Investigation on the Synergistic Complexation of Ni(II) with 1,10-Phenanthroline and Dithizone at Hexane-Water Interface Using Centrifugal Liquid Membrane-Spectrophotometry

Yoki Yulizar[1*)], Nerny Wahyuningsih[1], Novena Damar Asri[1], and Hitoshi Watarai[2]

1. Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Indonesia, Depok 16424, Indonesia
2. Institute for NanoScience Design, Osaka University, 1-3 Machikaneyama-machi, Toyonaka, Osaka 560-8531, Japan

*)E-mail: yokiy@ui.ac.id

Abstract

Complex formation of Ni(II) and 1,10-phenanthroline ($C_{12}H_8N_2$/Phen) with the addition of dithizone ($C_{13}H_{12}N_4S$/HDz) at the hexane-water interface has been studied by direct measurement spectrophotometry using the centrifugal liquid membrane (CLM) method. Ni(II) ion with Phen formed a cationic complex of $Ni(C_{12}H_8N_2)_2^{2+}$ or $NiPhen_2^{2+}$. That complex dissolved in the aqueous phase and had two UV absorption spectrum maxima wavelengths, λ_{max} 270 and 292 nm. Observation of complex formation was performed variations of pH and ligand concentration. The pH caused protonation that affected the amount of the formed complex. With the variations of ligand concentrations, the greater was the concentration of ligands the greater was the formed complex. Based on the Batch method, the HDz ligand addition into the $NiPhen_2^{2+}$ cationic complex produced ion association complex of $Ni(C_{13}H_{11}N_4S)_2(C_{12}H_8N_2)$ or $NiDz_2Phen$ at λ_{max} 403 nm, and was extracted in the organic phase. Measurement results using CLM method showed that $NiDz_2Phen$ complex was formed at hexane-water interface with λ_{max} 523 nm. Comparison of Phen with HDz ligand concentrations affected the initial formation rate of $NiDz_2Phen$ complex. The greater concentration of Phen ligand increased the initial rate of formation for synergistic complex. The obtained data using CLM method indicated that the synergistic complex formation rate constant of $NiDz_2Phen$ at the interface, k was 0.30/s.

Abstrak

Investigasi Pembentukan Kompleks Sinergis Ni(II) dengan _1,10-Phenanthroline_ dan _Dithizone_ pada Antarmuka Heksana-Air dengan _Centrifugal Liquid Membrane-Spectrophotometry_. Pembentukan kompleks Ni(II) dan _1,10-Phenanthroline_ ($C_{12}H_8N_2$/Phen) dengan penambahan _dithizone_ ($C_{13}H_{12}N_4S$/HDz) pada antarmuka heksana-air telah dipelajari dengan metode spektrofotometri melalui pengukuran langsung dengan metode _centrifugal liquid membrane_ (CLM). Ion Ni(II) dengan Phen membentuk kompleks kation $Ni(C_{12}H_8N_2)_2^{2+}$ atau $NiPhen_2^{2+}$. Kompleks tersebut terlarut dalam fasa air serta memiliki dua panjang gelombang maksimum, λ_{maks} yaitu 270 dan 292 nm. Pengamatan pembentukan kompleks dilakukan terhadap variasi pH dan konsentrasi ligan. Kondisi pH menyebabkan protonasi yang berpengaruh terhadap jumlah kompleks yang terbentuk. Pada variasi konsentrasi ligan, semakin besar konsentrasinya, jumlah kompleks yang terbentuk semakin banyak. Berdasarkan metode Batch, penambahan ligan HDz pada kompleks kation $NiPhen_2^{2+}$ menghasilkan kompleks asosiasi ion $Ni(C_{13}H_{11}N_4S)_2(C_{12}H_8N_2)$ atau $NiDz_2Phen$ yang memiliki λ_{maks} 403 nm, dan terekstrak dalam fasa organik. Hasil Pengukuran menggunakan metode CLM, diketahui kompleks $NiDz_2Phen$ terbentuk pada antarmuka heksana-air dengan λ_{maks} 523 nm. Perbandingan konsentrasi ligan Phen dengan HDz mempengaruhi laju awal pembentukan kompleks $NiDz_2Phen$. Semakin besar konsentrasi ligan Phen, laju awal pembentukan kompleks sinergis semakin cepat. Data yang diperoleh menggunakan metode CLM menunjukkan bahwa tetapan laju pembentukan kompleks sinergis $NiDz_2Phen$ pada antarmuka, k sebesar 0,30/s.

Keywords: 1,10-Phenanthroline, centrifugal liquid, dithizone, interfacial complexation, synergistic extraction

1. Introduction

Extraction behaviour of metal ions with ligand combinations has been studied in a liquid-liquid system [1]. The system has been applied in several areas such as in the processing of hazardous metal ions [2] and in recovering precious metals from industrial products [3]. During its development, it has been proven that the

addition of certain elements can cause synergistic reactions resulting in improved performance and efficiency of the extraction [4-10].

Watarai *et al*. [11] reported that the interface plays an important role in the formation of complexes from liquid-liquid extraction. The interface region between the aqueous phase and the organic phase has a thickness of ± 1 nm [12]. It has also been demonstrated that the complex formation of liquid-liquid extraction takes place through the interface [13-18]. This observation is an important finding in the study of liquid-liquid extraction. To date, many researchers have investigated the interface in their studies [19-22]. This proves the importance of the interface to study the reaction mechanism in the liquid-liquid extraction system.

The rate of synergistic extraction has been studied to observe the formation of Ni(II) complex with dithizone and 1,10-Phenanthroline [23] as well as the formation of Ni(II) complex with dithizone and 4.7-diphenil-1,10-Phenanthroline [24]. Both of these researches study the effects of phenanthroline on the rate of extraction of Ni(II) with dithizone in chloroform using the high speed stirring (HSS) method. The results showed that the synergistic extraction system can be considered as a combination of the chelate extraction system and ion association.

Starting from studies using indirect measurements, this research was conducted using direct measurements to study the kinetics and mechanism of Ni(II) complex formation with 1,10-Phenanthroline and dithizone at the hexane-water interface. Data was collected from a combination sequence of added ligands and the parameters that influence it. Our initial research [25] studied the formation of addition complex at the interface where 1.10 Phenanthroline ligand was added to Ni(II)-dithizone complex in a hexane-water system. The results showed a faster formation rate of complex.

This research studies the formation of a synergistic complex at the hexane-water interface through the addition of dithizone to the Ni(II)-Phenanthroline complex. The rate of interfacial complexation obtained was then compared with the rate of complex formation obtained from a previous study [25]. This study used direct measurements from the centrifugal liquid membrane (CLM)-spectrophotometry to observe formation of complexes and seek formation rate constants of complexes at the hexane-water interface. The study also investigated variations of ligand concentrations and pH that affect the rate of complex formation.

2. Experiment

Chemicals. 1,10-Phenanthroline monohydrate ($C_{12}H_8N_2.H_2O$/Phen) and dithizone ($C_{13}H_{12}N_4S$/HDz)

were purchased from Merck without any further purification. Phen was dissolved in water, while HDz in hexane. Hexane (Merck) was purified by fractional distillation. The aqueous phase was made using aquabides (Ikapharmindo Putramas). Stock solution of Ni(II) ion was prepared by dissolving $NiSO_4.6H_2O$ (Merck). All other chemicals used are analytical reagent grade.

Determining the molar ratio of Ni(II):Phen. 5 ml of solution containing Ni(II) ion 1.0×10^{-5} M (pH 3.88, ionic strength (NaCl) 0.1 M) was mixed with 5 ml Phen ligand in a sealed test tube (diameter 1.5 cm and height 15 cm), both in the aqueous phase. The mixture was shaken 15 minutes until it reached an equilibrium reaction. Measurements were taken with a UV-Vis spectrophotometer at wavelength, λ 190-800 nm (Hitachi, double beam with tungsten and deuterium lamp light sources). Ligand concentrations varied at 1.0×10^{-6}-4.0×10^{-5} M.

Batch methods. This method is used to study the behavior of complex formation of Ni(II) with Phen in the aqueous phase, and the formation of a synergistic complex (Ni:Phen) with HDz in a hexane-water system. The experiments were conducted with variations in pH and ligand concentrations.

Effect of pH on Ni(II):Phen complexation. 5 ml of solution containing Ni(II) ion 1.0×10^{-3} M (pH 2.06 measured by an electronic pH-meter (Ω Metro Ohm), ionic strength (NaCl) 0.1 M) was added a solution of Phen 1.0×10^{-5} M in a sealed test tube and shaken 15 minutes to reach equilibrium reaction. Measurements were performed with a UV-Vis spectrophotometer at λ 190-350 nm. The same experiment was repeated with a solution of Ni(II) with pH 3.01, 3.88, 4.92, and 5.90.

Effect of Phen concentration on Ni(II):Phen complexation. The experiments were performed in the same way as the pH variation experiments, using the pH optimum obtained from these experiments. The Ni(II) concentration used 1.0×10^{-3} M, ionic strength (NaCl) 0.1 M, the Phen concentration varied between 1.0×10^{-7}–1.0×10^{-5} M.

Synergistic complexation of Ni(II):Phen with HDz. 5 mL from the aqueous phase containing Ni(II) ion 1.0×10^{-3} M (pH optimum, ionic strength (NaCl) 0.1 M) was added the aqueous phase containing Phen 1.0×10^{-5} M in a sealed test tube and then shaken 15 minutes to reach equilibrium reaction. Solution absorbance measurements were made with UV-Vis spectrophoto-meter at λ 190-350 nm. To this solution, 5 ml of the organic phase containing HDz 1.0×10^{-5} M was then added, shaken for 1 h until a new equilibrium is reached, then left to settle until it separated. Each phase was measured with UV-Vis spectrophotometer at λ 300-800 nm.

Centrifugal liquid membrane (CLM) method synergistic complexation of Ni(II):Phen with HDz. Observations with CLM were performed on blanks and samples in cylindrical glass cells (diameter 19 mm, height 32 mm and thickness 1 mm). Blanks are only performed at the aqueous phase without reagents, whereas the three solution samples are performed for Phen, Ni:Phen complex, and Ni:Phen-Dz complex. Measurements of the blanks were performed with 150 μL aquabidest using a micro-syringe injected into a cylindrical glass cell attached to UV-Vis spectrophotometer photodiode array (single beam Hewllett-Packard Agilent 8453 A). The cells were then rotated at a speed of 10,000 rpm using NSK (Nakanishi Electer Emax) rotator equipped with traffo 2PF1020 type. The absorption spectrum is measured directly at λ 300-800 nm. Measurements of Phen ligands were carried out by injecting 50 μL of Phen 1.3×10^{-3} M, at the aqueous phase, into a cylindrical glass cell (at stop condition). The cylindrical glass cell was respun at a speed of 10,000 rpm. Absorption spectrum was measured again at λ 300-800 nm. Measurements of the Ni:Phen complex was conducted by injecting 50 μL of Ni(II) ions 5.0×10^{-3} M (pH optimum, ionic strength (NaCl) 0.1 M), from the aqueous phase, into a cylindrical glass cell (spinning at 10,000 rpm). Absorption spectrum is measured again at λ 300-800 nm. Measurement of Ni:Dz-Phen complex was conducted after the Ni:Phen complex formation reaction had reached equilibrium. 250 μL organic phase contain HDz 3.5×10^{-5} M was injected into a cylindrical glass cell (at a fixed rotational speed of 10,000 rpm). Absorption spectrum of complex was measured at λ 300-800 nm.

Effect of Phen concentration on synergistic complexation. Experiments were also conducted on blanks and samples. Blanks are only performed at the aqueous phase without reagents, whereas the three sample solutions are performed for Phen, Ni:Phen complex, and Ni:Phen-Dz complex. All experiments followed the same procedure as used in the previous experiments using concentrations of aqueous phase for Ni(II) 1.0×10^{-3} M, ionic strength (NaCl) 0.1 M, pH optimum, and concentration of organic phase HDz 3.5×10^{-5} M, but for measurements of the Phen ligand in the aqueous phase, the Phen concentration used was 1.0×10^{-5} M. The experiment was repeated for Phen concentrates of 1.9×10^{-4} M and 2.6×10^{-4} M.

3. Results and Discussion

Batch Method. Determining the molar ratio of Ni(II):Phen. The experiments aim to obtain a molar ratio between Phen ligands with Ni(II) ions to form a complex. The measurement results of UV-Vis absorption spectra show that Ni(II)-Phen complex has two maximum wavelengths; λ_{maks} at 270 and 292 nm.
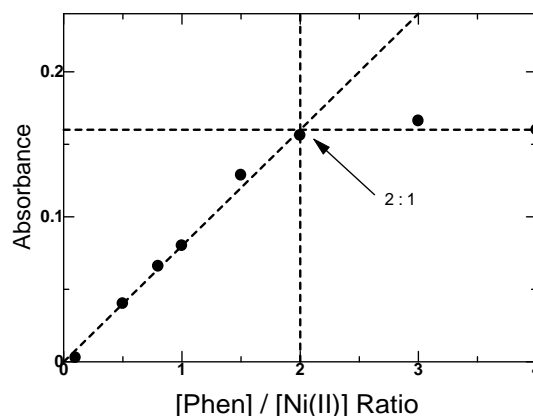

Figure 1. Relationship of UV-Vis Absorbance of Ni(II)-Phen Complex Formation on the Concentration Ratio [Phen]/[Ni(II)]; [Ni(II)] = 1.0 x 10⁻⁵ M, Ionic Strength (NaCl) 0.1 M, pH 3.88, [Phen] = 1.0 x 10⁻⁶- 4.0 x 10⁻⁵ M

To determine the molar ratio of Ni(II):Phen complex, it was analyzed for absorbance at λ_{maks} 292 nm.

The ratio of Phen and Ni(II) concentration ([Phen]/[Ni(II)]) on absorbance at λ_{maks} 292 nm is plotted on the graph (Figure 1). It can be seen that the increase in [Phen]/[Ni(II)] is accompanied by an increase in the absorbance of the complex. This shows that the more Ni(II)-Phen complex formed correlates with the greater concentrations of Phen used. However, when the ratio passed 2:1, the absorbance of the complex became constant. It shows that Ni(II) ion no longer reacts with Phen. Therefore, the use of Phen at higher concentrations had no effect on the amount of complex formed, so it was concluded that the molar ratio of Phen and Ni(II) is 2:1. Ni(II) ion binds to two Phen ligands to form cation complex $Ni(C_{12}H_8N_2)_2^{2+}$ or $NiPhen_2^{2+}$.

$$Ni^{2+} + 2\ Phen \rightleftharpoons NiPhen_2^{2+} \qquad (1)$$

Formation of Cation Complex, $NiPhen_2^{2+}$. In water solvent, Phen ligand has two λ_{maks} that is 228 and 264 nm with molar absorptivity, $\varepsilon = 3.72 \times 10^4$ and 2.59×10^4 $M^{-1}cm^{-1}$, respectively. Once added a solution of Ni(II) in a system containing Phen, it changes two λ_{maks} as shown in Figure 2.

Figure 2 shows the λ_{maks} complex at 270 nm, the λ_{maks} shift of Phen ligands at 264 nm react with Ni(II). In addition to the λ_{maks}, shift the complex has increased absorbance. Complexation reactions are also evidenced by the emergence of a new absorption at λ_{maks} 292 nm. The emergence of this absorbance proves the formation of the cation $NiPhen_2^{2+}$ complex. Therefore, the analysis performed on $NiPhen_2^{2+}$ complex is performed at λ_{maks} 292 nm.
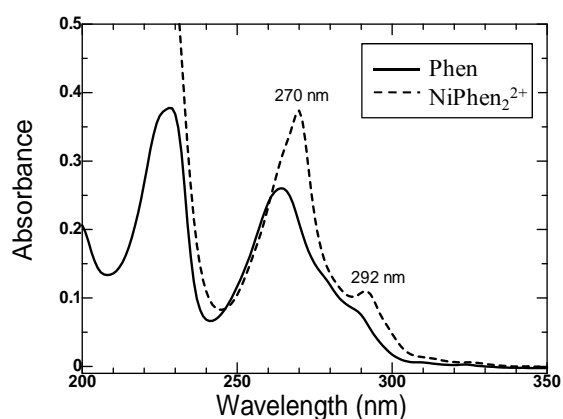
Figure 2. UV-Vis Absorbance Spectra of $NiPhen_2^{2+}$ Complex Formation; [Ni(II)] = 1.0 x 10^{-3} M, Ionic Strength (NaCl) 0.1 M, pH 3.88; [Phen] =1.0 x 10^{-5} M
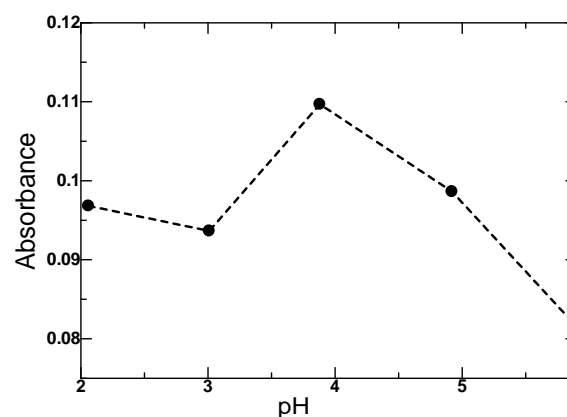

Figure 3. Relationships of UV-Vis Absorbance in Forming Cation $NiPhen_2^+$ Complex at λ_{maks} 292 nm on pH Variations. [Ni(II)] = 1.0 x 10^{-3} M, Ionic Strength (NaCl) 0.1 M; [Phen] = 1.0 x 10^{-5} M, and pH 2.06-5.90

Observations on the formation of cation $NiPhen_2^{2+}$ complex by measuring the UV-Vis absorption spectra is carried out on variations of pH and Phen ligand concentrations.

Effect of pH on the complexation of $NiPhen_2^{2+}$. The experiment was conducted to observe the effect of pH and to obtain the pH optimum for the formation of $NiPhen_2^{2+}$ complex. The results of observation illustrated in Figure 3, show that the formation of $NiPhen_2^{2+}$ complex reaches maximum absorbance that is pH optimum at pH 3.88.

At pH> 3.88 it can be seen that the concentration of H^+ ions reduces or increases OH^- ions which affect the amount of Ni^{2+} ions that react with a decline in Phen, so that the formation of $NiPhen_2^{2+}$ complex is small, as shown by the decrease in absorbance values (Figure 3). This is because the Ni(II) begins to hydrolyze and precipitate as $Ni(OH)_2$ at pH> 6.50 for the concentration of [Ni(II)] = 1.0 x 10^{-3} M.

At pH <3.88 it can be seen that the concentration of H^+ ions increases, affecting the amount of $NiPhen_2^{2+}$ complex formed to become less. This is due to the number of H^+ ions protonating the N atoms of the Phen ligand. At low pH, the concentration of H^+ in the solution is high, so that more protonation occurs. Protonation of the N atom blocks the binding of Ni(II) on the ligand, so that less of the the complex is formed. From the pH optimum of complexation, the pH is then used to observe the synergistic complexation of Ni:Phen with HDz.

Effect of Phen concentration on the complexation of $NiPhen_2^{2+}$. The experiment was to observe the effect of Phen concentration on the formation of cation $NiPhen_2^{2+}$ complex with conditions of ion concentration Ni(II)

1.0 x 10^{-3} M, ionic strength (NaCl) 0.1 M, and pH optimum 3.88. Variations in Phen concentration $1.0x10^{-7}$-1.0 x 10^{-5} M, showed that the greater the concentration of Phen used, the greater is the UV-Vis absorbance of formation of $NiPhen_2^{2+}$ complex. This is due to more Phen reacting with Ni(II) ion, thus forming more and more complexes.

Synergistic complexation of Ni:Phen with HDz. The addition of dithizone (HDz) ligand to the $NiPhen_2^{2+}$ complex cation produces ion association complex. HDz ligands containing N and S atoms form a covalent bond with $NiPhen_2^{2+}$ to become Ni $(C_{13}H_{11}N_4S)_2(C_{12}H_8N_2)$ or $NiDz_2Phen$ complex. Formation of synergistic $NiDz_2Phen$ complex extracted in the organic phase (hexane) is based on the determination of the molar ratio of [Ni(II)]:[HDz] = 1: 2 as $NiDz_2$ uses the Batch method in the solvent extraction system [25], and from previous studies in solvent extraction systems the $NiDz_2Phen$ complex is extracted in the chloroform phase [23].

$$NiPhen_2^{2+} + 2HDz \rightleftharpoons NiDz_2Phen + Phen + 2H^+ \quad (2)$$

Observation of UV-Vis absorption spectra of the complex in the aqueous phase and the organic phase using the Batch method is shown in Figures 4 and 5. Figure 4 (solid line) shows the absorption spectra of $NiPhen_2^{2+}$ complex observed after the addition of HDZ with λ_{maks} 270 and 292 nm in the aqueous phase. This spectrum is similar to the spectrum before the addition of HDz (dashed line) which is a $NiPhen_2^{2+}$ complex, but with much lower absorbance. Decrease in absorbance after the addition of HDz is because $NiPhen_2^{2+}$ reacts with HDz to form $NiDz_2Phen$, so the presence of residue $NiPhen_2^+$ does not react with HDz in the aqueous phase.
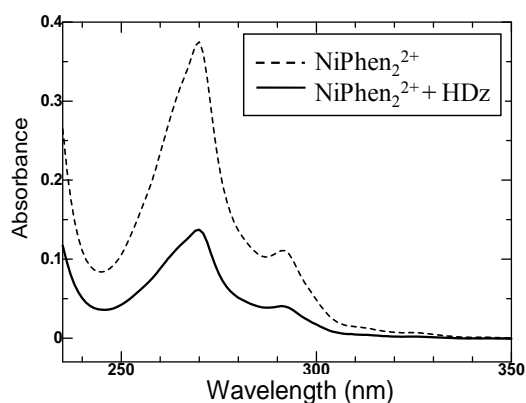
Figure 4. UV-Vis Absorption Spectra of NiPhen$_2^{2+}$ Complex in the Aqueous Phase Before and After the Addition of HDz to NiDz$_2$Phen Complex Formation. [Ni(II)] = 1.0 x 10^{-3} M; pH 3.88; Ionic Strength (NaCl) 0.1 M; [HDz] = 1.0 x 10^{-5} M; [Phen] = 1.0 x 10^{-5} M
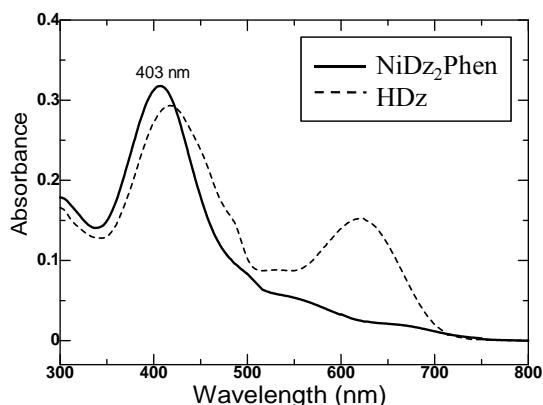

Figure 5. UV-Vis Absorption Spectra of the Formation of NiDz2Phen Complex in the Organic Phase, [Ni(II)] = 1.0 x 10^{-3} M, pH 3.88; Ionic Strength (NaCl) 0.1 M; [HDZ] = 1.0 x 10^{-5} M; [Phen] = 1.0 x10^{-5} M

Observations in the organic phase spectrum shows a new compound λ_{maks} 403 nm (Figure 5, solid line). This spectrum differs from spectrum HDz (dashed line) that has λ_{maks} 413 and 622 nm with ε dithizone in hexane phase 2.85 x 10^4 and 1.64 x 10^4 M^{-1}cm^{-1}, respectively. This spectrum was proposed as spectrum of ion association NiDz$_2$Phen complex extracted in the organic phase.

CLM Method. This method uses a high rotation speed (10,000 rpm) to produce ultra-thin membranes from two phases system. Each phase has a thickness of 131 μm, with an interfacial area of the two phases (S$_i$) 19.11 cm^2 and the specific interfacial area (S$_i$/V$_o$) 76.44 cm^{-1}. When measuring the absorption spectrum, the beam passes through the both phases of bulk and liquid-liquid interface in a cylindrical glass cell two times. Total absorption spectrum detected by UV-Vis spectrophotometer is at λ 300-800 nm [25].

Synergistic complexation of Ni:Phen with HDz. Results of the Batch method assume that NiDz$_2$Phen is extracted in the organic phase. This method is observed in the aqueous phase and organic phase. Confirmation and further observations on the complex adsorbed at the hexane-water interface is conducted by directly measuring with CLM method.

The formation of NiDz$_2$Phen complex begins with injecting the aqueous phase containing Phen into a cylindrical glass cell, followed by an aqueous phase containing Ni^{2+}. After reaching equilibrium reaction, the organic phase containing HDz is injected. After injection, the visible appearance of the spectra at λ_{maks} 523 nm increases absorbance exponentially with time (Figure 6). The spectra mentioned are spectra NiDz$_2$Phen. The spectrum has different λ_{maks} than the λ_{maks} obtained from the Batch method (403 nm). This proves that formation of NiDz$_2$Phen complex takes place at the hexane-water interface.

Figure 6 also shows spectra with λ_{maks} 413 nm which decreases exponentially with time. The spectra mentioned shows the presence of HDz that diminishes as it reacts with NiPhen^{2+} to form NiDz$_2$Phen. It can be seen that two spectra peaks appear, indicating that HDz instantly expires when it reacts with NiPhen^{2+}. This is due to the small concentration of HDz = 3.5x10^{-5} M.

This experiment observes changes in the visible region of the absorption spectra of NiDz$_2$Phen. Spectra changes of Phen and cation NiPhen^{2+} complex which absorbs in the UV region can not be observed because the CLM cylindrical glass cell used also absorbs UV light, thus distorting the measurement.

Research on synergistic NiDz$_2$Phen complex formation through ion association reaction (NiPhen^{2+} + HDz) is faster than previous studies [25] via addition reaction
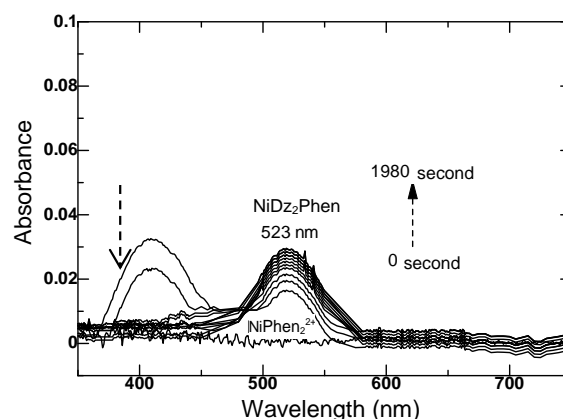

Figure 6. Formation Spectra of NiDz2Phen Complex at Hexane-water Interface with CLM Method; [Ni(II)] = 1.0 x 10^{-3} M, Ionic Strength (NaCl) 0.1 M, pH 3.88; [HDz] = 3.5 x 10^{-5} M; [Phen] = 2.6 x 10^{-4} M

(NiDz$_2$ + Phen). This is evident in the increase of NiDz$_2$Phen absorbance at λ_{maks} 523 nm. In the addition reaction, an increase in NiDz$_2$Phen absorbance is slow as the reaction equilibrium is reached after 1080 seconds. However, with the ion association reaction, the absorbance of the complex increases very rapidly and drastically. NiDz$_2$Phen complex reactions can reach equilibrium after 120 seconds (Figure 7). Further verification is done by comparing the initial reaction rate (r^o_{obs}) of both.

Calculation of r^o_{obs} performed using a second-order equation with *least squares* regression, where the increase in ion pair NiDz$_2$Phen absorbance (523 nm) at the initial state is expressed exponentially with time (Figure 7). Using equation $r^o_{obs} = $ (d [NiDz$_2$Phen]$_i$/dt), it obtained $r^o_{obs} = 8.54 \times 10^{-5}$ M/s. Compared to previous studies [25], an addition reaction (NiDz$_2$ + Phen) resulted in $r^o_{obs} = 1.11 \times 10^{-5}$ M/s. It can be seen that the combination of additional HDz or Phen ligands can affect the formation rate of NiDz$_2$Phen complex. In this study, the order of adding Phen to Ni(II) ion formed cations NiPhen$_2^{2+}$ complex that speeds up the reaction of NiDz$_2$Phen complex formation when treated with HDz.

Effect of Phen concentration on the synergistic complexation of NiDz$_2$Phen. The experiment aims to observe the effect of Phen concentration on the formation of NiDz$_2$Phen complex at the hexane-water interface. Observations were made by spectrophotometry at λ_{maks} 523 nm. The results of observations are shown in Figure 8. It appears that the greater concentration of Phen forms more NiDz$_2$Phen complex, as can be seen from the higher absorbance. This is due to increased concentration of Phen that forms greater initial amounts of NiPhen$_2^{2+}$ complex. NiPhen$_2^{2+}$ complex subsequently undergo ion association with HDz to form NiDz$_2$Phen that is adsorbed at the hexane-water interface.
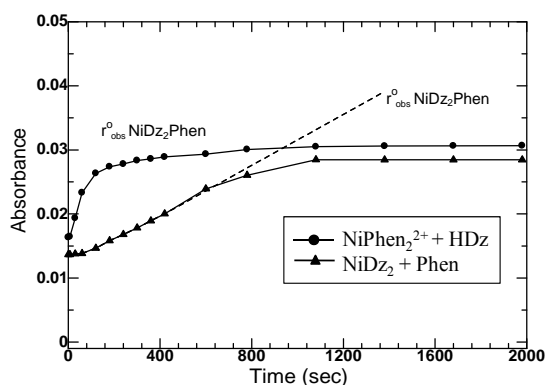

Figure 7. **Relationships of Ion Association Complex Absorbance and Addition Complex NiDz$_2$Fen [25] Exponentially with Time; [Ni(II)] = 1.0 x 10^{-3} M, Ionic Strength (NaCl) 0.1 M, pH 3.88; [HDz] = 3.5 x 10^{-5} M; [Phen] = 2.6 x 10^{-4} M**
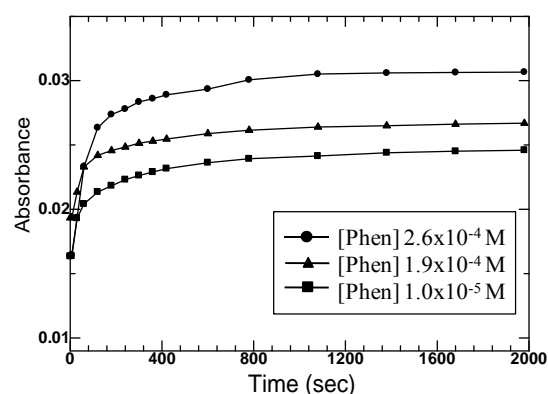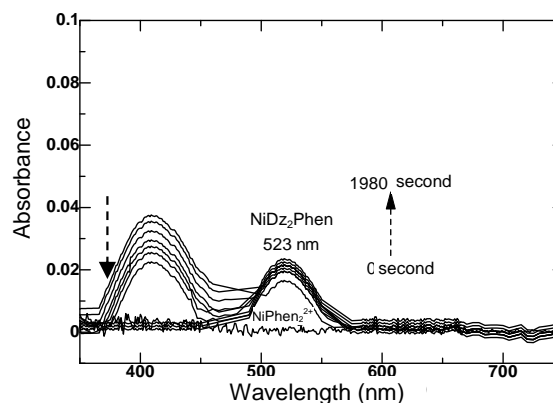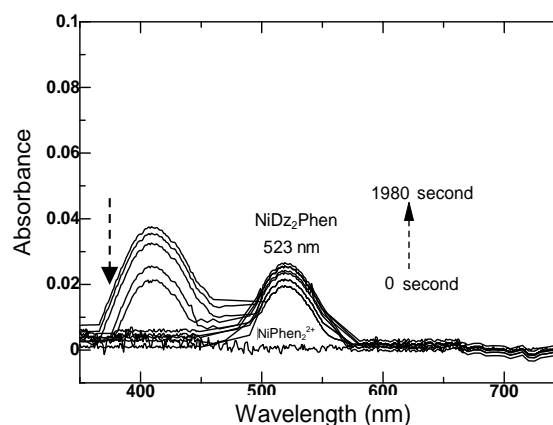

Figure 8. **Relationship of Synergistic NiDz2Phen Complex Absorbance Exponentially with Various Phen Concentrations; [Ni(II)] = 1,0 x 10^{-3} M, Ionic Strength (NaCl) 0.1 M; pH 3.88; [HDz] = 3.5 x 10^{-5} M, [Phen] = 1.0x10^{-5} - 2.6 x 10^{-4} M**

(a)

(b)

Figure 9. **Spectra of Formation of NiDz$_2$Phen at the Hexane-water Interface with the CLM Method Using [Phen] = 1.0 x 10^{-5} M (a) and [Phen] = 1.9 x 10^{-4} M (b); [Ni(II)] = 1.0 x 10^{-3} M, Ionic Strength (NaCl) 0.1 M, pH 3.88; [HDz]=3.5x10^{-5} M**

The extraction rate of NiDz$_2$Phen complex is determined by the concentration of HDz and Phen [23]. Formation of NiDz$_2$Phen complex is an equilibrium reaction that occurs through the formation of intermediate complex Ni(C$_{13}$H$_{11}$N$_4$S)(C$_{12}$H$_8$N$_2$)$_2^+$ or NiDzPhen$_2^+$ at the interface. If the HDz concentration is greater than Phen, the formation of intermediate NiDzPhen$_2^+$ complex is slower, so NiDz$_2$Phen in the organic phase is more dominant than NiDzPhen$_2^+$ at the interface. This is evident from the low absorbance and small gain, visible from the narrow distance between the peaks of the spectra that almost coincide (Figure 9a).

If the HDz concentrate is smaller than Phen, then the formation of intermediate NiDzPhen$_2^+$ complex is faster, so the NiDzPhen$_2^+$ at the interface is more dominant than NiDz$_2$Phen in the organic phase. This is evident from the high absorbance and large gain, visible from the wide distance between the spectral peaks (Figure 9b).

Spectra at λ_{maks} 413 nm show the amount of HDz during the reaction. With concentrations of HDz >> Phen the spectra decreased gradually (Figure 9a). At a concentration of HDz << Phen, the spectra decreased rapidly (Figure 9b). This is due to the small amount of HDz, so it instantly reacts with NiPhen$_2^{2+}$.

Figure 10 shows the relationship of NiDz$_2$Phen complex absorbance exponentially with time. It appears that the greater the concentration of Phen, the greater is the curve gradient. Based on this observation, the value of the formation rate constant (k) of ion association NiDz$_2$Phen complex at the interface can be calculated.

Using a second-order equation with *least squares* regression, as shown in Figure 7, r^o_{obs} = (d[NiDz$_2$Phen]$_i$/dt) at the initial state of the reaction (Fig 10) obtained 1.03 x 10^{-5} and 6.87 x 10^{-5} M/s, consecutively for the concentration of Phen 1.0 x 10^{-5} and 1.9 x 10^{-4} M.

Determining the formation rate constant value of ion association NiDz$_2$Phen complex at the interface, k is performed by plotting the r^o_{obs} value of the Phen concentration used. Based on this relationship, the resulting equation is a straight line y = 0.30x + 8.07x 10^{-6} (Figure 11). k was obtained at 0.30/s. Values of k showed ease in the formation of synergistic complexes to be adsorbed at the liquid-liquid interface. This rate constant value was smaller than the value of k between 0.91-85.40/s that were obtained from previous experiments on forming NiDz^{2}Phen complex in a chloroform-water system using HSS spectrophotometry method [23]. This value showed that the formation of complexes at the hexane-water interface (hexane, non-polar) was slower than at the chloroform-water interface (chloroform, semipolar). The slow complex formation
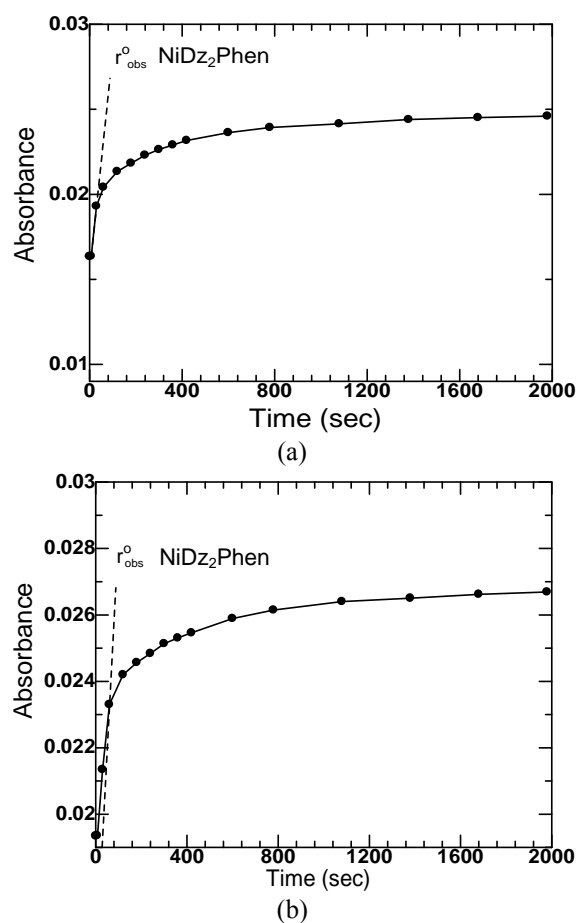
(a)

(b)

Figure 10. Relationship of NiDz$_2$Phen Complex Absorbance Value with CLM Method: [Phen] = 1.0 x 10^{-5} M (a) and [Phen] = 1.9 x 10^{-4} M (b); [Ni(II)] = 1.0 x 10^{-3} M; Ionic Strength (NaCl) 0,1 M; pH 3.88; [HDz] = 3.5 x 10^{-5} M
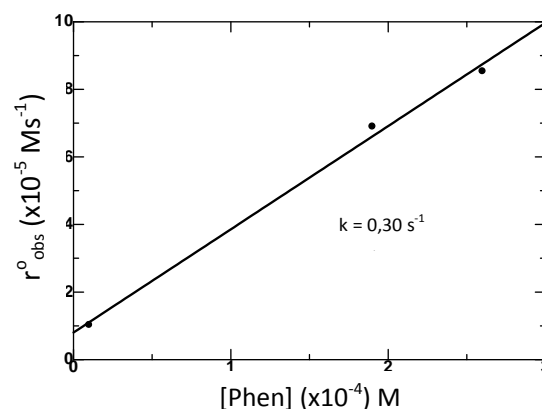

Figure 11. Relationship of r^o_{obs} NiDz$_2$Phen Complex to the Phen Ligan Concentration; [Phen] = 1.0 x 10^{-5} − 2.6 x 10^{-4} M

facilitates the observation of adsorbed complex at the interface. These results prove that the CLM spectrophotometry method can be applied to directly
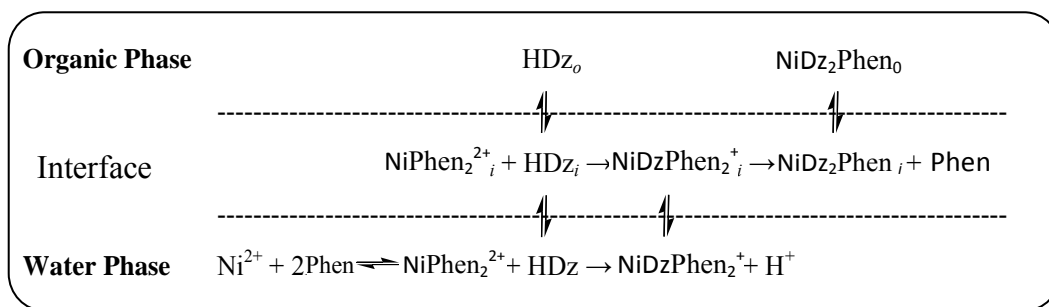
Organic Phase	HDz_o		$NiDz_2Phen_0$	
Interface	$NiPhen_2{}^{2+}{}_i + HDz_i \rightarrow NiDzPhen_2{}^{+}{}_i \rightarrow NiDz_2Phen_i + Phen$			
Water Phase	$Ni^{2+} + 2Phen \rightleftharpoons NiPhen_2{}^{2+} + HDz \rightarrow NiDzPhen_2{}^{+} + H^+$			

Figure 12. Formation Reaction Mechanism of Synergistic Complex between Ni(II), Phen with HDz at the Hexane-Water Interface

measure synergistic formation of complexes at the liquid-liquid interface.

Synergistic Complexation Reaction Mechanism. From the results of experiments and observations made above a reaction mechanism for the formation of $NiDz_2Phen$ complex from ions Ni(II), Phen and HDz in the aqueous phase, the organic phase and the hexane-water interface, can be proposed, as shown in Figure 12.

Synergistic complex formation occurs in three stages. First, the $NiPhen_2{}^{2+}$ complex in the aqueous phase reacts with HDz in the hexane phase to form intermediate $NiDzPhen_2{}^{+}$ complex at the hexane-water interface. Second, the intermediate complex undergoes disproportionation reactions to form neutral $NiDz_2Phen$ complex at the interface. Third, $NiDz_2Phen$ complex is desorbed from the interface and extracted into the organic phase. It appears that the formation of ion association complex occurs gradually in three places, the aqueous phase, the interface, and the organic phase.

4. Conclusions

The formation of synergistic $NiDz_2Phen$ complex at the hexane-water interface has been successfully studied directly using UV-Vis spectrophotometry associated with CLM method. Based on the Batch method, the cation $NiDzPhen_2{}^{+}$ complex has λ_{maks} 270 and 292 nm. The complex dissolved in the aqueous phase with pH optimum 3.88. $NiDz_2Phen$ complex formed at λ_{maks} 403 nm and extracted in the organic phase. Using the CLM method, $NiDz_2Phen$ complex formation was observed at λ_{maks} 523 nm. Differences in λ_{maks} obtained with the Batch method proves that formation of $NiDz_2Phen$ complex takes place at the hexane-water interface. The greater the concentration of Phen, the faster is the initial formation rate of $NiDz_2Phen$ complex. Based on the CLM method, the complexation rate constant value of ion association of $NiDz_2Phen$ at the interface, k is 0.30/s.

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