) ions (Hg(II)/**2** = 4.5 in molar ratio),[11] 54% of Hg(II) was transported by 96 h. For Co(II), Ni(II), Zn(II), Pb(II), Cd(II), and Ag(I) ions, single metal ion transport by **2** was also attempted under the same conditions. A small amount of Ag(I) was transported (12% by 24 h). None of other ions was transported at all even by 48 h. These results indicate that **2** transports only Hg(II) and Cu(II) ions efficiently. Competitive transport of Hg(II) and Cu(II) by **2** was also done. Figure 1 (A) shows time dependence of amount of Hg(II) and Cu(II) in the competitive experiment. The value of the selectivity for Hg(II) over Cu(II) was 1.9, which was calculated from the transported amounts by 6 h.

A modification of the structure of **2** was made to improve the Hg(II) selectivity over Cu(II). In our previous study of diamide derivatives **1**, Cu(II) transport ability of the carrier was affected by the acyl group on the 2-acylamino substituent.[12] Introduction of a bulky acyl group such as pivaloyl, *p*-toluoyl, thenoyl etc. into the 2-acylamino substituent caused lowering of Cu(II) transport ability. Therefore, we synthesized

Table 1. Amount of Hg(II) and Cu(II) transported through a $CHCl_3$ liquid membrane by 24 h[a]

Carrier	Hg(II) transported into the receiving phase, %	Hg(II) remaining in the source phase, %	Cu(II) transported into the receiving phase, %	Cu(II) remaining in the source phase, %
2	90	3	84	9
3	92	1	16	80
4	61	24	—	—
5	43	50	0	94

a) Initial transport conditions (25 °C); (Source phase) 10 mmol dm^{-3} $Hg(OAc)_2$ or $Cu(OAc)_2$, pH 6.2, 15 ml / (Liquid membrane) 0.3 mmol of carrier in 30 ml of chloroform / (Receiving phase) 0.05 mol dm^{-3} sulfuric acid 15 ml.

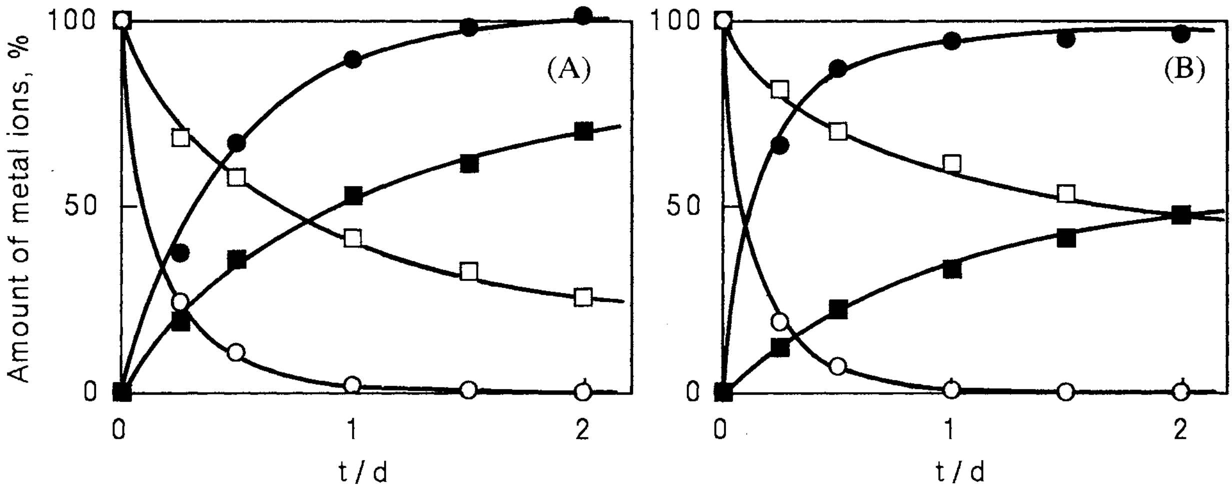

Fig. 1. Time dependence of amount of Hg(II) and Cu(II). (A), compound **2**; (B), compound **3**. -●-, Hg(II) transported into the receiving phase; -○-, Hg(II) remaining in the source phase; -■-, Cu(II) transported into the receiving phase; -□-, Cu(II) remaining in the source phase.

diamide compound **3** to suppress the Cu(II) transport. Cu(II) transport ability of **3** lowered very much as expected (see Table 1). On the other hand, **3** transported Hg(II) even faster than **2**. These results suggested that contribution of 2-acylamido substituent on the Hg(II) uptaking by diamides **2** and **3** is not so large as in Cu(II) transport by **1**. Figure 1 (B) shows the time dependence of Hg(II) and Cu(II) in the competitive transport experiment by **3**. High Hg(II) selectivity (Hg(II)/Cu(II) = 5.5) was observed, although Cu(II) transport rate increased a little compared with that of single Cu(II) transport. Thus, enhancement of the Hg(II) selectivity over Cu(II) was achieved.

Hg(II) transport ability of diamide **4** with two sulfur atoms was not good as those of **2** and **3**. In the Hg(II) transport experiment by **4**, Hg(II) complex appeared as white precipitate in a chloroform liquid membrane as time passed. Hence, transport efficiency became lower, and we concluded that **4** is not appropriate to use as a Hg(II) carrier.

Hg(II) transport experiment by compound **5** having a naphthyl group instead of a quinolyl group was carried out. Hg(II) transport ability of **5** was found to be lower than that of **2** as shown in Table 1. Consequently, large contribution of 8-quinolylcarbamoyl moiety on effective Hg(II) ion uptake by **2** and **3** seems likely. In addition, the existence of the interaction between sulfur atom and Hg(II) was suggested by the ^{1}H NMR spectrum of the 1 : 1 mixture of **2** and $Hg(OAc)_2$. Marked down field shifts were observed on the methyl and methylene protons next to sulfur atom in **2**[13) as reported already on other sulfur-containing ionophores.[4, 6) On the other hand, interaction between 2-acylamino substituent and Hg(II) seems to be relatively weak as mentioned already, although the broadening and downfield shift of the amido proton of 2-acylamino substituent was observed in the ^{1}H NMR spectrum of the mixture. Thus, in a liquid membrane, these diamides **2** and **3** seem to form a 1:1 complex with Hg(II) mainly by coordination of thioether and 8-quinolylcarbamoyl moieties,[14) although the precise mode of the coordination is still unclear. The results of the titration experiment using UV spectrometer also supported the formation of a 1:1 complex of **2** with Hg(II).

In conclusion, the present diamide compounds **2** and **3** from methionine were effective for the Hg(II) transport through liquid membranes. The selectivity of Hg(II) over Cu(II) was improved by introducing a bulky *p*-toluoyl group as the acyl group on the 2-acylamino substituent. The high selectivity and efficiency toward Hg(II) will make it possible to utilize these compounds as carriers for effective Hg(II) separation.

References

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8) All new compounds gave satisfactory spectroscopic and analytical data. Anal. for **2**. Found: C, 60.61; H, 6.00; N, 13.04%. Calcd for $C_{16}H_{19}N_3O_2S$: C, 60.55; H, 6.00; N, 13.04%. For **3**. Found: C, 67.17; H, 5.79; N, 10.57%. Calcd for $C_{22}H_{23}N_3O_2S$: C, 67.16; H, 5.89; N, 10.68%. For **4**. Found: C, 59.21; H, 4.96; N, 10.91%. Calcd for $C_{19}H_{19}N_3O_2S$: C, 59.21; H, 4.97; N, 10.90%. For **5**. Found: C, 64.27; H, 6.52 ; N, 8.89%. Calcd for $C_{17}H_{20}N_2O_2S$: C, 64.54; H, 6.37; N, 8.86%.

9) K. Hiratani, I. Nozawa, T. Nakagawa, and S. Yamada, *J. Membr. Sci.*, **12**, 207 (1982).

10) Reproducibility was confirmed as ±5% or better.

11) 15 ml of 30 mmol dm^{-3} $Hg(OAc)_2$ solution was used as a source phase and 0.1 mmol of **2** was used as a carrier.

12) K. Kasuga, T. Hirose, K. Takahashi, and K. Hiratani, 64th National Meeting of the Chemical Society of Japan, Niigata, October 1992, Abstr., No. II, p. 527.

13) Down field shifts: 0.29 and 0.22 ppm for each of two methylene protons and 0.26 ppm for methyl protons in $CDCl_3$.

14) The complex is supposed to include one acetate anion.

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