CHEMISTRY LETTERS, pp. 725-728, 1990.

N,N'-Bis(8-quinolyl)glutaramide as a Highly Selective and Effective Cu(II) Carrier for the Uphill Transport through Liquid Membranes

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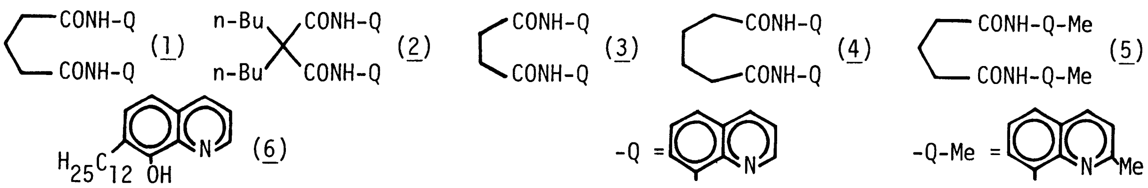
N,N'-Bis(8-quinolyl)glutaramide was found to be an excellent Cu(II) carrier through chloroform liquid membrane. It can selectively and efficiently transport only Cu(II) from aqueous solution containing Cu(II), Zn(II), Ni(II), and Co(II).

Carrier-mediated continuous solvent extraction, i.e., transport through liquid membranes, of metal ions is not only an attractive method for the separation and recovery of valuable resources,[1] but also of importance from the biological, medical, and environmental points of view. Although many carriers on the transport of alkali and alkaline earth metal ions through liquid membranes have been reported so far,[2] only a few synthetic carriers for the highly selective and effective uphill-transport of heavy metal ions have been developed.[3-6]

We report here on very selective and efficient Cu(II) transport behaviors of N,N'-bis(8-quinolyl)glutaramide(1) through liquid membranes. It has been so far well known that commercially available 7-alkyl-8-quinolinol(Kelex 100)(6) can work not only as an excellent Cu(II) selective extractant in the solvent extraction, but also as a Cu(II) selective carrier in the transport through liquid membranes.[7] Then, the transport ability of 1 was investigated comparing with that of 6. Diamide 1 was obtained in high yield from the reaction of glutaryl dichloride with 8-aminoquinoline in the presence of triethylamine in benzene. In a similar manner, diamides, 2 - 5, were also prepared to investigate the structural effect on the Cu(II) transport.[8]



The transport experiments were carried out by using a U-type glass cell across chloroform liquid membrane from the buffered aqueous source phase containing either a single heavy metal ion or plural ions of Cu(II), Ni(II), Co(II), and Zn(II) to the receiving phase containing 0.05 M(= mol dm^{-3}) sulfuric acid. The buffered aqueous source phase was adjusted to pH 6.2. The cell was kept at 25 ± 0.2 °C and the each phase was mechanically agitated at 200 rpm.[9] Table 1 shows the results of Cu(II) transport after 2 days along with the transport conditions.

Table 1. Amount of Cu(II) Transport through $CHCl_3$ Phase after 2 Days[a)]

Carrier	Cu(II) transported in the receiving phase,%	Cu(II) remaining in the source phase,%	Cu(II) existing in chloroform,%[b)]
1	63	25	2
2	0.2	94	6
3	29	63	1
4	6	93	1
5	2	97	1
6[c)]	34	≈0	66

a) Initial transport conditions(25 °C): (source phase) 10 mM $Cu(OAc)_2$, pH 6.2, 15 ml/(liquid membrane) carrier(0.3 mmol for 1 - 5 or 0.6 mmol for 6) in 30 ml of chloroform/(receiving phase) 0.05 M sulfuric acid 15 ml.

b) The values were calculated from Cu(II) amounts measured both in the receiving and the source phases.

c) Two equimolar amounts of 6 compared with others was used because 6 was a bidentate ligand.

In Table 1, glutaramide derivative(1) has apparently the most excellent Cu(II) transport ability among these carriers and can transport Cu(II) against its concentration gradient(see Fig. 1). The ability of the Cu(II) transport decreases in the following order: 1 > 6 > 3 >> 4 > 5 > 2. The transport ability clearly depends on the structures of diamides. It should be noticed here that 1 is superior to 6 in the Cu(II) transport under the same conditions, and 5 having 2-mehtyl group on the quinoline ring is considerably inferior to 1. In the latter case it can be considered that two methyl groups interfere with the formation of the stable Cu(II) complex. Although malonamide 2 can extract Cu(II) with excellent selectivity as recently reported,[10] it has little ability of Cu(II) transport through liquid membranes because 2 forms stable 1 : 1 complex with Cu(II). Succinamide 3 seems to be a fairly good carrier, but it is soluble to some extent in the acidic receiving phase, and then it is not appropriate as a carrier in the liquid membrane transport.

Figure 1 shows the time-dependence of the Cu(II) amount of transport by amides, 1 and 6. Initial transport rate of 6 seems comparable to that of 1. However, the Cu(II) amount of transport by 1 increases almost linearly almost linearly even after 2 days, whereas the rate of transport by 6 decreases with the time. In addition, the decreasing rate of Cu(II) in the source phase by 6 is remarkably rapid compared with that by 1. The curve of the decreasing amount with time by 1 in the source phase is symmetrical about the line corresponding to the increasing amount with time in the receiving phase, whereas Cu(II) amount in the source phase decreases very rapidly by 6 and becomes nearly 0% after 1 day. Then, a large portion of Cu(II) exists in chloroform phase and Cu(II) there is slowly released to the receiving phase(see in Table 1). This is supported by the observation that the color in chloroform containing 6 changes rapidly from colorless to yellowish brown and the color does not change during the transport experiment, while that containing 1 becomes only pale yellow during it. Furthermore, the single ion-transport of Ni(II), Co(II), and Zn(II) by 1 was attempted under the same conditions, but none of them could be transported at all. It should be noted in Fig. 1 that the amount of Cu(II) transported by 1 in the receiving phase after 1.5 days is apparently much more than that remained in the source phase and yet continues to increase even after 1.5 days. This fact means that 1 can work as a highly selective and effective Cu(II) carrier for the uphill transport through liquid membranes.

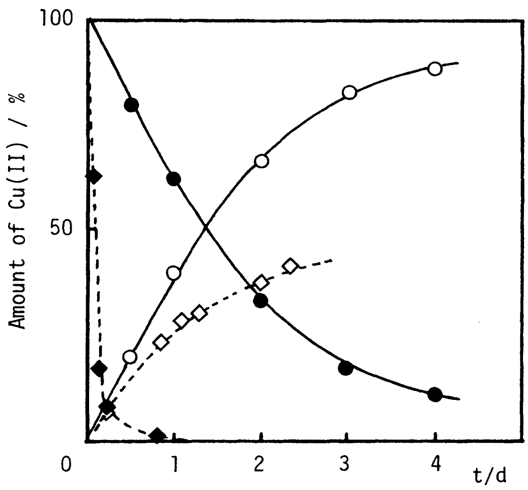


Fig. 1. Time dependence of Cu(II) transport through $CHCl_3$ membrane; transport conditions see in Table 1. 1 : —○— (Receiving phase) and —●— (Source phase), 6 : —◇— (Receiving phase) and —◆— (Source phase).

Next, in the competitive transport of Cu(II), Ni(II), Co(II), and Zn(II) by 1 and 6 from the source phase (pH 6.2) containing 10 mM of each metal ion, 0.3 mmol of glutaramide(1) in 30 ml of $CHCl_3$ transported only 54% of Cu(II) after 2 days under the same conditions described above, while 0.6 mmol of Kelex 100(6) in 30 ml of CHCl transported not only 20% of Cu(II) but also 34% of Zn(II), and a small amount of Ni(II)(<1%) and negligible amount of Co(II)(≈0%). Additionally, 1 transported only Cu(II) more than 90% after 2 days even from the solution containing a mixture of

1 mM of Cu(II) and 10 mM of each of Ni(II), Co(II), and Zn(II).

In conclusion, it is elucidated that glutaramide 1 can transport Cu(II) with high selectivity and efficiency through liquid membranes from the source phase in the range of nearly neutral pH to the acidic receiving phase, and the uphill transport of Cu(II) with 1 can be easily realized by keeping the pH difference between the source phase and the receiving one. This compound could be a potential candidate as a carrier to be applied for the practical use of Cu(II)-separation.

References

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(Received February 1, 1990)