METAL ION UPTAKE AND RELEASE WITH 2,2'-BIPYRIDINE DERIVATIVES BY pH SWITCHING

Shinsaku SHIRAISHI, Noriyuki KISHII, and Koji ARAKI
Institute of Industrial Science, The University of Tokyo,
7-22-1 Roppongi, Minato-ku, Tokyo 106

We found that 6,6'-diamino-2,2'-bipyridine (DABP) has high complex formation constant at neutral pH with several heavy metal ions, especially with cupric ion, and that the complexing ability greatly degreases on acidifying. In this study, we synthesized lipophilic derivatives of DABP along with other lipophilic derivatives of 2,2'-bip-ridine, and examined their ability to transfer metal ions to and fro between organic and aqueous phases by pH swiching in the aqueous phase.

6-Bromo-6'-hexyloxy-2,2'-bipyridine (I) and 6,6'-dihexyloxy-2,2'-bipyridine (II) were prepared from 6,6'-dibromo-2,2'-bipyridine and 1-hexanol. 6-Amino-6'-dodecylamino-2,2'-bipyridine (III) and 6,6'-bis(dodecylamino)-2,2'-bipyridine (IV) were obtained by N-alkylation of DABP with dodecyl bromide. These compounds are soluble in organic solvents such as benzene, hexane and chloroform but insoluble in water. Structures of these compounds were confirmed by PMR, IR, and mass spectra and elementary analyses; (I) mp 54.5-55.5 °C, M^+334.065(334.0727), (II) mp 77.5-79 °C, M^+356.2354(356.2556), (III) mp 72-73.5 °C, M^+354.2693(354.2786), (IV) mp82-5 °C, M^+522.4532(522.4665)

Metal ions in an aqueous solution was extracted with an organic solution containing I-IV by shaking the two solution. The metal ion extracted in the separated organic layer was reversely released into water. The amounts of metal ions extracted from or released into aqueous phase was determined by colorimetric method. Table shows the extraction and release of cupric ion with (I)-(IV)/chloroform systems. The ligands (III) and (IV) showed efficient extracting ability at pH 7.1 and efficient release at pH 2.8. This suggests the participation of the amino groups on 6 and 6' positions in complexation and release processes.

Table Extraction and Release of Cupric Ion from and into aqueous layer
(% of the Cu^{2+} based on the initial content)

	pH of aqueous phase	Ligand in organic phase				
		none	I	II	III	IV
Extraction[a]	2.8	t[c]	3	t	8	7
	7.1	8	13	11	73	71
Release[b]	7.1	t	t	t	t	t
	2.8	3	1	2	46	32

a) Extraction from a 10 ml buffer solution containing 2.5 x 10^{-7} mol of Cu^{2+} with 10 ml of $CHCl_3$ containing 2.5 x 10^{-7} mol of ligand by shaking for 30 min.
b) Release from 3 ml of the $CHCl_3$ layer extracted at pH 7 into 5 ml of a buffer solution of pH indicated.
c) t means trace amount.