Interfacial adsorption and complexation in liquid–liquid extraction systems

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Abstract: The interfacial adsorptivity of 2-hydroxyoximes and pyridylazo-ligands and the complexation rate of the ligands with Ni(II) ion at the liquid-liquid interfaces were measured by a high-speed stirring method. From the results, principal adsorption equilibria and rate-determining steps in the extraction mechanisms were determined. The observed adsorptivity and reactivity of the ligands at the interface were discussed by the aide of molecular dynamics simulations. It was found that the location of the adsorbed ligand within the interfacial layer, which was thinner than 1 nm, could determine the interfacial reactivity of the ligands and the extraction rate of the Ni(II) ion.

INTRODUCTION

The interfacial adsorption of extractants and the complexation at the liquid-liquid interfaces are recognized as essential elementary processes in the kinetics of solvent extraction of metal ions (ref.1). However, experimental techniques available for the measurements of the interfacial reaction were very limited. Our recent efforts to develop new experimental principles for the study of interfacial complexation kinetics produced a high-speed stirring method (ref.2), a two-phase stopped flow method (ref.3), a centrifugal liquid membrane method (ref.4) and a time-resolved total internal reflection spectrofluorimetry. These methods have revealed kinetic interfacial mechanisms in some representative solvent extraction systems including chelate extraction, ion-association extraction and synergic extraction of metal ions. However, the molecular mechanism of the interfacial complexation are still hardly understood because of the lack of the knowledge concerning the molecular structure of the liquid-liquid interfaces. In the present study, we proposed an application of molecular dynamics (MD) simulations for understanding what happened at the interface during the kinetic process of the solvent extraction.

2-Hydroxyoximes, e.g. 5-nonylsalicylaldoxime (P50), 2-hydroxy-5-nonylacetophenone oxime (SME529) and 2-hydroxy-5-nonylbenzophenone oxime (LIX65N), are widely used as commercial extractants of Ni(II),
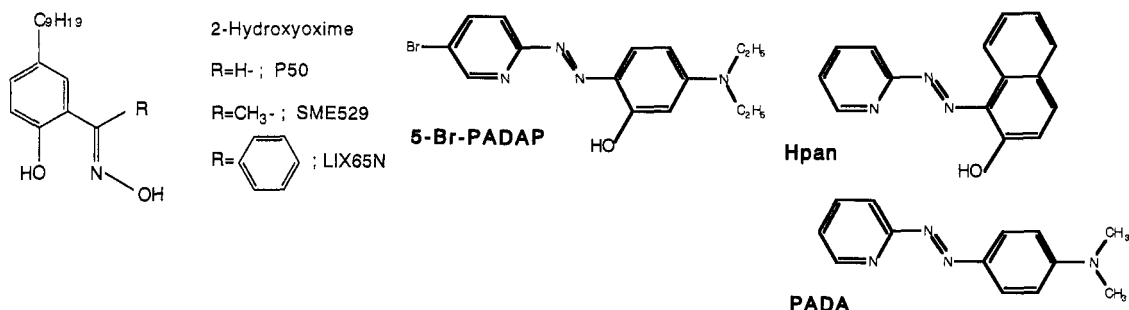
Cu(II) and Co(II). These extractants adsorbed at the interface even in its neutral form. The high-speed stirring method revealed that the reaction between the dissociated form and metal ions at the interface was the rate determining-step of the extraction rate of Ni(II) (ref. 5). 1-(2-Pyridylazo)-2-naphthol (Hpan) is one of the most widely used pyridylazo-ligands in the extraction colorimetry and complexometric titration of metal ions. However, the extraction rate with Hpan was rather slow for some metal ions such as Ni(II) and Pd(II). 2-(5-Bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP), is relatively new colorimetric reagent which is more sensitive than Hpan. Here, the extraction kinetic mechanism of Ni(II) with 5-Br-PADAP (ref. 6) and the catalytic effect of 4-(2-pyridylazo)-N,N-dimethylaniline (PADAP) on the extraction of Ni(II) with Hpan (ref. 7) which were investigated by a high-speed stirring spectrometry are discussed under the light of MD simulation.

EXPERIMENTAL

High-speed stirring method

The heptane phase or toluene phase (45ml) and the same volume of aqueous phase were stirred at the rate of 4700-5000 rpm in a vessel thermostated at 25 0.1, 5 ml of ligand solution was added, and then 5 ml of nickel solution was spiked into the mixture to initiate the extraction of Ni(II). The organic phase was continuously separated by means of a Teflon phase separator, being introduced into a flow cell mounted in a diode-array spectrophotometer and returned to the vessel by a pump. The interfacial amount of the extractant or complex was determined from the absorbance change resulting from the alternated stirring between 200 rpm and 5000 rpm. The high-speed stirring of the two phase system increased the interfacial area about 500 times. From the continuous decrease of the extractant or the increase of metal complex in the organic phase, the extraction rate was determined.

Molecular dynamics simulation

The liquid-liquid interfaces of heptane/water and toluene/water were simulated by the use of the DREIDING force field on the software of Cerius2 version 3.5. The position and the orientation for 500 molecules of water and 62 molecules of heptane or 100 molecules of toluene were optimized in a cell (ca. 25x 25x 57) at 300K. The density vs distance profile showed a clear interface with a thickness of ca. 10 in both systems. In the simulation of the adsorptivity of extractant, one molecule of the extractant was introduced into the two-phase system and the calculation was carried out at the time step of 1fs over the period of 100-800ps. The charge distribution of the extractant was optimized by MOPAC PM3,

RESULTS AND DISCUSSIONS

Interfacial complexation of Ni(II) with 2-hydroxyoxime

From the analysis of the experimental results of the stirring effect, the adsorption constants of the 2-hydroxyoximes in their neutral form were determined in the frame of the Langmuir isotherm. The adsorption constants (K') of the neutral forms were all in the order of 10^{-3} cm which corresponded to ca. 20 % adsorptivity for the initial amount of the extractant. The rate determining step of the extraction in heptane/water system was the formation rate of the 1:1 complex between the dissociated form and Ni(II) ion at the interface. The complexation rate constants of the dissociated form with Ni(II) ion at the interface were in the order of 10^5 M^{-1}s^{-1} for the three extraction systems, regardless of the large difference in the distribution constants (log K_D) ; 3.36 for P50, 3.99 for SME529 and 5.69 for LIX65N (ref.5). The complexation rate constants at the interface did not differ from those in bulk aqueous solutions.

MD simulation of 2-hydroxyoxime systems

It was found that the interfacial adsorption of the 2-hydroxyoxime was primarily important step in the kinetic process of the extraction of the metal ion. So, we tried to simulate the behavior of LIX65N in heptane/water interface. Figure 1 shows a typical snap shot after 200ps, where the polar groups of -OH and =N-OH of the adsorbed LIX65N molecule are in the aqueous phase side of the interface and ready to react with metal ion in the aqueous phase. This is the reason why the extractant could react with Ni(II) ion at the interface with almost the same reaction rate constant with in aqueous phase.

MD simulation was further applied for the estimation of the stabilization energy at the interface (ref.8). First, a MD simulation was carried out to obtain an equilibrated configuration of the extractant and solvent

molecules. Second, a spherical region with the radius of 8.5 around the center of mass of the extractant molecule was defined, then the internal energy of the spherical region (E_1) was calculated by molecular mechanics as shown in Fig. 2. The surroundings of the spherical region were fixed during the molecular mechanics calculation. Third, removing the extractant molecule from the spherical region, the energy of the residual solvent molecules in the spherical region (E_2) and the energy of the removed extractant molecule in a vacuum (E_0') were calculated. Finally, by the relations:

$$E_i = E_1 - E_2 - E_0' \tag{1}$$
$$E_i = E_i(\text{int}) - E_i(\text{org}) \tag{2}$$

the solute-solvent interaction energy in bulk phases and interface, E_i (kcal/mol), and the adsorption energy from a bulk phase to the interface, E_i (kcal/mol), were calculated. For example, the value of E_i for LIX65N was calculated to be -6.6 kcal/mol, and well explained the interfacial adsorptivity of LIX65N observed experimentally .
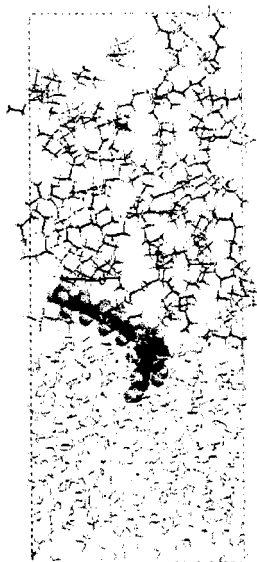

Fig. 1 MD simulation of the adsorption of LIX65N at heptane/water interface after 200ps. The polar moiety of LIX65N is accommodated in the aqueous phase so as to react with Ni(II) ion in the aqueous phase.
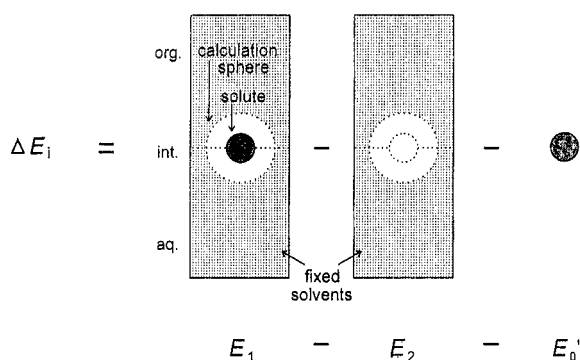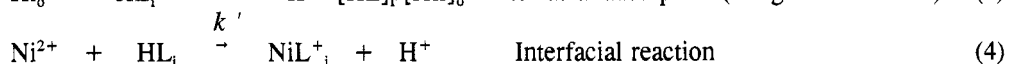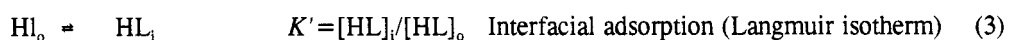
Fig. 2 Calculation of solute-solvent interaction energy of a solute at the liquid-liquid interface or in the bulk organic phase

Interfacial complexation of Ni(II) with pyridylazo-ligand

Among the three pyridylazo-ligands examined in this study, only 5-Br-PADAP showed significant adsorption at the interface of heptane/water under high-speed stirring conditions (5000rpm). In the toluene/water system, the adsorptivity was significantly reduced. Hpan and PADA did not adsorb at all at the heptane/water and toluene/water interfaces. By the use of Langmuir isotherm, the adsorption parameters, $K'A_i$, of 5-Br-PADAP (HL) at the heptane/water and toluene/water interfaces were obtained as 4.4 x 10^{-2} dm³ and 4.3 x 10^{-4} dm³, respectively (ref. 6). The A_i is the total interfacial area under the high-speed stirring (ca.2x10⁴cm²). The smaller adsorption constant in toluene/water system seems correspond to the larger distribution constant; log K_D(toluene/water) = 4.78 and log K_D(heptane/water) = 3.22.

When heptane solution of 5-Br-PADAP and aqueous solution of Ni^{2+} were stirred, the ligand in the organic phase was continuously consumed according to the complexation, but no extraction of the complex was apparent . This meant that the complex formed was completely adsorbed at the interface. The complex was extracted very slowly from the toluene system. The experimental results from the two systems were analyzed taking into account the interfacial adsorption of the ligand and the complexations at the interaface and the aqueous phase. It was assumed that the systems followed the following scheme:
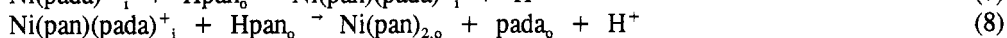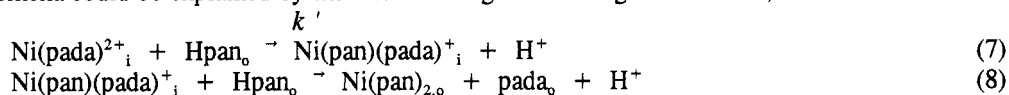
$$HI_o \rightleftharpoons HL_i \qquad K' = [HL]_i/[HL]_o \quad \text{Interfacial adsorption (Langmuir isotherm)} \quad (3)$$

$$Ni^{2+} + HL_i \xrightarrow{k'} NiL^+_i + H^+ \qquad \text{Interfacial reaction} \quad (4)$$

$$Ni^{2+} + HL \xrightarrow{k} NiL^+ + H^+ \qquad \text{Aqueous phase reaction} \quad (5)$$

On this basis the initial rate of consumption of HL_o should obey the equation:

$$r^o = -d[HL]_o/dt = \frac{V}{V+K'A_i}\left(\frac{k}{K_D} + \frac{k'K'A_i}{V}\right)[Ni^{2+}][HL]_o \qquad (6)$$

where V refers to the volume of the organic phase and k and k' to the 1:1 formation rate constants in the bulk aqueous phase and at the interface respectively. The value of k was determined in aqueous solution by a stopped-flow spectrometry under the conditions where the formation rate was independent of pH and found to be 5.3×10^2 $M^{-1}s^{-1}$. The experimentally obtained kinetic results in the liquid/liquid systems were well explained by the above equation. Values of k' were 3.8×10^2 $M^{-1}s^{-1}$ for heptane/water and 1.8×10 $M^{-1}s^{-1}$ for toluene/water. These results meant that the extent of the interfacial reaction as a percentage the total reaction was 99.9% in heptane/water and 94.5% in toluene/water.

Catalytic effect of PADA on the extraction fo Ni(pan)₂

1. The extraction rate of Ni(pan)₂ into toluene is very slow even under a high-speed stirring conditions and high pH. However, the addition of PADA, even as dilute as 10^{-5} M, accelerated the extraction rate about ten times. At this time, there was no change in the extracted species and no consumption of PADA after the extraction, but a significant decrease in the organic phase concentration of PADA was observed during the stirring. Analyses of the experimental results suggested the interfacial adsorption of $Ni(pada)^{2+}$ complex which was rapidly formed in the aqueous phase. Thus, the catalytic phenomena could be explained by the interfacial ligand-exchange mechanism,

$$Ni(pada)^{2+}_i + Hpan_o \xrightarrow{k'} Ni(pan)(pada)^+_i + H^+ \qquad (7)$$
$$Ni(pan)(pada)^+_i + Hpan_o \rightarrow Ni(pan)_{2,o} + pada_o + H^+ \qquad (8)$$

The value of k' was taken to be 90 $M^{-1}s^{-1}$ (ref. 7).

MD simulation of pyridylazo-systems

The MD simulation approach was extended to the explanation of the solvent effect of heptane and toluene on the interfacial reaction of 5-Br-PADAP with Ni(II) ion. In the heptane system, the interfacial rate constant, k', was almost consistent with the one in aqueous solution. However, the value of k' at the toluene/water interface was about 5 % of the value observed at the heptane/water interface.

The MD simulation was started by putting one molecule of 5-Br-PADAP at the center of the interface. The averaged location of the ligand after 100 ps in the two liquid-liquid systems were obtained. In heptane/water system, a 5-Br-PADAP molecule stayed at the interfacial region during the simulation almost parallel to the interface. The diethylamino group interacted with water molecules and was preferentially attracted to the interface (or repelled from the heptane phase because of its poor solubility). This must be the reason why it could react with Ni^{2+} ion with almost the same rate constant in the aqueous solution. On the other hand, the result of MD simulation in toluene/water system showed that 5-Br-PADAP was still located near the interface, but completely surrounded by toluene molecules. It can be imagined that the 5-Br-PADAP molecule at the interface can react with a Ni^2 ion in the aqueous phase, but the probability is greatly reduced because of the solvation by toluene molecules. Thus, the experimentally observed solvent effects in the interfacial complexation rate could be explained from the MD simulations of the microenvironment of the interfacially adsorbed 5-Br-PADAP. As for the extraction mechanism of Ni(II)-Hpan-PADA, the key processes were no adsorptivity of PADA (Fig. 3) and strong adsorptivity of $Ni(pada)^{2+}$. MD simulations could explain also these difference very satisfactorily.

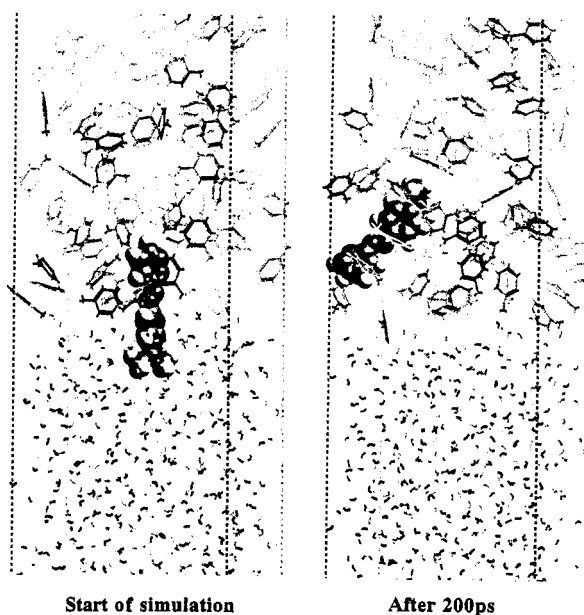**Start of simulation**   **After 200ps**

Fig. 3 PADA is not restricted at the toluene/water interface.

Complexation mechanism of pyridylazo-ligands

Chelate formation rate constants of Ni^{2+} aqua ion are usually in the order of 10^4 $M^{-1}s^{-1}$. However, the rate constant for reaction between Ni^{2+} and 5-Br-PADAP or Hpan is in the order of 10^2 $M^{-1}s^{-1}$, a hundred times smaller than the exchange rate of the hydrated water. The slow reaction rate of pyridylazo-ligands was correlated with the strength of intramolecular hydrogen bonding of -OH····N- which was correlated with pK_a. Therefore, the rate-determining step was thought to be a ring-closure process.

CONCLUSION

The kinetic mechanism of the extraction of Ni(II) with 2-hydroxyoximes and pyridylazo compounds were elucidated from the experimental measurements using the high-speed stirring method. MD simulation can show that:

(i) an adsorbed ligand or complex could take a favorable orientation at the interface;

(ii) the location of the adsorbed ligand at the interfacial region depended on the nature of organic solvent;

(iii) the location of the coordinating atom in the adsorbed ligand determined its reactivity with metal ion in the aqueous phase.

In addition MD simulation can be used to estimate the adsorption energy, or stabilization energy from solute-solvent interaction energies at the interface and in the bulk phases.

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