Lithium(I) Porphyrin Complex for the Spectrophotometric Determination of Lithium Ion in Aqueous Solution

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A water-soluble octabromoporphyrin has been synthesized and developed for the determination of lithium ion in aqueous solution. The porphyrin reacts with lithium ion in alkaline solution to form the lithium complex along with a shift of absorption maximum to shorter wave length. But sodium and potassium ions do not react with the porphyrin. The equilibrium constant of the Li(I) porphyrin complex was determined and applied to the determination of lithium(I) in natural water. Interference of metal ions was removed by ligand buffer of Mg-EDTA complex.

Keywords lithium, porphyrin, spectrophotometric method

Porphyrrins have been used for the determination of a trace amount of metal ions, especially transition metal ions, due to the high molar absorptivities of metalloporphyrins reaching several hundred thousand mol\(^{-1}\) dm\(^3\) cm\(^{-1}\) at 400-500 nm (the Soret band). Banks and Bisque were the first to propose porphyrin as a reagent for zinc(II) in 1957 but little work was done until some twenty years later by Ishii and Yotshuyanagi's groups, who published a series of papers dealing with use of porphyrins for the determination of Cu, Pb, Cd and Zn. However, porphyrins have not been used for the determination of Li due to a difficulty in the formation of Li-porphyrin complex in aqueous solution.

We synthesized a new water-soluble porphyrin with eight bromine atoms at \(\beta\)-pyrrole position. The bromine atoms decrease the basicity of the porphyrin by their electron withdrawing and make it easy to form Li-complex in alkaline solution.

In this paper we report a first colorimetric method for the determination of lithium ion in the presence of a large excess of sodium and potassium ions using a water-soluble porphyrin. The equilibrium constant of the lithium porphyrin complex was determined and the results were applied to the determination of lithium ion in some natural water samples.

Experimental

Apparatus

Absorption spectra were recorded on a Shimadzu UV-2100 and a Jasco Ubest spectrophotometers. The pH values were determined with a radiometer Ion 85 analyser with a combined electrode (GK2401C). A 1.000 \(\times\) 10\(^{-2}\) mol dm\(^{-3}\) nitric acid solution containing 0.09 mol dm\(^{-3}\) sodium nitrate was employed as the standard hydrogen ion concentration (\(-\log[H^+] = 2.000\)). From the pH meter reading in various electrode system was calibrated in terms of \(-\log[H^+]\) at an ionic strength of 0.1 mol dm\(^{-3}\) (HNO\(_3\)-NaNO\(_3\)). All experiments were carried out at 25 °C.

Synthesis of the Porphyrin

2,3,7,8,12,13,17,18-Octabromo-5,10,15,20-tetrakis(4-sulfonatophenyl)-21H,23H-porphyrin (H\(_2\)obtpps\(_4\), Fig. 1). Tetraphenylporphyrin (H\(_2\)tpp, 1g, 1.63 mmol) was brominated to afford 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetraphenylporphyrin (H\(_2\)obtpp, 1) by treating it with N-bromosuccinimide (NBS, 3 g, 16.8 mmol) instead of bromine previously reported in dibromomethane which was sufficiently dried by molecular sieve (4 A) before use. The crude product gave three bands on an activated alumina chromatography (300 mesh, Wako, Japan) using chloroform as an eluent and the first band was collected. Yield was 53 %. The compound 1 was sulfonated in concentrated sulfuric acid. The product was precipitated by careful addition of small amount of water and purified by a Sephadex column LH-20 which was soaked in a water-methanol (7:3) mixed solvent. Absorption maximum-wave length (log \(\varepsilon/mol^{-1}\) dm\(^3\) cm\(^{-1}\) and \(1^H\) NMR data (\(\delta ppm\)) of the final product, H\(_6\)obtpps, were as follows: 376 (4.54), 478 (5.30), 657 (4.25), and 760 nm (4.07) in aqueous solution at pH 7.0; 8.62 (d, 8H, o-H of phenyl) and
Reagents
Sodium nitrate used for adjusting ionic strength was purified by solvent extraction using phenyl-diazenecarbothionic acid 2-phenylhydrazide (dithizone) in carbon tetrachloride to remove transition and heavy metal ions like Cu(II), Zn(II), Fe(II), and Pb(II), and followed by recrystallization from hot water. Otherwise these metal ions form their metalloporphyrins in alkaline pH. Other metal nitrates were of analytical-reagent grade and were used without further purification. The buffer solutions were prepared by addition of nitric acid or sodium hydroxide to solutions of sodium acetate for pH 4-6, 2-morpholinoethanesulfonic acid (MES) for pH 6-7, 2-(4-(2-hydroxyethyl)-1-piperazinyl)ethanesulfonic acid (HEPES) for pH 7-8.5 and sodium borate for pH 8.5-10 (Wako Pure Chemical Industry, Osaka, Japan). All solutions were prepared in water treated by a Mill-Q SP TOC (Nippon Millipore Ltd., Japan).

Results and Discussion

Acid-Dissociation Constant of H4obtpps2-
Absorption spectra of the porphyrin were measured in various pH values at ionic strength of 0.1 mol dm⁻³ (NaNO₃) and at 25 °C. The absorption maximum-wave lengths were observed in three pH regions: 490 and 740 nm at pH lower than 2, 478 and 657 at pH 6-8.2 and 502 and 745 nm at pH higher than 11 (Fig. 2). The change in absorbance suggests three steps for the acid-dissociation equilibrium and their equilibrium constants as given as follows:

\[
\begin{align*}
H_4P^2^- & \rightleftharpoons H_3P^- + H^+; \ pK_{a1} = 1.96 \pm 0.06 \\
H_3P^3^- & \rightleftharpoons H_2P^4^- + H^+; \ pK_{a2} = 4.83 \pm 0.04 \\
H_2P^4^- & \rightleftharpoons HP^5^- + H^+; \ pK_{a3} = 10.02 \pm 0.02
\end{align*}
\]

where \(H_2P^4^-\) denotes free-base form of the porphyrin which is main chemical species in neutral pH. The acid-dissociation constants of the porphyrin were determined by using a nonlinear least-squares minimization program in two pH ranges: one region is 1-8 and other is pH 8-13. The octabromo groups lower the basicity of the porphyrin by their electron-withdrawing effect, and the deprotonation process of the free-base form, \(H_2obtpps4^+\), producing \(Hobtppss^-\) occurred at pH 10.

Formation of Lithium(I) Porphyrin.
Lithium hydroxide reacted with \(H_2obtpps4^-\) to shift the absorption spectrum towards shorter wavelength. But sodium hydroxide and potassium hydroxide did not alter the absorption spectra (Fig. 2). The absorption maximum-wave length (log \( \varepsilon \)mol⁻¹ dm³⁻¹ cm⁻¹) of the lithium(I) porphyrin complex are 490.5 nm (5.31) and 734 nm (4.36). Non-brominated porphyrin, i.e., \(H_2tpps4^-\), did not give any spectral change even in 0.1 mol dm⁻³ LiOH. This is a unique behavior of \(H_2obtpps4^+\). Absorption spectra were measured at different concentrations of lithium ion (10⁻⁵-10⁻² mol dm⁻³) and sodium hydroxide (pH 11.7-12.3) and the results suggest the following reaction for the formation of lithium-porphyrin complex:

\[
\begin{align*}
Li^+ + HP^5^- & \rightleftharpoons LiP^5^- + H^+
\end{align*}
\]
One lithium ion reacts with HPS' to form LiP5" by releasing one hydrogen ion. The equilibrium constant of eq. 5 was found to be log(Kip) = -8.8±0.02 at 25 °C and 1 = 0.1 mol dm⁻³ (NaNO₃).

Porphyrins form stable complexes with transition and heavy metal ions, but lithium(I) porphyrins are very unstable. Arnold et al. isolated Lithium porphyrins and reported that one lithium can be bound to all four nitrogens in the porphyrin in polar solvent and two lithiums can be interacted with the porphyrin nitrogen in nonpolar solvents. 19,20

The formation constant of metalloporphyrin is dependent on the ionic radius of metal ions due to the restricted porphyrin-core size (400 pm in diameter). 5,6 Since the ionic radius of lithium(I) (73 pm) is comparable to that of zinc(II) (74 pm), the lithium ion may be incorporated well in the porphyrin core like zinc(II). 8 However, sodium and potassium ions did not form stable complexes with the porphyrin under the same experimental conditions because of the large ionic radii of sodium (113 pm) and potassium (151 pm). 7 The octabromo groups decrease the basicity of the porphyrin so that the proton in the pyrrole group is released even at pH 10. That makes it easy for lithium ion to react with the porphyrin.

It is interesting to know how [LiP]₅⁻ is stable compared to lithium(I) crown-ether complexes. Although the equilibrium constant for the reaction

\[ \text{Li}^+ + \text{P}^6^\cdot \rightleftharpoons \text{LiP}^5^- \]

was not able to be determined, the conditional formation constant defined by \[ K = \frac{[\text{LiP}^5^-][\text{Li}^+]}{[\text{P}^6^-]} \] was calculated as \(10^{4.21}\) in 0.1 mol dm⁻³ NaOH from the formation constant (K) of LiP₅⁻ and acid-dissociation constant of H₂obtpps₄⁻ (pKₐ3) values, where \([\text{P}^6^-] \) denotes the total concentration of the porphyrin unbound to lithium(I). The equilibrium constant is much larger than the formation constant of Li with crown-ethers. 9

The above results were applied to the determination of lithium ion in aqueous solution. The following procedure was used on the presence of lithium(I). A 5-cm³ water sample containing 0.07-7 µg of lithium(I) was taken into a 10-cm³ calibrated flask. Then, 1 cm³ of N,N'-1,2-ethanediylbis[N(carboxymethyl)-glycinato)magnesium ([Mg(edta)]₂⁻), solution (CMg = 1.1 x 10⁻² mol dm⁻³; CH₂edta = 1.0 x 10⁻² mol dm⁻³), 1 cm³ of H₂obtpps₄⁻ (3.8 x 10⁻⁵ mol dm⁻³), and 0.5 cm³ of 1 mol dm⁻³ NaOH were added to the flask. Distilled water was added to the mark (10 cm³) and absorbance at 490 was measured against a blank solution. A calibration graph was linear over the range of 1 x 10⁻⁶ - 1 x 10⁻⁴ mol dm⁻³ of lithium(I) with a correlation factor of 0.967. Lithium ion less than a
few ppm level was determined spectrophotometrically in aqueous solution.

**Effect of Foreign Ions on the Determination of Li**

Since the porphyrin forms stable complexes with transition and heavy metal ions, these metal ions were masked by addition of [Mg(edta)]\(^{2-}\) solution as a ligand buffer. Nakagawa and Tanaka have proposed the use of a ligand buffer solution for the polarographic determination of zinc(II) in the presence of cadmium(II).\(^{10}\) We determined the optimum condition for the ligand buffer solution to mask transition and heavy metal ions for the determination of lithium in a sample solution. In order to mask metal M completely as possible, most of M (zinc(II), copper(II)) should be the form of [M(edta)]\(^{2-}\) and lithium should be free ion. Magnesium(II) used as a component of the ligand buffer for masking the metal M should satisfy the conditions: \(K_{M(\text{edta})} > K_{Mg(\text{edta})} > K_{Li(\text{edta})}\). The formation constants (logarithmic values) of copper(II), zinc(II), magnesium(II) and lithium(II) are 18.70, 16.44, 8.83 and 2.79, respectively.\(^{11}\) Thus, [Mg(edta)]\(^{2-}\) completely masks metal ions, such as copper(II) and zinc(II). The results are listed in Table 1. Cations and anions usually encountered in environmental samples are masked by [Mg(edta)]\(^{2-}\). Since the high concentration of mercury(II) was not be completely masked by [Mg(edta)]\(^{2-}\), NaCN was used to mask mercury(II). Such high concentration of mercury(II) must be very rare cases in environmental samples and the addition of NaCN may not be required for the determination of lithium in environmental samples.

**Determination of lithium in some natural water samples**

The present method was applied to the determination of lithium ion(I) in a sea water and a hot spring water samples. Large amounts of sodium ion did not interfere with the determination of lithium ion for the present method, but magnesium(II) ion interfere a little. Thus, an equivalent amount of H\(_4\)edta to the total magnesium ion was added to mask magnesium in the sea water sample.

Lithium ion in the sea water sample was determined by standard addition method using a calibration graph measured at the same ionic strength as the sea water (Fig. 5). The concentration of lithium was found to be \((1.99 \pm 0.04) \times 10^{-5}\) mol dm\(^{-3}\). The concentration of lithium ion was checked by a flame photometry and the concentration was \((1.57 \pm 0.09) \times 10^{-5}\) M. The small difference in the concentration of lithium by two methods may arise from an interference of sodium ion in the flame method. The concentration of lithium in the hot-spring water was very low and was not able to be determined by the present method, but a recovery test using the hot-spring water was sufficient: zinc and iron metal ions in the hot-spring water were completely masked by [Mg(edta)]\(^{2-}\).

**Summary**

Present work proposes the first example for the direct spectrophotometric determination of lithium in water using a water-soluble porphyrin. The method is sensitive, simple and selective analytical method by a use of ligand buffer of [Mg(edta)]\(^{2-}\). The method will be developed to a flow injection analysis.

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**References**