Chinese Chemical Letters Vol. 13, No. 10, pp 1003 – 1004, 2002 1003
http://www.imm.ac.cn/journal/ccl.html

Liquid Membrane Transport Behavior of Functional Substituted Crown Ethers for Amino Acids

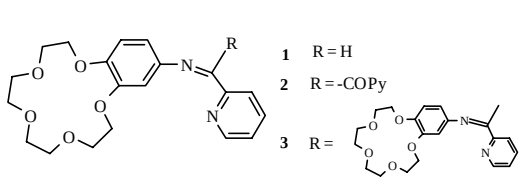
Xin Cheng LIAO, Xing Wang WANG, Jing Chao TAO*

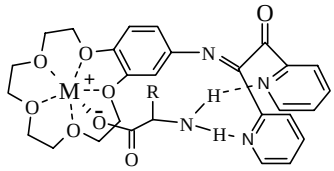
Department of Chemistry, Zhengzhou University, Zhengzhou 450052

Abstract: Three functional substituted crown ethers were synthesized as liquid membrane transport carriers for amino acids. The result obtained shows that this kind of ditopic ligands can transport sodium salt of amino acids in good rate value especially the one with two pyridinyl groups as binding site outside the macrocycle.

Key words: Crown ether, amino acid, membrane transport, co-ordination.

Crown compounds offer a variety of interesting functions based on their specific bindings of organic guest species[1,2]. In particular, they can act as carriers in ion-extraction, membrane transport, and phase-transfer reactions. In contrast to the large variety of synthetic ionophores for cation transport, there are only a few examples of synthetic ″anion transport ionophores″. Therefore, it appears highly desirable to search for a new class of ionophores with excellent transport abilities for amino acids, nucleic acids, and other interesting anionic guests. Although the physico-chemical features and biological importance of membrane transport have long been recognized, design and synthesis of carrier molecules for transporting amino acids have only recently developed[3]. In this paper the membrane transport behavior for some amino acids of three new functional substituted crown compounds with pyridyl group(s) as proton binding site outside the macrocycle, **1~3**, was discussed.





4

It was shown from our study[4] that the three functional substituted crown ethers could be easily prepared by treating 4′-aminobenzo-15-crown-5 and corresponding carbonyl compounds in alcoholic solvent. All the three ligands could form hetero-dinuclear or hetero-trinuclear complexes with alkaline and transition metal cations. Since the binding site outside the macrocycle takes important role in the complex formation, we can imagine that this kind of compounds may be used as ionophores in

membrane transport of amino acids or other anionic guests. In some biological systems, amino acids are believed to be carried with cations such as Na^+ and K^+ ions by a common ionophore. The sodium salts of some amino acids such as tryptophane, phenylalanine, methionine and histidine were thus selected as guest molecules for the anion transport study.

The transport was carried out through a CH_2Cl_2 membrane separating two aqueous solutions as described previously[5]. The apparatus described by Ramdani[6] was used. Source phase: aqueous solution (15mL) of sodium salt of amino acid (1×10^{-3}mol/L) and nitrate(0.1mol/L). Membrane: CH_2Cl_2 solution (45mL) of the ligand to be studied (5×10^{-3} mol/L). Receiving phase: distilled water (15mL). The transport experiments were performed at 25 ± 1°C. The appearance of the anionic amino acid in the receiving phase was detected by UV spectroscopy.

Table 1 Transport rate values of carrier **1~3** for amino acids in 10^{-8} mole/h

		Phenylalanine	Tryptophane	Methionine	Histidine
	1	38.8	22.9	13.5	6.0
ν	**2**	83.5	36.8	22.4	18.5
($\times10^8$ mol / h)	**3**	65.5	31.4	14.5	12.8

The transport abilities of macrocycles **1~3** toward the sodium salts of amino acids were studied and the transport rate values are given in **Table 1**. As was shown that there was no transport of any amino acid salts across the membrane in the condition used in the absence of the carrier. All the three macrocyclic carriers showed much higher transport rate for phenylalanine than other amino acids studied, indicating that there may be stronger interaction between carrier and phenylalanine induced by hydrogen bonds, charge transfer as well as π-π interaction. Comparing the three carriers, it is found that compound **2** showed better transport ability for each amino acid, indicating that the formation of hydrogen bonds between the amino group and the binding site outside the macrocycle takes important role in the transport procedure (**4**). In addition, proper geometrical fitting between binding sites of guest and carrier was an essential factor in promoting amino acids transport.

Acknowledgments

We are grateful to the National Natural Science Foundation of China (29872034) and the Natural Science Foundation of Henan Province for the financial support.

References

1. P. Molenveld, S. Kapsabelis, D. N. Reinhoudt, *J. Am. Chem. Soc.*, **1997**, *119*, 2948.
2. J. S. Seo, R. C. Hynes, D. Villiams, J. Chin, *J. Am. Chem. Soc.*, **1998**, *120*, 9943.
3. Y. N. Belokon, K. L. Prilula, V. I. Tararov, D. G. Gosev, V. M. Belikov, *J. Chem. Soc., Dalton Trans.*, **1990**, 1873.
4. J. C. Tao, Y. J. Wu, S. J. Xu, D. P. Zou, *Chin. Chem. Lett.*, **2001**, *12*, 479.
5. J. C. Tao, Y. J. Wu, J. Y. Song, *Polyhedron*, **1999**, *18*, 1015.
6. A. Ramdani, G. Tarrago, *Tetrahedron*, **1981**, *37*, 991.

Received 17 January, 2002