Effect of Surfactants on the Kinetics of Nickel(II) Extraction by 2-Hydroxy-5-nonylacetophenone Oxime (LIX 84) in an n-Heptane/Water System

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The initial reaction rates of the extraction of nickel(II) by 2-hydroxy-5-nonylacetophenone oxime (HNAPO) in a two-phase oil/water system was measured using a total internal reflectance static transfer cell. A two-step reaction mechanism between nickel(II) and HNAPO was found to satisfactorily explain the observed initial reaction rate ($R_{\text{int}}$). The addition of neutral surfactants, nonionic octaethylene glycol mono-n-dodecyl ether and zwitterionic n-dodecylmethyl-3-ammonio-1-propanesulfonate, decreased $R_{\text{int}}$, which could be accounted for with a competitive surface adsorption model. The presence of the anionic surfactant sodium dodecyl sulfate accelerated and then decelerated $R_{\text{int}}$, while the cationic surfactant dodecyltrimethylammonium chloride caused a decrease. The effects of these charged surfactants were accounted for using a combination of a competitive surface adsorption model and the Boltzmann distribution of charged species.

Introduction

Species separated using solvent extraction have to move from the bulk phase to the near the phase boundary or interface, react with a chelating agent (soluble in the second phase) to form a complex that is soluble in the second phase, and then move into the second bulk phase. This complex process of mass transfer and chemical reactions in a heterogeneous system means that the interfacial zone plays an important role in the overall process. Typical chelating agents, or extractants, utilized are interfacially active; therefore, alteration of the physicochemical properties of the interfacial zone can affect extraction.

2-Hydroxy-5-nonylacetophenone oxime (HNAPO), Figure 1, is a complexing agent commonly used to extract nickel(II) and is the active ingredient of the industrial extractant LIX 84 (Cognis Corp.). It will also extract copper(II), cobalt(II), palladium(II), and zinc(II) under the appropriate conditions. Previous studies have shown that the complexity of nickel(II) with HNAPO is an interfacial reaction, and is therefore a suitable system for observing the effect of interfacial physicochemical properties on extraction reaction rates.

The aim of this study is to observe the effects of various measurable interfacial physicochemical properties on metal ion extraction kinetics in a two-phase oil/water system. This builds on a previous work studying the same extraction process within a micellar phase. The reaction mechanism and characteristic rate constants for nickel(II) extraction by HNAPO were determined in a two-phase, n-heptane/water system. Neutral surfactants, n-dodecylmethyl-3-ammonio-1-propanesulfonate (DDSA) and octaethylene glycol mono-n-dodecyl ether (C12E8), were added to determine the effects of interfacial area competition between the surfactants and the extractant. Ionic surfactants, sodium dodecyl sulfate (SDS) and dodecyltrimethylammonium chloride (DTAC), were utilized to determine the influence of the interfacial electrostatic surface potential on reaction kinetics, in addition to interfacial area competition.

Experimental Section

Chemicals. Dodecylmethyl(3-sulfopropyl)ammonium (DDSA) and nickel perchlorate hexahydrate (analytical reagent grade) were obtained from Aldrich Chemical Co. Inc. SDS, perchloric acid, ethanol, and sulfuric acid of analytical grade were from BDH Ltd., England. DTAC was from TCI, Japan, and C12E8 from Nikko Chemicals Co. Ltd., Japan. HNAPO was obtained by purification from an industrial sample of LIX 84i (courtesy of Cognis Corp.), as described previously.

As the pH extraction isotherm for the Ni2+/HNAPO extraction system is located relatively close to a neutral pH, the pH can undergo significant changes during extraction if the solution is not buffered. Although buffers can interact with the metal ions, their...
use in this system cannot be avoided. As described previously, all aqueous-phase systems were buffered using a 0.01 M perchloric acid/triethanolamine (analytical reagent grade, Ajax Chemicals, Australia) buffer system (pH range similar to that of the hydrochloric acid/triethanolamine system of 6.9–8.5). Sodium perchlorate monohydrate (analytical reagent grade, Ajax Chemicals, Australia) was used to maintain constant ionic strength. Small pH adjustments were made to the buffered solution using concentrated sulfuric acid and sodium hydroxide (analytical reagent grade, Ajax Chemicals, Australia) solutions. All chemicals were used as supplied, with the exception of the extractant, HNAPO, which was purified.

Total Internal Reflectance Static Transfer Cell. The total internal reflectance static transfer cell (TIRSTC) uses the same phenomenon as that of infrared ATR techniques. Instead of a solid phase being used, as for ATR, the difference in the optical density of water and organic solvents is utilized to achieve total internal reflectance. The technique samples the entire organic phase and not just the interface; therefore, the data collected contain a component due to the metal–extractant complex as it diffuses into the bulk phase from the interface. The advantages of the TIRSTC are that the hydrodynamics of the system are characterized as mass transfer occurs by diffusion, neither phase is agitated, and the interfacial area is accurately known, therefore overcoming the major problems associated with other two-phase kinetics techniques.

The TIRSTC consisted of a Teflon-coated vessel (185 mm × 95 mm × 95 mm, horizontal cross sectional area 0.0176 m²) to hold an organic and aqueous phase, as shown in Figure 2. Light enters the cell through an optical fiber at 80°30′, relative to the horizontal, into the organic phase and is totally internally reflected off the organic/aqueous-phase interface (on the basis of the refractive indices of ηorg-heptane = 1.38764 and ηwater = 1.33299 at 20 °C, the critical angle, θc, is 72°27′). The interfacially reflected beam is reflected back toward the interface again by a parallel mirror (suspended within the organic phase) and then allowed to bounce off the interface once more. The light beam was then collected by a second optical fiber at 80°30′. The light beam sampled the entire organic phase, allowing the concentrations of species in the bulk organic phase to be monitored using UV–vis spectroscopy. A single-beam Multispec spectrograph (Oriel Instruments) with an Instaspec II diode array detector (Oriel Instruments) was used to monitor the UV–vis spectrum. Light from the xenon lamp was passed through a UV-cutoff filter prior to entering the TIRSTC.

Phase volumes of 710 and 200 cm³ for the aqueous and organic phases, respectively, resulted in a 40 mm thick aqueous phase and 15 mm total organic-phase thickness (with the mirror immersed within the organic phase). Under these conditions the path length was determined to be 15.2 cm. This path length was independently measured using additions of a Ni(NAPO)2/n-heptane stock solution, where NAPO is the deprotonated form of HNAPO, to the cell and measuring the organic-phase absorbance using both the TIRSTC and a separate twin-beam spectrophotometer. The organic phase, composed of the appropriate concentration of HNAPO in n-heptane, was introduced using small volumes of 1.5 M HNAPO in n-heptane stock solution. The aqueous phase was NiClO4·0.01 M HClO4/triethanolamine, and NaClO4 as required to adjust the ionic strength. As required, surfactants were added from 1.0 M stock solutions.

Before the experiments were performed, the cell was thoroughly washed with water and n-heptane to remove contaminants. Since the spectrophotometer used was a single-beam instrument, a reference scan was required, and this was taken using the following procedure with no extractant present in the organic phase. The aqueous phase was added first and allowed to settle for 15 min to minimize convection currents. The organic phase was then poured onto the Teflon baffle over a period of 4 s and allowed to run onto the surface of the aqueous phase via an “L”-shaped baffle. The L-shaped baffle was used to minimize the vertical liquid motion in the aqueous phase produced by the addition of the organic phase. Once major disturbances on the interface subsided (~2 s from the point of all organic having entered the cell), the UV–vis spectrum sampling commenced.

As reported in a previous study, the nickel/NAPO complex in n-heptane absorbs in the UV–vis region with no interference from the free HNAPO, λmax = 387 nm, εmax = 3700 M⁻¹ cm⁻¹. Spectra obtained from the TIRSTC as a function of time were converted to complex concentration using the Beer–Lambert law. The initial reaction rate, Rinit, was obtained using a smoothed curve tangent over the initial 300 s.

### Results and Discussion

#### Identification of the Reaction Mechanism and Rate Constants

A series of experiments were performed by varying the proton, nickel ion, and HNAPO concentrations independently. The influence of the proton concentration on the extraction kinetics is shown in Figure 3. Increasing the nickel ion concentration, pH, or HNAPO concentration increased the rate of Ni(NAPO)2 complex formation.

The reaction mechanism at the free oil/water interface should be similar to the mechanism at the micelle/aqueous interface, implied by the reacting species being unchanged and the reaction environment being similar. Several authors, however, have noted that this might not be the case due to a change in dimensionality of the reaction and the physicochemical environment at the locus of the reaction. It could be argued that this can be accommodated by ensuring that the concentration and rate constants utilized are consistent with the environment in which they are occurring. Therefore, the proposed mechanism for the extraction of nickel(II) by HNAPO in n-heptane/aqueous

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The effect of proton concentration on the kinetics of nickel-(II) extraction by HNAPO in the two-phase system. Aqueous phase of 0.01 M HClO₄/triethanolamine and 3.4 × 10⁻⁶ M Ni(ClO₄)₂ at the appropriate pH. Organic phase of n-heptane with 6.8 × 10⁻³ M HNAPO. Key: (○) pH 6.5, (△) pH 7.0, (□) pH 7.4, (◇) pH 8.0.

System⁴⁰ is shown by eqs 1–4.

\[
\text{HNAPO}_{\text{org}} \rightleftharpoons \text{HNAPO}_{\text{ad}}
\]

\[
\text{Ni}^{2+}_{\text{aq}} + \text{HNAPO}_{\text{ad}} \rightleftharpoons \text{Ni(NAPO)}^+_{\text{ad}} + \text{H}^+_{\text{aq}}
\]

\[
\text{Ni(NAPO)}^+_{\text{ad}} + \text{HNAPO}_{\text{ad}} \rightleftharpoons \text{Ni(NAPO)}_{2,\text{ad}} + \text{H}^+_{\text{aq}}
\]

\[
\text{Ni(NAPO)}_{2,\text{ad}} \rightleftharpoons \text{Ni(NAPO)}_{2,\text{org}}
\]

and has the same reaction steps as that in a micellar system.¹¹ The subscript “aq” denotes the aqueous phase, the subscript “ad” denotes adsorbed at the aqueous/organic interface, the subscript “org” denotes the organic phase. \( k_1 \) (M⁻¹ s⁻¹) and \( k_2 \) (M⁻¹ s⁻¹) are the forward reaction constants, \( k_{-1} \) (M⁻¹ s⁻¹) and \( k_{-2} \) (M⁻¹ s⁻¹) are the reverse reaction constants, Ni(NAPO)⁺ is the intermediate 1:1 complex, and Ni(NAPO)₂ is the 1:2 complex. A mechanism including the deprotonated form (NAPO⁻) of the ligand is not valid under the conditions studied, with the concentration of this particular form being negligible (bulk aqueous-phase \( pK_a = 12.3^{10} \)), and variation in the ionic strength has no influence on the rate of reaction.

Using the steady-state approximation for the intermediate species Ni(NAPO)⁺, and assuming that the reaction is not diffusion controlled, the initial rate reaction equation can be derived as eq 5. Since the surface excess has units of mol m⁻², this must be converted to mol dm⁻³ to be consistent with the other species concentration terms in eq 5. This is achieved by introducing a surface area per phase volume factor, \( S \), defined as the oil/water interfacial surface area (m²) divided by the oil phase volume (dm³). For the TIRSTC and conditions used in this study, \( S \) was calculated as 0.088 m²/dm³. Linearizing eq 5 to eq 6 enables the fitting of the experimental data, where \( X = [\text{H}^+_{\text{aq}}]/[\text{Ni}^{2+}_{\text{aq}}] S T_{\text{HNAPO}}^2 \) (M⁻²) and \( Y = 1/[\text{Ni}^{2+}_{\text{aq}}] S T_{\text{HNAPO}} \) (M⁻²).

\[
\frac{d[Ni(NAPO)_{2,\text{org}}]}{dt}(t \rightarrow 0) = \frac{k_1 k_2 [\text{Ni}^{2+}_{\text{aq}}] S T_{\text{HNAPO}}^2}{k_{-1} [\text{H}^+_{\text{aq}}] + k_2 S T_{\text{HNAPO}}}
\]

(5)

\[
\frac{1}{R_{\text{int}}} = \frac{k_{-1}}{k_1} X + \frac{1}{k_1 Y}
\]

(6)

The n-heptane/aqueous-phase extraction data were fitted using the equation \( Z = a X + b Y \), where \( Z = 1/R_{\text{int}}, \ a = k_{-1}/k_1 k_2, \) and \( b = 1/k_1 \). A plane with \( a = 3.48 \times 10^{-3} \) (standard error \( 5 \times 10^{-5} \)) and \( b = 0.363 \) (standard error 0.08) was fitted to the data, with \( R^2 = 0.94 \). Using these fitted values of \( a \) and \( b \), \( R_{\text{int}} \) can be calculated and compared with the experimental data. The theoretical modeling of the initial reaction rate, using eq 5, was found to provide a satisfactory fit to the experimental data, with deviations being randomly distributed over the studied range. Therefore, the proposed reaction mechanism, eqs 1–4, and the subsequent initial reaction rate equation, eq 5, correlate with those observed experimentally. The fitted values of \( a \) and \( b \) enable the determination of \( k_1 \) as 2.76 M⁻¹ s⁻¹ and \( k_{-1}/k_2 \) as 9.58 × 10⁻⁴.

Utilizing a two-phase system imposes limitations on the concentrations accessible. These are due to the long light beam path length (small adjustments to this can be made via the organic-phase height), therefore requiring lower concentrations to keep absorption levels down. Additionally, diffusion in either phase may be the limiting reaction step. Experimental restriction to low HNAPO concentrations renders the saturated interface phenomenon inaccessible.

Additionally, the extraction process has to be reaction, not diffusion, controlled. The short time predictive equation for a process (within an oil/water metal extraction system) that is diffusion-controlled¹⁶ predicts that the concentration of the complex in the organic phase is proportional to \( t^{1/2} \). Therefore, a \( \log \)–log plot of \([\text{Ni(NAPO)}]_{\text{org}} \) versus time will have a slope of 0.5 if the process is diffusion-controlled. All reaction kinetics measured in the TIRSTC were found to be reaction-controlled initially; however, some reaction conditions caused a shift to diffusion control at around 500 s. The transition from reaction to diffusion control is a result of either saturation of the interface by Ni(NAPO)₂ or depletion of HNAPO at the interface or a combination of both. Consequently, only the initial periods of the extraction reaction within the TIRSTC can be modeled using the reaction mechanism only, and the initial reaction rate measured is characteristic of the chemical reaction.

Errors, in terms of random noise and between experiments, were observed for the kinetic curves. The errors are due to the macroheterogeneous nature of the n-heptane/aqueous system; particularly any disturbance at the interface can dominate the data since only a relatively small surface area is involved. The deviations observed, for example, the “hump” in Figure 3 for 3.4 \( \times 10^{-6} \) M Ni(ClO₄)₂ around 200–400 s, could not be totally eliminated. These deviations may be caused by the movement of discrete volumes of organic phase within the TIRSTC having higher concentration than the bulk average.

**Effect of Neutral Surfactants.** As determined previously,²⁴ neutral surfactants are significantly more surface-active than HNAPO. The consequence of this is that the surfactant molecules will be preferentially absorbed at the free oil/water interface compared to HNAPO, reducing \( \Gamma_{\text{HNAPO}} \) and the reaction rate. To

calculate the surface excess of components when there are two competing surface-active species present, a model was developed.\(^\text{24}\) The model assumes ideal enthalpy and entropy of mixing, and eq 7 predicts the surface fraction of surfactant 1 when

\[
\theta_1 = \frac{\Gamma_1}{\Gamma_{\text{max}1}} = \frac{K_1 \phi_1 (1 - \phi_2)}{(1 - \phi_1)(1 - \phi_2) + K_1 \phi_1 (1 - \phi_2) + K_2 \phi_2 (1 - \phi_1)} \quad (7)
\]

competing with surfactant 2, where \(\theta_1\) is the available surface fraction for surfactant 1 to absorb onto, \(\Gamma_1\) is the surface excess of surfactant 1, \(\Gamma_2\) is the surface excess of surfactant 2, \(\Gamma_{\text{max}1}\) is the maximum surface excess of surfactant 1, \(K_1\) and \(K_2\) are constants, \(\phi_1\) is the volume fraction of surfactant 1, and \(\phi_2\) is the volume fraction of surfactant 2. The constants \(K_1\), \(K_2\), and \(\Gamma_{\text{max}1}\) are determined in a single surfactant system using a linearized Langmuir isotherm.\(^\text{24}\)

The concentration of the extractant and complex at the interface is fitted by eq 7, for a system with two competing surfactants. A problem that is encountered experimentally with the addition of surfactants, both neutral and ionic, is the formation of small emulsion droplets at the interface. Small numbers of droplets can scatter the reflected light and cause the absorbance to fluctuate significantly as they move around.

The additions of DDSA, see Figure 4, and C\(_{12}\)E\(_8\)\(^\text{25}\) both decreased the rate of extraction. DDSA completely inhibited the extraction reaction when the bulk aqueous concentration of the surfactant reached 2.4 \(\times\) 10\(^{-4}\) M, while C\(_{12}\)E\(_8\) only required 3.0 \(\times\) 10\(^{-7}\) M. This dramatic difference in concentration required to stop the extraction reaction is due to the higher surface activity of C\(_{12}\)E\(_8\). The higher surface activity of C\(_{12}\)E\(_8\) is indicated by its lower CMC, 10\(^{-3}\) M versus 10\(^{-3}\) M for DDSA,\(^\text{26}\) and the larger \(K\) used for the surface adsorption isotherm, 7 \(\times\) 10\(^5\) versus 3.8 \(\times\) 10\(^3\). The addition of a nonionic surfactant has previously been found to decrease the initial extraction rate of copper(II) by 2-hydroxy-5-nonylbenzophenone oxime.\(^\text{27}\)

**Effect of Charged Surfactants.** The addition of charged surfactants has two effects on the kinetics of extraction. First, there is the competition for interfacial area, as observed for neutral surfactants above. Second, the concentration of charged aqueous-phase species at the interface is altered by the electrostatic surface potential generated by the charged surfactant.

The presence of charged surfactants at the oil/water interface will introduce an electrostatic surface potential due to the presence of theionic functional groups. The induced local change in the concentrations of charged species in the aqueous phase was calculated using a Boltzmann distribution.\(^\text{28}\) This was found to be valid for this same extraction system in a micellar phase.\(^\text{11}\)

DTAC was found to decrease the extraction rate with increasing concentration and required a concentration, 7.0 \(\times\) 10\(^{-4}\) M, to shut down the reaction similar to that for DDSA, 2.0 \(\times\) 10\(^{-4}\) M. This similarity can be accounted for by the fact that DTAC is not as interfacially active as DDSA, with \(K\) values of 3.5 \(\times\) 10\(^5\) and 3.8 \(\times\) 10\(^3\), respectively. Therefore, DTAC does not displace HNAPO at the interface to the same degree as DDSA, with the positive surface potential then making up for the difference in surface activity. A cationic surfactant has also been observed to decrease the initial reaction rate of copper(II) extraction by 2-hydroxy-5-nonylbenzophenone oxime.\(^\text{27}\) Conversely, the addition of SDS to the aqueous phase initially increased the rate of extraction, and then decreased it, as shown by Figure 5. This observed trend is a result of the competition between the two phenomena influencing the reaction rates: the enhancement from the negative electrostatic surface potential, which increases the concentration of nickel(II) (and decreases \([H^+]\)) at the


interface, and inhibition due to displacement of HNAPO at the interface by SDS. Initially it would appear that the addition of SDS could halt the extraction if the concentration was high enough. However, this is unlikely to occur as even if there is a very small concentration of HNAPO present at the interface, the rate of reaction is still significant due to the elevated concentration of nickel(II) cations at the interface. SDS concentrations above 7.0 x 10^-4 M were not experimentally obtainable (due to formation of stable emulsion droplets, as mentioned previously) to enable full exploration of this phenomenon. The same increase, and slight decrease at higher SDS concentrations, has also been previously observed for the copper(II) extraction by 2-hydroxy-5-nonylbenzophenone oxime in an n-heptane/aqueous system.27

**Modeling Effects of Interfacial Competition.** Equation 7 does not consider the change in concentration of reacting species at the oil/water interface, and as such it is not suitable to determine \( R_{\text{int}} \) for systems containing additives such as surfactants. Using the surface adsorption model, the value of \( \Gamma_{12} \) can be corrected and the prediction of the experimental \( R_{\text{int}} \) is improved, as shown by Figure 6. The prediction of \( R_{\text{int}} \) for DDSA is satisfactory; however, in the case of C12E8 the fitting is poor. It appears that C12E8 adsorbs to the interface more strongly and therefore reduces the concentration of HNAPO to a larger degree than the surface adsorption model predicts and was found previously;24 the reason for the discrepancy is unclear.

Figure 6 also indicates that adjustment of the interfacial concentration of HNAPO only is insufficient when charged surfactants are involved. Correctly, the \( R_{\text{int}} \) for DTAC is overestimated (with the actual interfacial concentration of Ni^{2+} lower due to the positive electrostatic surface potential), and for SDS it is underestimated (with the actual interfacial concentration of Ni^{2+} being lower due to the negative electrostatic surface potential).

Plotting the experimental \( R_{\text{int}} \) against the surfactant surface fraction, Figure 7, allows easy identification of the surface competition phenomena. The additions of DTAC and C12E8 both slow the initial reaction rate to an extent, indicating that the surface activity and surface potential of DTAC have an effect similar to that of the higher surface activity of C12E8. In contrast, SDS does not show any sign of being able to halt the reaction, even at over 95% coverage. For the zwitterionic surfactant DDSA, it can be clearly seen that there is a gradual slowing of \( R_{\text{int}} \) until the extraction reaction is halted at over 95% coverage of the interface.

**Modeling Effects of Electrostatic Surface Potential.** The concentrations of charged species at the oil/water interface can be calculated using the Boltzmann distribution, requiring knowledge of the interfacial electrostatic surface potential, which can be calculated using Gouy–Chapman theory, eq 8.

\[
\Psi = \frac{2kT}{ze} \sinh^{-1} \left( \frac{\alpha}{(8e_0\epsilon_0 kTn_0)^{1/2}} \right) \tag{8}
\]

\[
\sigma = \epsilon \Gamma \sigma_s \tag{9}
\]

where \( e \) (C) is the electronic charge, \( \epsilon_0 \) (C^2 J^-1 m^-1) is the permittivity of free space, \( n_0 \) (m^-3) is the number volume density of the background 1:1 electrolyte, \( \Gamma \) (m^-2) is the surface excess in number area density, \( \sigma \) (C m^-2) is the surface charge density, and \( \sigma_s \) is the degree of surfactant ionization.

The surface charge density can be estimated using eq 9 if the degree of surfactant ionization is known. Surfactant ionization for SDS has been determined29,30 and could be used to estimate values of \( \sigma_s \); however, no data are available for DTAC. Additionally, the effect of the presence of another surface-active species on surfactant ionization has not yet been explored. Therefore, it is not currently possible to calculate the electrostatic surface potential of the free oil/water interface reliably using these theories.

To determine if the Boltzmann distribution can account for the changes in \( R_{\text{int}} \), the electrostatic surface potential required to adjust the calculated \( R_{\text{int}} \) (with interface competition included)


to the experimental values was calculated; see Figure 8. If the electrostatic surface potentials from Figure 8 are used to calculate $R_{\text{int}}$, then the data points for DTAC and SDS in Figure 6 will fall directly on the line. The presence of SDS requires a zero surface potential from a concentration of $10^{-5}$ M, followed by a rapid increase at higher concentrations. This variation in surface potential for SDS at the oil/water interface is counter to that measured for stabilized decane emulsion droplets, which was found to remain constant at $-100$ to $-125$ mV between $10^{-5}$ and $10^{-3}$ M SDS. However, $R_{\text{int}}$ remaining constant as the SDS surface fraction approaches 1.0 (see Figure 7) implies that the electrostatic surface potential is increasing the interfacial concentration of nickel(II) and is counteracting the reduction in $\Gamma_{\text{HNAPO}}$ due to surface competition with the SDS. The addition of DTAC requires an electrostatic surface potential of $+20$ mV at a very low concentration, $10^{-7}$ M. The behavior of the electrostatic surface potential at higher concentrations is not observable, so it cannot be determined if it follows the same trend as SDS with a significant increase in the size of the electrostatic surface potential.

Conclusions

The nickel(II)/HNAPO extraction kinetics within the two-phase system $n$-heptane/aqueous has been examined using the TIRSTC. A mechanism involving a two-step reaction between the nickel ion and the extractant satisfactorily explains the observed initial reaction rate. From the initial reaction rate data, $k_1$ (forward reaction rate constant for formation of the 1:1 complex) was determined as $2.8 \text{ M}^{-1} \text{s}^{-1}$ and the ratio of $k_{-1}$ (backward reaction rate constant for formation of the 1:1 complex) to $k_2$ (forward reaction rate constant for formation of the 1:2 complex) as $9.6 \times 10^{-4}$. The addition of neutral surfactants, nonionic ($\text{C}_{12}\text{E}_8$) and zwitterionic (DDSA), decreased the initial reaction rate, which was modeled using a surface adsorption model to calculate the interfacial concentration of HNAPO, $\Gamma_{\text{HNAPO}}$. The presence of the anionic surfactant SDS accelerated and then decelerated the reaction rate, while the cationic surfactant DTAC caused a decrease. The effects of these charged surfactants can be accounted for using a surface adsorption model and the Boltzmann distribution of charged species. The predicted electrostatic surface potential of the free oil/water interface required for agreement with the experimental $R_{\text{int}}$ was calculated and found to be reasonable.

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