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Kinetic and mechanism formation reaction of complex compound Cu with di-n-buthildithiocarbamate (dbdte) ligand

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Abstract Synthesis of complex compound is one field of research which intensively studied. Metal-dithiocarbamate complexes find wide-ranging applications in nanomaterial and metal separation science, and have potential use as chemotherapeutic, pesticides, and as additives to lubricants. However, the information about is reaction kinetic and mechanism are very much lacking. The research and analyzes results show that reaction synthesis ligand DBDTC and complex compounds Cu-DBDTC. Optimum reaction condition of formation of complex compounds Cu with DBDTC at pH=3, [DBDTC] = $4 \cdot 10^{-3}$ M, and the time of reaction 5 minutes. Based the analysis varian reaction of complex compounds at pH 3 and 4, difference significance at the other pH: 5; 5,5; 6; 6,5 ; 7; and 8. The various of mole with reactants comosition difference sigbificance, those the time reaction for 5 and 6 minutes difference by significance with the other time, it is 3,4,8, and 10 minutes. The great product to at condition pH 6, the time optimum at 5 minutes and molar ratio of logam: ligand = 1:2. The reaction kinetic equation of complex compound Cu with chelating ligand DBDTC is $V=0.917106 [Cu^{2+}]^{0.87921} [DBDTC]^{2.03021}$. Based on the kinetic data, and formed complex compounds estimation, the mechanism explaining by 2 stages. In the first stage formation of [Cu(DBDTC)], and then [Cu(DBDTC)₂] with the last structure geomethry planar rectangle. The result of this research will be more useful if an effort is being done in reaction mechanism by chemical computation method for obtain intermediate, and for constant "k" in same stage, k₁.k₂. and compound complex constanta (β).

Introduction

The development of more reliable methods of analysis to determine the levels of metal ions at low concentrations including copper (Cu) is still continuing. The selection of low-concentration analysis method is also adjusted to the condition of the equipment in the laboratory in the hope of obtaining representative resultan [1]. An analytical method always involves the preparation stage of the sample, which includes dissolving the solid sample, pre-separation filtering, and concentration content. The process of pre-separation and concentration concentration is often done by extraction. Before the process of extraction takes place generally the metals with low concentrations are converted first into organic complex compounds that have polarity according to the polarity of the organic solvent extractor. Solvent extraction with the formation of chelate complex compounds proved to have remarkable success in the process of separation of metal ions [2-3].

The di-n-butyldiethylthiocarbamate (DDTC) is capable of forming a neutral and powerful complex compound with a number of metal ions such as Hg, Pb, Cd, Co, Ni, and Cu [4-7]. Generally the metal



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ions with dialkilditiokarbamat form a colored compound, and slightly soluble in water and its solubility will increase in a relatively less polar organic solvent if the chain is longer [8]. The complex can be determined directly by spectrophotometry After going through the extraction into an organic solvent. This DDTC ligand has long been used in analytic applications ie the extraction and determination of metal ions such as those of Wytenbach and Bajo [9]; Sanzalone and co-worker [10], Lo and co-worker [11]. Various things have been done on the use of ligand dialkilditiokarbamat, but still limited to DDTC, whereas other homologues such as di-n-propilditiokarbamate, And di-n-butilditiokarbamate can be used and also can be synthesized The latter two ligands have a good prophylactic because they have longer chains so their solubility is expected to increase, and the efficiency of the extraction is also increased, thus the complex compound formed by this extraction also has Better prospects [12-14]

The synthesis of complex compounds is always related to the development of analytical procedures that always attract the attention of researchers. In developed countries research in the field of synthesis of complex compounds has been done intensively and can now be synthesized various complex compounds that are useful in various industries, however information on kinetics and mechanisms of reaction is still very less. The kinetics information and the mechanism of complex forming reactions are very useful chemical data, for example in chromatographic separation, kinetic factors and complex stability are essential in regulating the interactions between metal complexes and components in chromatographic systems (stationary phase and mobile phase).

Based on the description of the above background then the problem to be solved in this research is to know how the kinetics equation of the reaction of the formation of complexes Cu with di-n-buthyldithiocarbamate.

Methods

The first stage, at this stage will be synthesized ligand di-n-buthyldithiocarbamate according to procedures Taufan and co-worker [15] that is from the reaction between di-n-butyl amin with karbondisulfida. Into the erlenmeyer flask placed on a large glass beaker filled with 5 mL of concentrated karbondisulfide was then added 6.25 mL concentrated NH_4OH , shaken gently. While continuously shaken, it was added dropwise in thick n-butylamin as much as 13.75 mL. Once the pasta is formed, the paste continues to stir slowly until it becomes a crystal. The formed crystals are dried in a wind-blown way. The synthesis results were tested for their efficacy by thin layer chromatography (TLC), and characterized by melting point determination, UV-VIS spectroscopy method and Infrared spectroscopy method. (2) The second stage, at this stage will be determined the factors that can affect the results of complex forming reactions.

The formation of complex Cu compounds with di-n-butilditiokarbamate was carried out by extraction, according to Taufan and co-worker (15) procedures. It is therefore necessary to specify the optimization of extraction which includes: pH of solution, reaction concentration, and reaction time. Analysis of reaction product was done by spectroscopic method of uv-vis and atomic absorption spectroscopy (SSA). The synthesis results were tested for their efficacy by thin layer chromatography (TLC) and characterized by uv-vis spectroscopy method and infrared spectroscopy and from the determination of coordination number using Job method.

Results and Discussion

Characterization of Complex Synthesis Result

Cu-DBDTC chelate complex is black after evaporation of the extractants. The extraction was carried out under optimum conditions of pH 6.5; Concentration of DBDTC 4×10^{-3} M; And 5 minute rection time. The purity test with TLC obtained only one spot which indicates there is only one component, this means the result of the reaction is relatively pure. Melting point of Cu-DBDTC compound is 74-76 ° C.

The formation of DBDTC complex compounds with Cu^{2+} metal ions is based on the interaction of Cu^{2+} ions with in-n-butylthiocarbamate (DBDTC⁻) ions. The DBDTC⁻ ion is obtained in the dissolution of ammonium dibutildithiocarbamate salt. DBDTC ions act as ligands forming neutral chelate complexes with Cu^{2+} ions in a chloroform solvent.

Kinetics Study of Reaction Formation Compound Cu-DBDTC Complex

The general aim of kinetic experiments is to determine the form of the reaction rate equations. The rate reaction equation in this study is determining use differentiation method. The rate equation of Cu-DBDTC complex can be written mathematically as follows

$$v = k[A]^m[B]^n \quad (1)$$

where k is the reaction rate constant, $[A]$ is the concentration of Cu^{2+} , $[B]$ is the concentration of DBDTC, m and n is the order of the reaction. The logarithm form of equation 1 is

$$\log v = \log k + m \log [A] + n \log [B] \quad (2)$$

The determination of the reaction order is determined by finding the initial rate one of reactant and the concentrations of other reactants are fixed. The graph of concentration versus time is obtained from the experimental data to determine the initial rate. A graph of initial rate versus concentration (Figure 1) is created to determine the value of intercept and slope, as well as the order of the reaction. Based on the graph, the value of reaction order in Table 1 is obtained.

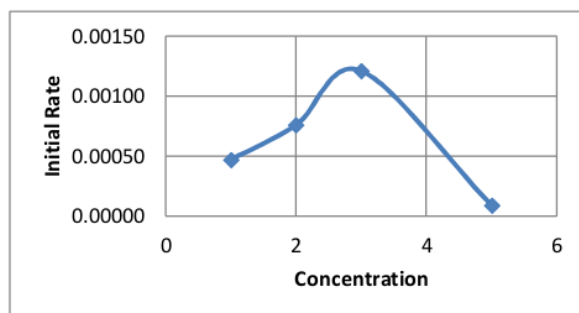


Figure 1. Graph initial rate vs concentration

Table 1. Reaction order at various pH

pH	Orde Reaksi	
	Cu^{2+}	DBDTC
6.0	1.03365	2.24132
6.5	0.87921	2.03021
7.0	0.88919	2.20839

The rate reaction constant can be obtained by substituting the initial concentration of the order of each order in equation 1 into equation 3. The reaction order price is selected at pH 6.5 because it is the optimum condition of Cu-DBDTC complex formation. The price obtained is $k = 0.917106$.

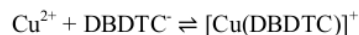
$$v = k [\text{Cu}^{2+}]^{0.87921} [\text{DBDTC}]^{2.03021} \quad (3)$$

by substituting the value of k in equation 3, is obtained

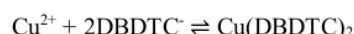
$$v = 0.917106 [\text{Cu}^{2+}]^{0.87921} [\text{DBDTC}]^{2.03021} \quad (4)$$

The Mechanism of Cu-DBDTC Complex Formation Reaction

The theoretical study on the mechanism of reaction of Cu-DBDTC complex formation is based on 3 things: 1) data of reaction kinetics, 2) from value of n (coordination number) obtained by job method, and 3) from value of k. The mole ratio of Cu²⁺ and DBDTC is 1: 2 (based on equation 4) and the total order is 3. Based on this comparison then the complex molecular formula formed is Cu (DBDTC)₂ with a square planar geometry structure. The mechanism of formation of complex compounds Cu (DBDTC)₂ is



Then, the overall reaction is



The determination of n (coordination number) in this research by continuous variation method (job method). Graph obtained by entering data of mole fraction of DBDTC ligand and absorbance of Cu-DBDTC complex. Based on the graph obtained by curve intersection at 1.86 ≈ 2 approaching model of ML_n stoichiometric structure with n = 2. Based on the result it can be concluded that the complex molecular formula is Cu(DBDTC)₂ and this is in accordance with the kinetic data. Another fact that supports the above reaction mechanism is the value of k at different pHs are constant, same as the order of reaction.

Cu (DBDTC)₂ complex compounds are theoretically expected to have 4 coordination numbers based on the valence bond theory. The Cu²⁺ ion has an electron configuration of 1s² 2s² 2p⁶ 3s² 3p⁶ 3d⁹, thus the coordination bond between the bidentate ligand and the central atom is possible to form the sp³ tetrahedron orbitals. However, this contradicts the results of the Huheey experiment (1983) which states there has never been any compounded Cu-shaped complex of tetrahedron.

The experiment results of Van Lenthe [16] showed that diethyldithiocarbamate is strong ligand, so DBDTC which is homologous ligand in this study was also strong ligand. Theoretically it can be expected that the Cu complex species will have Cu molecular formula (DBDTC)₂ with square planar dsp² hybridization.

Conclusion

The conclusions obtained from this study are: (1) the synthesis results of Cu-DBDTC complex compounds according to the character of the compound. (2) the optimum conditions of complex shielding between Cu²⁺ and Di-n-butylidithiocarbamate (DBDTC) were achieved at pH 6.5; [DBDTC] = 4 x 10⁻³ M; reaction time 5 minutes; and the mole ratio of the metal: mol ligand is 1: 2. (3) the kinetic equation obtained is v = 0.917106 [Cu²⁺]^{0.87921} [DBDTC]^{2.03021}. (4) Mechanism of reaction of complex formation of Cu (DBDTC)₂ covering 2 stages. The first stage is formed [Cu (DBDTC)]⁺, then formed [Cu (DBDTC)₂] with possible geometry structure is square planar.

However, it is still need to clarify the reaction mechanism by chemical computation method to prove the existence of intermediates, determination value of k at each stage (k₁ and k₂), and the value of constituent of complex formation.

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