

[Ca(2,2'-bipyridine)₃]²⁺-Montmorillonite: A Potentiometric Sensor for Sulfide ion

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Abstract—Sulfide ion (S^{2-}) is one of the most important ions to be monitored due to its high toxicity, especially for aquatic organisms. In this work, [Ca(2,2'-bipyridine)₃]²⁺-intercalated montmorillonite was prepared and used as a sensor to construct a potentiometric electrode to measure sulfide ion in solution. The formation of [Ca(2,2'-bipyridine)₃]²⁺ in montmorillonite was confirmed by Fourier Transform Infrared spectra. The electrode worked well at pH 4-12 and 4-10 in sulfide solution 10^{-2} M and 10^{-3} M, respectively, in terms of Nernstian slope. The sensor gave good precision and low cost.

Keywords—2,2'-bipyridine complexes, montmorillonite potentiometry, sulfide ion.

I. INTRODUCTION

SULFIDE ion (S^{2-}) is found in both natural and waste waters, it is one of the most important ion to be monitored due to its high toxicity for aquatic organisms. The toxicity of sulfide ion is attributed to the releasing of hydrogen sulfide (H_2S) which is a colorless, very poisonous, flammable gas with a characteristic foul odor of rotten eggs. At a low concentration, H_2S can produce personal distress, while at high concentration, it can result in loss of consciousness, permanent brain damage or even death through asphyxiation. Various methods have been used to determine sulfide ion, such as spectrophotometric, fluorescence, chemiluminescence, inductively coupled plasma-atomic emission spectroscopy (ICP-AES), atomic absorption spectrometry, flow injection analysis (FIA), ion chromatography, and electrochemical methods and so on, articles of these techniques are cited by Huang *et al.* [1].

Montmorillonite, a 2:1 layered silicate clay mineral has versatile uses, due to its adsorption and cation exchange properties as well as high surface area. Montmorillonite has been studied in various fields, as bleaching agent, especially for cooking oil [2-7]. It can also be used to adsorb wide varieties of species such as heavy metal ions, organic and biocide molecules as well as surfactants [8-16]. Recycle of spent clay from the oil refining industry was studied [17].

Transition metal complexes of 2,2'-bipyridine have been studied extensively, they have been widely discussed for applications in biodiagnostics, photovoltaic and organic light-emitting diode [18,19]

A number of montmorillonite-modified electrodes and electrochemical sensors have been reported, these included the use of a carbon paste modified electrode for the determination of 2-nitrophenol in a flow system by different pulse voltammetry [20], sorption and determination of Hg(II) on clay modified carbon paste electrodes [21], electrocatalysis reduction of molecular oxygen on a sodium montmorillonite-methyl viologen carbon paste chemically modified electrode [22], modified electrodes based on mixed bentonite vanadium (V) oxide xerogel [23], Al-pillared acid-activated montmorillonite modified electrodes [24], in situ spectroelectrochemical studies of phenothiazine dyes at clay coated electrodes [25], sensors and biosensors based on clay-modified electrodes-new trends [26], chitosan-clay nanocomposites: application as electrochemical sensors [27], a selective modified-porphyrin carbon paste electrode for determination of Mn(II) by using anodic stripping voltammetry [28]. Previously in our labs, we modified [Zn(8-hydroxyquinoline)₂]-intercalated bentonite as film for the measurement of dissolved oxygen by fluorescent method [29] and CdS-intercalated bentonite/ carbon composite as electrode for the determination of sulfide ion in water [30,31].

We have also prepared [Ca(2,2'-bipyridine)₃]²⁺-intercalated montmorillonite by modification of an *in situ* solid-solid reaction, from natural Ca(II)-montmorillonite and 2,2'-bipyridine and used it as a sensor to construct a potentiometric electrode by mixing with artificial graphite, polytetrafluoroethylene (PTFE) and carboxymethyl cellulose (CMC). The electrode was used to measure anions in aqueous solution, found most sensitive to S^{2-} ion. The % recovery and reproducibility gave satisfactory results, the electrode was also used to measure sulfide ion in natural water samples successfully [32].

In this work, we confirmed the coordination of 2,2'-bipyridine with Ca^{2+} in the interlayer space of montmorillonite by the lowering of vibrational frequencies of 2,2'-bipyridine compared with the non-bonded molecule. The precision of the slope and pH effect were also studied.

II. EXPERIMENTS

A. Chemicals and apparatus

Ca-montmorillonite from Lopburi province, Central Thailand, was provided by Klong Yang Co., Ltd., with cation exchange capacity (CEC) 64 meq/100g. The chemical composition of the montmorillonite was determined by X-ray fluorescence spectrometer, Philips, PW 1480. The result is shown in Table 1. All other chemicals were analytical grade. 2,2'-bipyridine (Fluka), Carboxymethyl cellulose (CMC, 3%), polytetrafluoroethylene (PTFE, 60%, Dupont), artificial

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graphite (Thai Carbon and Graphite), acetone (Merck), sodium sulfide (Na_2S , Panreac), hydrochloric acid (HCl, Merck), sodium hydroxide (NaOH, Merck), acetone (CH_3COCH_3 , QR&C) and deionized water.

Ion meter (ORION, 420A) was used to measure potential of the solution, using silver-silver chloride electrode as a reference electrode. The 744 pH meter (Metrohm) was used to measure pH of solution. Infrared spectra of the samples in the 4000 to 400 cm^{-1} were obtained from Fourier Transform Infrared Spectrometer, Perkin Elmer model System 2000 FTIR, using KBr disc method.

TABLE I
CHEMICAL COMPOSITIONS OF THAI BENTONITE

Compositions as oxide	%
SiO_2	68.65
Al_2O_3	0.14
TiO_2	13.73
Fe_2O_3	1.18
MnO	0.07
MgO	2.22
CaO	2.79
Na_2O	<0.1
K_2O	0.6
P_2O_5	<0.05
Loss On Ignition	7.2
H_2O	2.84

B. Preparation of $[\text{Ca}(2,2'\text{-bipyridine})_3]^{2+}$ -intercalated montmorillonite sensor

The preparation of $[\text{Ca}(2,2'\text{-bipyridine})_3]^{2+}$ -intercalated montmorillonite was modified from an *in situ* solid-solid reaction [33], using natural Ca(II)-montmorillonite and 2,2'-bipyridine as follows. Ca(II)-montmorillonite sample which has been washed, dried and passed through 90 μm sieve was mixed with 2,2'-bipyridine in a 1:3 mole ratio of Ca^{2+} : 2,2'-bipyridine (5.0:0.5 g). The mixture was ground manually in an agate mortar at room temperature for about 30 min. The resulting greyish powder was washed with acetone to remove excess 2,2'-bipyridine, it turned to pale pink after standing at room temperature. The intercalation of $[\text{Ca}(2,2'\text{-bipyridine})_3]^{2+}$ in the interlayer space of montmorillonite has been confirmed by powder XRD. The existence of 2,2'-bipyridine in montmorillonite has been confirmed by determination of the C:N ratio of the product using CHN analyzer, and compared with that in the 2,2'-bipyridine molecule [32].

C. Construction of $[\text{Ca}(2,2'\text{-bipyridine})_3]^{2+}$ -montmorillonite/Carbon composite electrode.

A 0.2 g $[\text{Ca}(2,2'\text{-bipyridine})_3]^{2+}$ -montmorillonite was mixed with artificial graphite in agate mortar and ground for 15 min. The mixture was then transferred to a small vial containing glass beads and shake manually for about 1.5 hr. $[\text{Ca}(2,2'\text{-bipyridine})_3]^{2+}$ -montmorillonite/graphite mixture was then mixed thoroughly with a mixture of CMC/PTFE and put in a mold made of Pyrex tube (1 cm long, 6 mm in diameter). The mold was then heated at 70°C in an oven for 15-30 min. The $[\text{Ca}(2,2'\text{-bipyridine})_3]^{2+}$ -montmorillonite/graphite composite

was then taken off from the mold and dried at 70°C in an oven for 6 hr., before polishing with fine grain sand paper. The cylindrical shape sensor was then inserted in Pyrex glass tube (6 inches long, 6 mm diameter) and sealed with silicone. Na_2S solution (0.1 M) was added in the tube as internal electrolyte. Copper wire was used for electrical contact and silver-silver chloride electrode was used as a reference electrode.

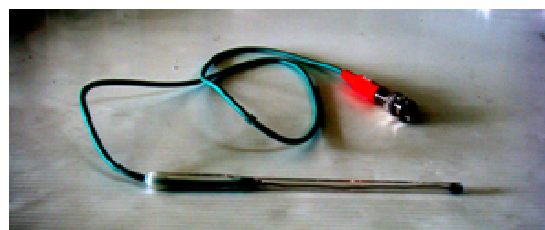


Fig. 1 A photograph of the electrode

D. pH effect

The effect of pH to the response of sensor was tested in the pH range 2-12 by using 2 concentrations of sulfide solution, 1×10^{-2} M and 1×10^{-3} M, 0.01-1 M HCl or NaOH were used to adjust the pH of the solutions.

III. RESULTS AND DISCUSSION

Infrared spectra of Ca-montmorillonite and $[\text{Ca}(2,2'\text{-bipyridine})_3]^{2+}$ -intercalated montmorillonite are shown in Fig. 2a and 2b respectively. The assignment of the bands is in Table 2.

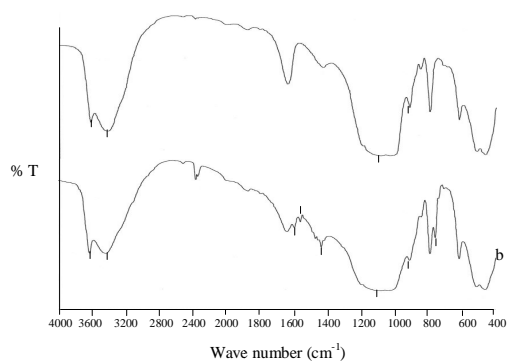


Fig. 2 FT IR spectra of Ca(II)-montmorillonite (a) and $[\text{Ca}(2,2'\text{-bipyridine})_3]^{2+}$ -intercalated montmorillonite (b)

As can be seen in Table 2, the vibrations due to Si-O, Si-OH or Si-O-Al at the surface of montmorillonite are not changed. We found that the vibrations of bondings in 2,2'-bipyridine shifted to lower frequencies, compared to non-bonded molecule, which is consistent with those has been done by Erdem *et al.* [34] where 2,2'-bipyridine-bentonite (montmorillonite) was used to adsorb Cu(II) and they found some interaction between Cu(II) and 2,2'-bipyridine.

The existence of stretching vibrations of C-C of aromatic ring as well as the C-C and C-N ring stretching of 2,2'-bipyridine in the spectrum of $[\text{Ca}(2,2'\text{-bipyridine})_3]^{2+}$ -montmorillonite (Fig.2b) is an obvious evidence for the

intercalation of 2,2'-bipyridine in the montmorillonite, these bands were not found in the spectrum of Ca-montmorillonite (Fig.2a). The C-C and C-N ring stretching vibrations of non-bonded 2,2'-bipyridine in montmorillonite (or DP-bentonite in [34]) were found at 1587, 1531, 1472 and 1459 cm^{-1} and they shifted to 1577, 1502, 1477 and 1453 cm^{-1} after DP-bentonite was used to adsorb Cu(II) ion [34], in our work we found these bands at 1577, 1472 and 1459 cm^{-1} which are closed to those in the Cu(II) loaded DP-bentonite. The lowering of stretching vibrations of 2,2'-bipyridine in montmorillonite confirmed the coordination of 2,2'-bipyridine to Ca^{2+} in montmorillonite, in our work.

TABLE II
ASSIGNMENT OF IR SPECTRA OF CA- MONTMORILLONITE AND
[Ca(2,2'-BIPYRIDINE)₃]²⁺-MONTMORILLONITE
COMPARED WITH THOSE IN [34]

Vibration	Wave number (cm^{-1})		
	A* (this work)	B* (this work)	C* [34]
$\nu_{\text{Si-OH}}$	3625	3622	3623
$\nu_{\text{O-H}}$ (water)	3434	3439	3433
$\nu_{\text{Si-O}}$ (out of plane)	1093	1093	1087
$\nu_{\text{Si-O}}$ (in plane)	1039	1039	1039
$\delta_{\text{SiO-H}}$	917	912	915
$\delta_{\text{Si-O-Al}}$	523	523	523
$\delta_{\text{Si-O-Si}}$	467	467	467
$\nu_{\text{C-H}}$ (aromatic ring of bipyridine)	-	3067	3101
$\nu_{\text{C-C}}, \nu_{\text{C-N}}$ of bipyridine ring	-	1577, 1472, 1459	1577, 1502, 1477, 1453

*A = Ca-montmorillonite (this work)

*B = [Ca(2,2'-bipyridine)₃]²⁺- montmorillonite (this work)

*C = Copper(II) loaded DP -bentonite [34]

*spectrum of 2,2'-bipyridine is not shown here

For the precision of slope, a selected electrode was used to determine the slope for 10 times. Satisfactory results were obtained, the average slope was 29.572 ± 0.3552 and %RSD was 1.2011.

pH effect studies

The results of the effect of pH which was studied in pH range 2-12 was shown in Fig.3

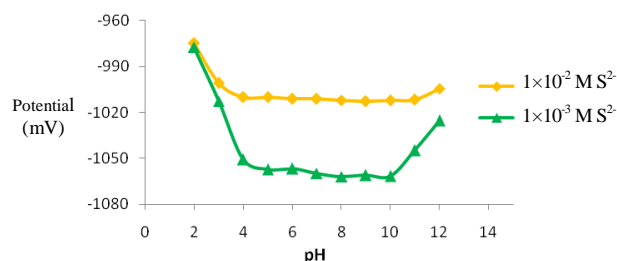


Fig. 3 Effect of pH to the response of sensor [Ca(2,2'-bipyridine)₃]²⁺-montmorillonite in 1×10^{-2} M and 1×10^{-3} M of S^{2-} solution

As can be seen in Fig.3, the response of sensor remains almost constant in the pH range 4-12 and 4-10 for 1×10^{-2} M

and 1×10^{-3} M of S^{2-} solution, respectively. The variations of potential out of these pH may be due to the interference of the adjusting HCl or NaOH to the sulfide solutions [35] and this interference decreases when sulfide concentration increased from 1×10^{-3} M to 1×10^{-2} M

Since in most cases, aqueous solution will have pH between 4-8. Studies of sulfide solutions at pH 4 and 8 were performed to confirm the response of the sensor, 3 electrodes were used to test for 4 replicates of each pH solution. Average slopes of each electrode are plotted vs numbers of the electrodes, the results are shown in Fig. 4 and 5.

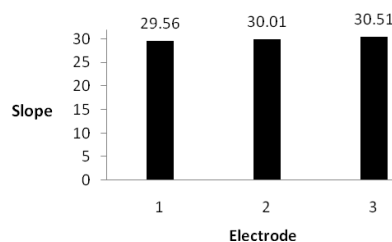


Fig. 4 Average slopes of 3 electrodes at pH 4

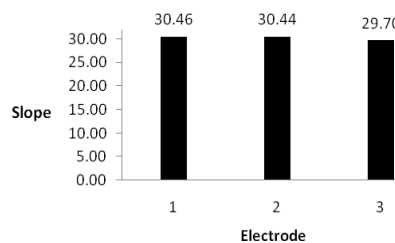


Fig. 5 Average slopes of 3 electrodes at pH 8

As in Fig. 4 and Fig.5 the slopes are closed to theoretical value of 29.5 according to Nernst's equation for S^{2-} , a two minus charge ion. This implies that the electrode can be used to measure S^{2-} in solution of pH 4-8 with high confidence.

IV. CONCLUSION

A potentiometric sensor was prepared from an intercalation compound of montmorillonite, [Ca(2,2'-bipyridine)₃]²⁺-montmorillonite. The formation of the complex was confirmed by lowering of stretching vibrations of bonding in 2,2'-bipyridine ligand, this is consistent with other techniques which have been done before. The electrode works well in sulfide solution of pH 4-8. Apart from a good precision of Nernstian slope, the electrode is easy to construct and very low cost.

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