Asian Journal of Chemistry; Vol. 25, No. 3 (2013), 1467-1470

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2013.13080

Synthesis and Property Study of N,N-Dithiocarboxy Diethylenetriamine Ethyl Polymer

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(*Received*: 19 November 2011; *Accepted*: 12 September 2012) AJC-12139

In this research, the synthesis and property of N,N-dithiocarboxy diethylenetriamine ethyl polymer were investigated. The polymer was synthesized through one-step reaction of diethylenetriamine, carbon disulfide with 1,2-dichloroethane, with the reaction time and required temperature being reduced significantly compared with that of traditional two-step reaction. Such factors as addition of sodium-hydroxide and its adding procedure, adding procedure of carbon disulfide, addition of diethylenetriamine, reaction temperature and reaction time were studied in details. Physical and chemical characteristics of this polymer were determined taking advantage of IR, UV and melting point test. Heavy-metal-ion absorbing property of this polymer was studied intensively. The results showed that several kinds of heavy metal ions could be significantly absorbed with the produced polymer, among which Ag^{+}, Cu^{2+} and Zn^{2+} could be absorbed most effectively. The absorption ability of this polymer was maximized when the pH value was controlled at 5.

Key Words: Trapping and absorption agent, Heavy metal ions, Diethylenetriamine ethyl polymer, Synthesis.

INTRODUCTION

Polymeric chelating agent is a kind of important trapping and absorption agent for heavy metal ions, through the effect of which, various heavy metal ions in solutions can be concentrated and enriched because of the effect of chelating functional groups. Chelate complexes can be formed gradually by chelating certain kinds of heavy metal ions with aminodithioformic groups which contain the coordination atoms, such as sulphur and nitrogen. But alkali metal and alkali-earth metal ions have no response to such groups. The aminodithioformic heavy-metal-ion trapping and absorption agents possess high absorption capacity to heavy metal ions[1-7], whose structure can be illustrated in Fig. 1. The chelate mode of the aminodithioformic agents with bivalent metal ions[6-8] is shown in Fig. 2.

Some trace heavy metal ions in water can be absorbed stably and efficiently by the aminodithioformic polymer. It has been used widely and potentially in the control of the water pollution. It paves the new way and provides the new technology of heavy metal pollution control.

Synthesis of dithiocarbamates polymer can be realized by the reaction of amine with carbon disulfide to form dithiocarbamates structure[6]. In order to increase the relative molecular

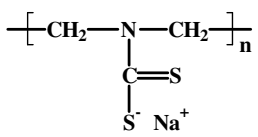

Fig. 1. Structure of aminodithioformic heavy-metal-ion trapping and absorption agents

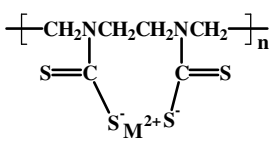

Fig. 2. Chelate mode of the aminodithioformic agents with bivalent metal ions

mass of this kind of compound, it is necessary to proceed cross linking reaction before or after indrafting dithiocarbamates structure. Thus the cross structure unsolvable in water is formatted[6-8,9,10]. Multivariant halogenated hydrocarbon, diisocyanate and methylbenzene are often used as cross-linking agent.

Some researchers produced N,N-dithiocarboxy diethylenetriamine ethyl polymer through two-step reactions[4,6-9]. The synthesis procedure was as follows: the intermediate product (N,N-dithiocarboxy diethylenetriamine) was obtained from the

reaction of carbon disulfide with diethylenetriamine in certain condition in 4 h and polyethylene N,N-dithiocarboxy diethylenetriamine was synthesized by reaction of 1,2-dichloroethane with the intermediate product in alkalinity condition in 4-5 h. The synthesis time and drawing filtering time were quite long and the operation was complicated, with high reaction temperature[6,8,11,10,16,12-15]. By changing the addition and the adding sequence of sodium-hydroxide, the two-step reactions could be converted into one-step reaction and the reaction time was saved for 2.5 h. The drawing filtering procedure and washing procedure of the intermediate product were not demanded. The operation time was reduced significantly by the contraction of the operation procedure. The reaction condition was more moderate by reducing the reaction temperature from 75-90 ºC.

The chelate complexes were formatted by N,N-dithiocarboxy diethylenetriamine ethyl polymer synthesized with a new method in this study. Generally speaking, most heavy metal ions, such as Cu^{2+}, Ag^{+} and Zn^{2+} were extraordinarily stable. The polymer can also absorb such heavy metal ions (for example Cu^{2+}) which exist in the form of stable complex (for example EDTA and citrate acid) in water. The merits of the trapping and absorption agent synthesized in this paper were as follows: the operation was quite simple and the heavy metals absorbed by the agent could not be released again from the mud. The risk of secondary pollution was reduced significantly. At present, with environmental protection being the hot point both from the aspect of the public and from the view of researchers, there must be a wide applications for N,N-dithiocarboxy diethylenetriamine ethyl polymer.

EXPERIMENTAL

Diethylenetriamine was obtained from No. 3 chemical agent factory of Yixing. Carbon disulfide and 1,2-dichloroethane were provided by Chengdu chemical agent factory. The solvents were all of technical grade. All aqueous solutions and standards were prepared by using distilled water. The pH of the metal ions solution was adjusted by using ammonia-ammonium chloride buffer solution of different pH value.

General procedure: N,N-Dithiocarboxy diethylenetriamine ethyl polymer was synthesized by 1,2-dichloroethane and the intermediate product which was synthesized by diethylenetriamine and carbon disulfide in alkaline medium. The main route of synthesis is as follows:

$$NaOH + H_2NCH_2CH_2NHCH_2CH_2NH_2 + CS_2 \rightarrow NaS_2CNHCH_2CH_2NHCH_2CH_2NHCS_2Na \quad \text{Step 1}$$

$$NaS_2CNHCH_2CH_2NHCH_2CH_2NHCS_2Na + ClCH_2CH_2Cl \rightarrow NaS_2CNHCH_2CH_2NHCH_2CH_2NHCS_2CH_2CH_2 \quad \text{Step 2}$$

A three mouth glass flask of 500 mL was used as the reaction vessel. Distilled water (100 mL) and sodium-hydroxide (12.0 g) were added into the glass in cold water bath. After cooling to the room-temperature, diethylenetriamine (10.75 mL) was charged. Carbon disulfide was added at the speed of two drops every minute. The dark yellow solution was obtained after the reaction of one and a half hours under the condition of room-temperature. The reaction vessel was removed into 75 ºC hot water bath, after which the reaction lasted for 4 h after the addition of 1,2-dichloroethane at the same speed of carbon disulfide. Then the milky solution was obtained. All procedures were carried out in stirring condition. The white powder was achieved by drawing filtration and washing for three times with water and absolute ethyl alcohol.

Absorption experiments: The mixtures of the synthesized absorber (0.200 g) and metal ion solution (Ag^{+}, 0.05 mol/L; Cu^{2+}, 0.05 mol/L; Zn^{2+}, 0.05 mol/L; Hg^{+}, 0.05 mol/L, respectively) was stirred for 1 h by the electromagnetic stirring machine. The solution was left untouched until it became separated into layers. The surplus ion concentration was assayed by dithizone method. The absorption capacity was obtained by the change of the heavy mental ion concentration. The formula was as follows:

$$Q = \frac{[V(C_0 - C)]}{M}$$

where Q, C_0, C, M and V represent the absorption capacity, unabsorbed and absorbed heavy mental ions concentration, the absorbent weight and the capacity of the heavy mental ions solution, respectively.

Copper(II) adsorption experiments were carried out at nine different stirring time periods, namely 10, 15, 20, 25, 30, 35, 40, 45, 55 and 60 min. The operation was almost the same as the abovementioned steps of absorption capacity studies.

All pH value studies were carried out by using ammonia-ammonium chloride buffer solution of different pH value of 3.0, 3.5, 4.0, 4.5, 5.0 and 5.5. So the absorption capacities of copper(II) at different pH value were obtained. The operation was also alike with the step of absorption capacity studies.

RESULTS AND DISCUSSION

Effect of addition and adding sequence of sodium-hydroxide: The synthetic reaction of the dithiocarbamates is nucleophilic reaction. The alkaline medium is different with the different qualitative of the N,N-substituting group. In this reaction nitrogen atom has stronger mucleophilic capability because the substitute is electron-repelling group. So in this experiment, sodium-hydroxide was used to maintain the alkaline medium so that the reaction was preceded more easily. In absorbent synthetic step, sodium-hydroxide was added first in order to make the intermediate in form of sodium salt exist in solution. So the two step reaction was improved to one-step reaction. The time of synthetic reaction was saved for 2.5 h. The operational procedures were reduced because the steps of drawing filtering and cleaning of the intermediate were not needed and the operation time was reduced further. In Fig. 3, effect of the sodium-hydroxide addition on productive rate was displayed and it was showed the optimized dosage of sodium-hydroxide was 12.0 g.

Effects of addition of diethylenetriamine: In adsorbent synthesis experiments, the productive rate of the polymer was affected by the addition of diethylenetriamine. The effects were shown in Fig. 4. From the results, it was clear that the productive rate of the polymer was affected more significantly when the diethylenetriamine addition was below the theoretical addition than when it was above the theoretical addition. But in order to improve the purity of the product, the adding dosage should

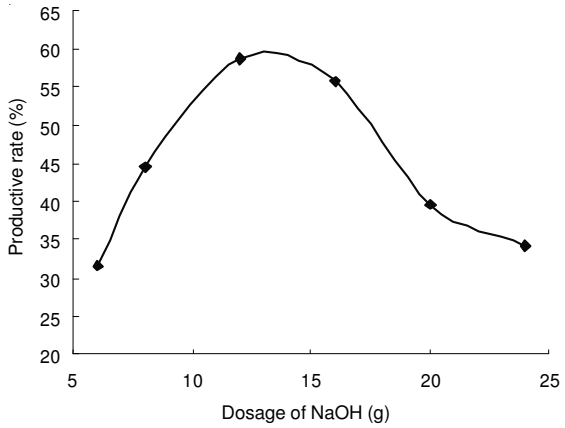

Fig. 3. Effect of NaOH dosage on productive rate

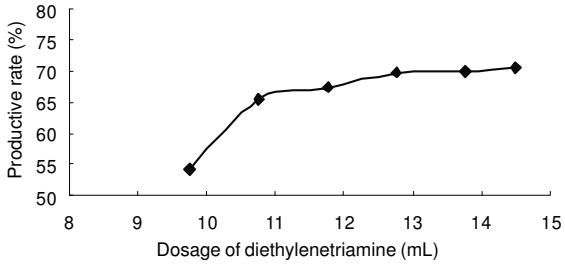

Fig. 4. Effect of diethylenetriamine dosage on productive rate

be equal to the theoretical value to ensure that the reaction can be sufficiently complete because the second procedure might be affected significantly by the addition in the first procedure. The reaction condition was with strong alkalinity because of the addition of sodium-hydroxide in the first step. It was not necessary to enhance the alkalinity by the addition of diethylenetriamine. So the cost was lowered and the operation procedures were simplified.

Effects of adding sequence of carbon disulfide: The effects on the product purity and complexation were studied by the adding sequence of carbon disulfide in adsorbent synthesis experiments. If carbon disulfide was added before the adding of diethylenetriamine, the colour of the product was faint yellow and the product could be divided into two layers. The upper layer was faint yellow small particles and the other layer was white power. But if carbon disulfide was added drop by drop before the adding of diethylenetriamine, the product was pure white power. So the latter adding sequence of carbon disulfide was adopted in this experiment.

Effects of reaction temperature: The reaction temperature was controlled lower for carbon disulfide, which made it easy to lower the boiling point and volatility. But the reaction speed was slowed down if the temperature was too low. The system temperature increased because of the heat released after sodium hydroxide being solved. So the system must be cooled before adding diethylenetriamine and cooling water was circulated while carbon disulfide was added drop by drop.

Effect of reaction time: Several different reaction times were tested in this study, namely 1, 1.5, 2 and 3 h. It was found that in the one-step synthesis reactions, the reaction was speeded up because of the adding of sodium hydroxide. 1.5 h was sufficient for the synthesis of the products from one-step reaction.

Structural analysis of synthesis product

IR spectra characterization: IR spectra were recorded on a Magna-IR spectrometer in the range of 4000-500 cm^{-1} by using KBr as dispersant. The characteristic absorption frequency was listed in Table-1. It was evident that the weak bands characteristic of S-H and N-H in parahelium appeared at about 3560 and 3300 cm^{-1} individually because the carbon chains achieved was longer than that achieved through two-step synthesis reaction. Furthermore, bands characteristic of N-C=S, C=S and S-CH_2 appeared at 1496, 1230 and 1425 cm^{-1}, respectively. The IR spectra were coincident to the IR spectra in the literature[1]. Based on this evidence, the presence of the polymer was confirmed.

TABLE-1
INFRARED SPECTRA (cm^{-1}) ANALYSIS OF PRODUCT

Absorption peak	1496	1230	1425	1186
Groups	N-C=S	C=S	S-CH_2	C-N-C

UV-VIS spectra characterization: The semi-manufactured product was used to detect the UV-VIS absorption spectra because the product could not solve in many kind of solvents. UV-VIS spectra were recorded on a UV-VIS spectrometer model TU-1810 in the range of 400-200 nm by using sodium-hydroxide as solvent and distilled water as reference. The UV-VIS spectra was shown in Fig. 5 and the characteristic absorption frequency was listed in Table-2. The spectra shows that there were double bond structures characteristic partly between carbon and nitrogen as well as between carbon and sulphur, which was an evidence for the presence of mine functional groups in semi-manufactured product.

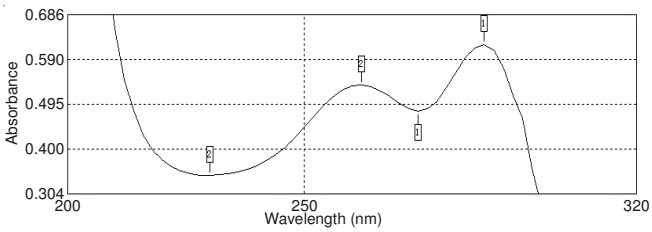

Fig. 5. Ultraviolet spectrogram of the intermediate product

TABLE- 2
ULTRAVIOLET SPECTRA ANALYSIS
OF INTERMEDIATE PRODUCT

Absorption peak	Description
262 nm	The π-π^* transition of N···C···S group
288 nm	The n-π^* transition of CS_2 group

Determination of melting point apparatus: The melting point was determined on a melting point apparatus model XRC-1 in 120-250 ºC range using NaOH as solvent and distilled water as reference. The product melted at *ca.* 151ºC and changed into black solid when the temperature increased to 210 ºC.

Absorption property of the polymer

Absorption capacity: According to the steps for absorption capacity studies, the absorption capacities of heavy metal ions were examined and the results were shown in Table-3. It was evident that the absorbent was able to act as a powerful absorber for such ions as Ag^+, Cu^{2+} and Zn^{2+}. The reason might

be that the complex formed through the combination of the absorber and the ions of Ag^+, Cu^{2+} and Zn^{2+} was more stable than that formed through the combination of the absorber and Hg^+, which could not be absorbed significantly by this product.

TABLE-3
ADSORPTION PROPERTY OF THE POLYMER FOR HEAVY METAL IONS

Metal ions	Ag^+	Cu^{2+}	Zn^{2+}	Hg^+
Absorption capacity (mmol g^{-1})	4. 54	1.43	1.75	0.85

Absorption kinetic curve of copper(II): The absorption curve of copper(II) obtained in the step of kinetic curve studies was shown in Fig. 6. The absorbing speed was quick in the first 30 min and the absorption became balanced after reacting for 50 min.

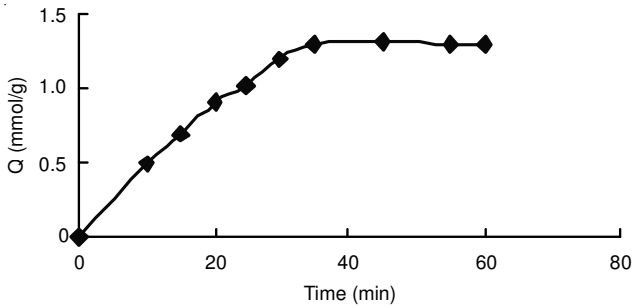

Fig. 6. Influence of time on Cu^{2+} adsorption capacity

Effects of pH value on absorbent capacity: In Fig. 7, the effect of pH on absorbent capacity for copper(II) was illustrated. The absorbent capacity to copper changed obviously with the change of pH value. The maximum absorbent capacity was obtained when pH value was 5.

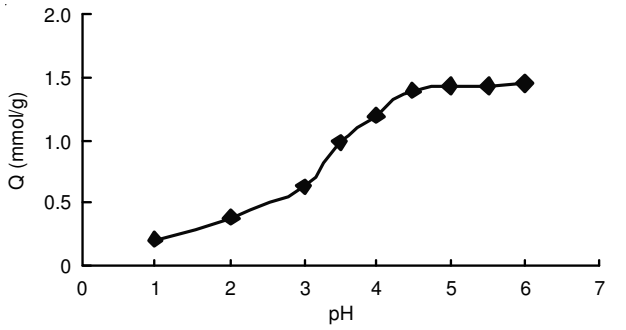

Fig. 7. Influence of pH on Cu^{2+} adsorption capacity

Conclusion

N,N-Dithiocarboxy diethylenetriamine ethyl polymer can be produced effectively through one-step reaction of diethylenetriamine, carbon disulfide and 1,2-dichloroethane in low temperature condition, the reaction time of which can be reduced significantly compared with that of traditional two-step reaction. Mean while, the required temperature of one-step synthesis reaction was reduced from 90-75 ºC. The structure of N,N-dithiocarboxy diethylenetriamine ethyl polymer synthesized in this study was detected, which was characterized by longer carbon chains and the presence of polymer as powerful absorbent. The absorption property of the polymer was studied preliminarily, which suggested that the synthesized polymer had good absorbent capacity for the absorbing of many kind of metal ions, among which, the absorbent capacity for copper ions was as high as 1.43 mmol g^{-1}. It was especially powerful for the absorbing of noble metal ions such as Ag^+, the absorbing capacity was as high as 4.54 mmol g^{-1}. N,N-Dithiocarboxy diethylenetriamine ethyl polymer can be used as a potential in the treatment of industrial wastewater polluted by metal ions provided that the synthesis process be optimized further.

ACKNOWLEDGEMENTS

This work was supported by the National Natural Science Foundation of China (NSFC, No. 51078366 , 21177164) and the National Science and Technology major water special project in Water Pollution Control and Governance (No. 2009ZX07424-004).

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