Continuous Electrochemically Modulated Complexation Separations Process

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A continuous electrochemically modulated complexation (EMC) process was devised to extract and concentrate a class of heterocyclic nitrogen compounds. This design is composed of flow-through electrolysis cells for redox modulation and cycling of the complexing agent and hollow-fiber membrane modules for phase contacting. The extent of both extraction and concentration was found to depend mainly on the magnitude of the distribution coefficients for both steps. Experimental results and modeling of this continuous EMC process are reported, as well as potential applications for this process for other separations.

Introduction

Recently, the National Research Council (NRC, 1987) released a report which targeted high-priority research needs and opportunities in chemical separations. The report concluded that in the future separation processes will be critical in such areas as the environmental remediation. The NRC report also stated that electrochemical-driven separations represent a promising research area that has received relatively little attention. Most of the reports in this area are studies of rate processes. The removal of carbon dioxide has been addressed due to its industrial and biological importance (Kimura et al., 1973; Barrer et al., 1980; Gros et al., 1980; Kang and Winnick, 1985). Winnick and coworkers have investigated the case of an electrochemical cell that concentrates sulfur dioxide and carbon dioxide (Lin and Winnick, 1974; Winnick et al., 1974; Townley and Winnick, 1981, 1983).

In earlier publications (Koval et al., 1990; Jemaa et al., 1991, 1992), we have reported a cyclical process that allows certain heterocyclic nitrogen compounds to be removed selectively from a feed hydrocarbon phase and to be concentrated subsequently in a receiving hydrocarbon phase. The process involves reactive extraction of nitrogen heterocycles into an aqueous phase that contains a water-soluble iron porphyrin, FeTPPS. The FeTPPS acts as a complexing agent for the heterocycles, and the magnitude of the FeTPPS-heterocycle interaction can be modulated by electrochemical cycling between the Fe(II) and Fe(III) redox states. The overall process is referred to as electrochemically modulated complexation (EMC). When operated as an equilibrium-stage process, EMC has been analyzed from both a mass balance and energy point of view.

In previous research on electrochemical separation processes, there is no indication of how an EMC-type process might be operated continuously, even though a continuous process is industrially attractive. In this work, we report the design of a continuous EMC process and discuss its capabilities. The process employs hollow-fiber membrane modules for phase contacting and flow-through electrolysis cells for redox cycling of the complexing agent. The process is analyzed in terms of the mass-transfer resistance of each of these elements. The main objective of this work is to provide the fundamental basis for a continuous process that can be employed for the selective separation and concentration of solutes, presuming that the appropriate complexing agent is available.

Process Description

A pictorial diagram of the electrochemically modulated complexation process is shown in Figure 1. The complexing agent, dissolved in the contacting (aqueous) phase, is electrolyzed to its high solute affinity redox state in step 1. The solute is extracted from a feed (hydrocarbon) phase by partitioning into the contacting phase via reaction with the complexing agent in step 2. In step 3, the complexing agent is electrolyzed to its

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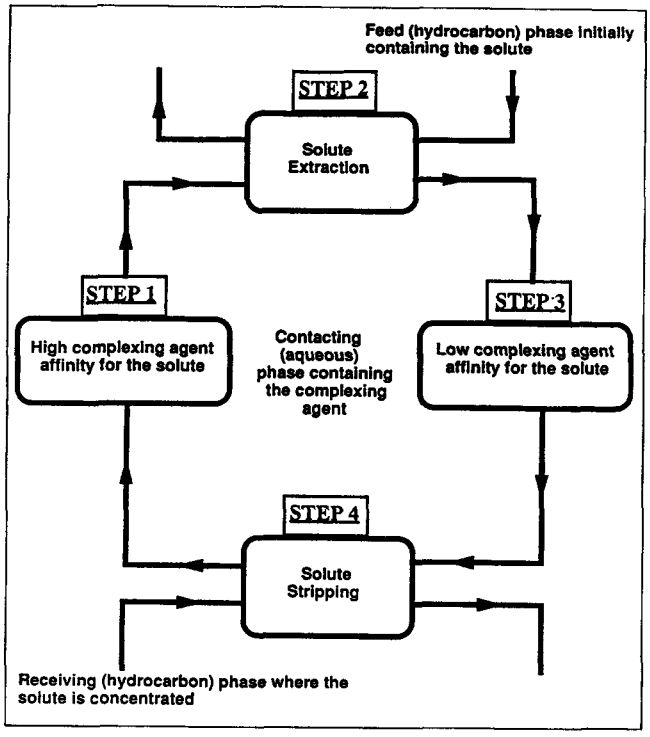


Figure 1. Electrochemically modulated complexation process for the selective extraction and subsequent concentration of a solute.

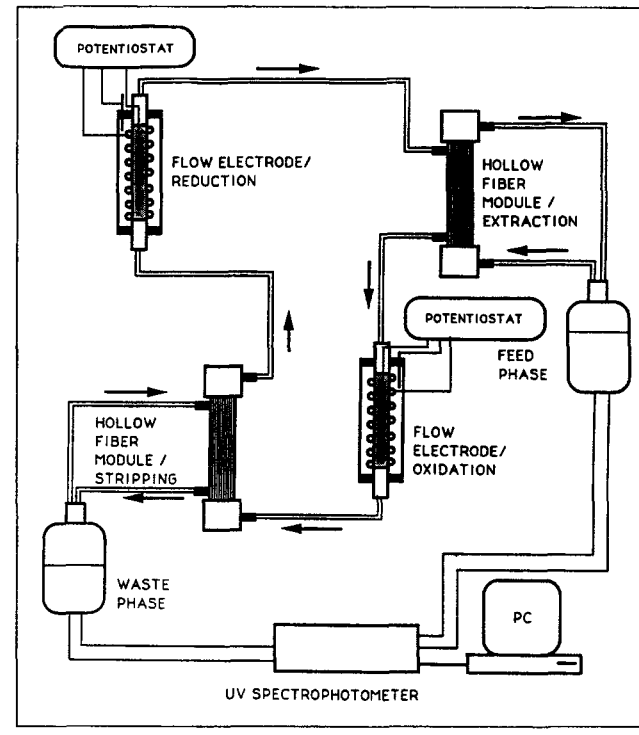


Figure 2. Experimental apparatus.

low solute affinity redox state. The solute partitions into the receiving phase upon contact with the aqueous solution in step 4. The contacting phase is then recycled.

In an EMC process, the complexing agent has to meet four requirements:

1. The complexing agent must be soluble only in the contacting (aqueous) phase to prevent any loss.
2. The complexing agent must have a solute binding site and undergo a chemically reversible redox cycle in the presence and absence of the solute.
3. A considerable difference must exist in the affinity of the solute for the complexing agent in its two oxidation states.
4. The kinetics of the solute-complexing agent reaction should be sufficiently rapid with respect to interfacial mass transfer.

Water soluble derivatives of metalloporphyrins satisfy all the above criteria (Walker, 1973; Smith, 1975; Ellis et al., 1980, Lever and Gray, 1983; Yamamoto, 1986). Specifically, the iron porphyrin was used as a complexing agent in this experimental work. Information related to its binding mechanism with nitrogen compounds is available elsewhere (Drew, 1989; Drew et al., 1990).

Two partition coefficients (K_r and K_o) play an important role in the process. They are defined as the ratios of the total solute concentration in the contacting to that in the feed (and receiving phase), when the carrier is in the reduced (or oxidized state), respectively.

A complete diagram for the experimental apparatus is shown in Figure 2. The complexing agent, dissolved in the contacting (aqueous) phase, passes through a porous electrode to produce the Fe(II) form with a high affinity for the solute. The aqueous phase is then contacted with the feed phase in a hollow-fiber contactor to extract solute. The contacting phase is next passed through a second flow electrode to produce the Fe(III) (low solute affinity form of the complexing agent). The receiving phase, where solute will be concentrated, is subsequently contacted with the aqueous phase in a second hollow-fiber contactor.

Experimental Setup

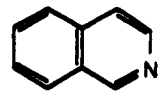
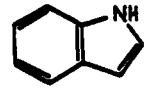
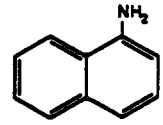
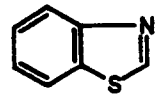
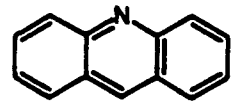
Chemicals

The complexing agent was synthesized as the sodium salt of iron(III)tetraphenyl(*p*-sulfonato)porphyrin, $Na_3Fe(III)TPPS$, as described elsewhere (Fleischer et al., 1971; Drew, 1989). The solvent 2,2,4-trimethylpentane (isooctane), and the solutes isoquinoline, acridine, indole, 2-aminonaphthalene, and benzothiazole (Aldrich Chemical Company, Inc.) were used as received. Structures of the solutes are contained in Table 1. Isooctane was the organic feed and receiving phase. These solutes are model compounds that represent various classes of compounds found in coal and crude oil. Their choice was based on availability and safety. The complexing agent was dissolved in an aqueous solution of 0.1-M boric acid (Sigma Chemical Company) and 0.95-M sodium perchlorate (Fisher Scientific). The pH was adjusted to 9.2. At these conditions, the solution ionic strength was 1.0 M.

Electrode construction

One important aspect of this work is the design of the electrochemical cells. Flow through a porous electrode is one type

Table 1. Heterocyclic Nitrogen Compounds Employed in This Work

Compound	Structure
Isoquinoline	
Indole	
2-Aminonaphthalene	
Acridine	
Benzothiazole	

of cell for electrochemical conversion. The electrode behaves as a packed-bed chemical reactor where the reactant is supplied at one end by bulk convective flow and exits at the other end. Different electrochemical cell designs and various analyses concerning flow-through porous electrode are presented elsewhere (Alkire and Gracon, 1975; Sioda, 1972). The working electrodes used in this study were composed of vitreous glass carbon flakes (Electrosynthesis Co., Inc.) placed between two nichrome screens that acted as supports. The carbon flakes were contained in a plastic tubing having an internal diameter of 1.0 cm and a thickness of 0.6 mm. A nichrome wire was embedded in the porous electrode to insure good electrical contact. Holes of approximately 1 mm diameter were drilled around the plastic tubing, and a porous membrane (M.W. cutoff = 12000–14000, Fisher Scientific) was wrapped around the outer tubing surface. This membrane allowed ionic conduction between the outer and inner solution. The counter-electrode was a stainless-steel screen wrapped around the outer surface of the plastic tubing. Electrical contact was made directly to the metal screen. The potentials were measured against a silver nitrate electrode. The electrolysis potentials were applied with the aid of potentiostats manufactured in-house from a standard design.

Hollow-fiber modules

Hollow-fiber modules are promising contactors for a variety of purposes. They present some advantages over conventional extraction units such as the freedom to vary the individual phase flow rates without concern for flooding, no density difference requirements for either solution, and most important, a large surface area per unit volume.

The hollow-fiber modules employed during the course of this study were obtained from Hoechst Celanese. These membranes are hydrophobic and are constructed of polypropylene. Each module is composed of 2,500 fibers placed in a Teflon tube which is 2.5 cm in diameter and 20.3 cm long. These fibers have an internal diameter of 413 micron and a wall thickness of 30 micron. The pores in the membrane are approximately 0.03 micron in diameter. To change the hydrophobicity of the fibers, the membrane is wetted with ethanol and rinsed with distilled water (Duharon and Cussler, 1988).

Equipment

The concentrations of individual solutes were measured using a Hewlett-Packard HP8452A diode array UV-Visible spectrophotometer run with HP89531A MS-DOS UV/VIS operating software on a Zenith Z286 PC. For experiments involving a mixture of solutes, a Hewlett-Packard HP5890 gas chromatograph was employed to separate the solutes and measure their concentrations.

Electrode Performance

The reduction and oxidation of the complexing agent occur in two different flow electrodes. The amount of complexing agent reduced or oxidized is a function of different parameters such as flow rate and electrode length. Further analysis of flow through a porous electrode is provided elsewhere (Sioda, 1973; Alkire and Gracon, 1978). Figure 3 shows the measured cell current vs. the aqueous-phase flow rate for different electrode lengths. The solid line in the graph indicates 100% reduction (or oxidation). At low flow rates, all the reactants that entered the reactor underwent electrochemical reaction. Deviation from the solid line was observed as flow rates increased. This deviation is due to the fact that the residence time was not large enough for all of the solute to reach the surface of the carbon and react. As indicated by Figure 3, an increase in the electrode length causes the electrolysis to approach 100% efficiency, since the residence time and the surface area of the electrochemical reactor have increased. In this work, flow rates of less than 25 mL/min were usually used so that the complexing agent was kept in the reduced form for the extraction step or oxidized form for the stripping step.

Modeling

The mass-transfer mechanism in each hollow-fiber module

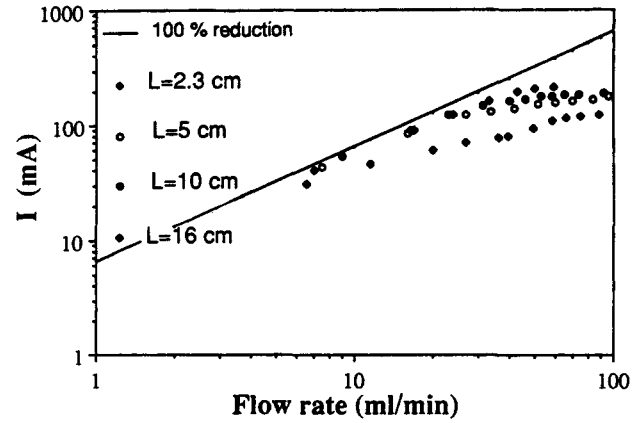


Figure 3. Limiting currents observed in porous electrodes as a function of flow rates for different electrode lengths.

is a function of three resistances. One of these resistances is due to the flow outside the fibers, the second is due to the membrane itself, and the third resistance is due to the solution flowing inside the fibers.

In the hydrophilic module, where the extraction of solutes from the feed phase takes place, the organic phase flows inside the fibers while the aqueous phase loaded with the complexing agent flows outside the fibers. The nitrogen compounds diffuse from the bulk feed phase to the membrane wall. Secondly, they dissolve and react with the complexing agent in the contacting phase filling the pores of the fibers before crossing the thickness of the membrane. Finally, they diffuse from the outer wall to the bulk of the aqueous phase.

In the hydrophobic module, stripping of the solutes occurs. The aqueous phase flows inside the fiber, while the organic solution flows on the shell side. The nitrogen compounds diffuse from the bulk aqueous phase, through the membrane, and to the bulk organic receiving phase.

The two overall mass-transfer coefficients for each hollow-fiber module, defined as K_{or} during the extraction step (based on the organic phase) and K_w during the release step (based on the aqueous phase), are employed in this model. According to Prasad and Sirkar, K_{or} for a hydrophilic membrane with an organic phase flowing inside the fibers can be described by the following expression (Prasad and Sirkar, 1987):

$$\frac{1}{K_{or}} = d_i\left[\frac{1}{d_i k_{of}} + \frac{1}{m d_{lm} k_m} + \frac{1}{m d_o k_{wf}}\right] \tag{1}$$

For a hydrophobic membrane, where an aqueous phase flows inside the fibers, K_w is written as:

$$\frac{1}{K_w} = d_i\left[\frac{m}{d_o k_{of}} + \frac{m}{d_{lm} k_m} + \frac{1}{d_i k_{wf}}\right] \tag{2}$$

In Eqs. 1 and 2, m is the distribution coefficient when no complexing agent is present in the system. It is defined in the same manner as K_r and K_o. If a complexing agent is present in the system, then m is replaced by K_r in Eq. 1 and K_o in Eq. 2. The constants d_i, d_o, and d_{lm} are the inside, outside, and the log mean fiber diameters, respectively. The variables k_{of}, k_{wf}, and k_m are the organic film, the aqueous film, and the membrane mass-transfer coefficients, respectively. These coefficients have been correlated as a function of Sherwood, Schmidt and Reynolds number. Again, according to Prasad and Sirkar, the mass-transfer coefficients inside and outside the fiber and within the membrane itself are expressed as:

$$Sh = 1.62\left(\frac{d^2 v}{lD}\right)^{1/3} \tag{3}$$

$$Sh = 5.9\left(\frac{d_e}{l}\right)\left(\frac{d_e v}{\nu}\right)^{0.6}\left(\frac{\nu}{D}\right)^{1/3} \tag{4}$$

$$k_m = \frac{D_w \epsilon_m}{h\tau} \quad \text{(hydrophilic)} \tag{5}$$

$$k_m = \frac{D_o \epsilon_m}{h\tau} \quad \text{(hydrophobic)} \tag{6}$$

where D_w and D_o are the solute diffusion coefficients in the aqueous and organic solutions. The constant ϵ is the membrane porosity, h is the thickness of the membrane, and τ is the tortuosity factor. Equations 3 and 4 were obtained by Prasad and Sirkar after conducting a series of experiments on a similar module and represent a good approximation of the mass-transfer coefficient inside and outside the fiber. These correlations are employed to compute the overall mass-transfer coefficients (K_{or} and K_w) and to develop a model capable of predicting the behavior of the system.

The method employed is general and applicable to both liquid-liquid extraction and gas absorption. Any chemical reaction effects are lumped with the mass-transfer coefficients. The main assumption in this model is that the concentrations in the feed and receiving reservoirs are changing slowly compared to those in the modules. It is valid if the reservoir volume is much larger than the extraction module volume, which is the case here. A mass balance on each organic reservoir and on each hollow-fiber module yield the following set of equations:

$$\frac{C_f^l - C_f^{l*}}{C_f^0 - C_f^{0*}} = \exp\left[\frac{4K_{or}l}{dv_f}\left(1 - \frac{Q_f}{K_r Q_a}\right)\right] \tag{7}$$

$$\frac{C_r^l - C_r^{l*}}{C_r^0 - C_r^{0*}} = \exp\left[\frac{4K_w l}{dv_{aq}}\left(1 - \frac{K_o Q_a}{Q_r}\right)\right] \tag{8}$$

$$Q_a[C_a^l - C_a^0(t-a)] = Q_f(C_f^l - C_f^0) \tag{9}$$

$$Q_a[C_a^l(t-a) - C_a^0] = Q_r(C_r^l - C_r^0) \tag{10}$$

$$V_f\frac{dC_f^l}{dt} = Q_f(C_f^0 - C_f^l) \tag{11}$$

$$V_r\frac{dC_r^0}{dt} = Q_r(C_r^l - C_r^0) \tag{12}$$

The subscripts f, a, and r stand for feed, aqueous and receiving phases, respectively. The superscripts 0 and 1 stand for the entrance and exit of the hollow-fiber modules. $C^*_{f(r)}$ is the feed (receiving)-phase concentration which would be in equilibrium with the aqueous-phase concentration. The velocities inside the fibers of the feed and aqueous phases are denoted by v_f and v_{aq}, respectively. V_f and V_r are the feed- and receiving-phase reservoir volumes, respectively. The constant a is a time lag which is the time required for the aqueous phase to reach the second hollow-fiber module after exiting from the previous one.

A knowledge of the magnitude of the distribution coefficients is mandatory to evaluate the overall mass transfer parameters. The individual mass-transfer coefficients were calculated using the correlations presented earlier. The membrane characteristics were provided by Hoechst Celanese. This set of equations was solved numerically for the different concentrations as a function of time. The main variables of interest are the solute concentrations in the organic phase reservoirs. The same approach and model was used to predict the behavior of a mixture of compounds. The effect of different parameters was also investigated.

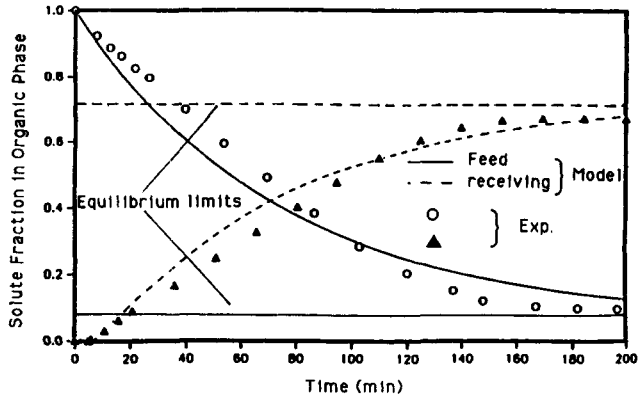


Figure 4. Extraction and concentration of isoquinoline.

$K_r = 1.90$, $K_o = 0.23$, $Q_a = 16.5$ mL/min, $Q_f = 19.0$ mL/min, and $Q_r = 19.0$ mL/min.

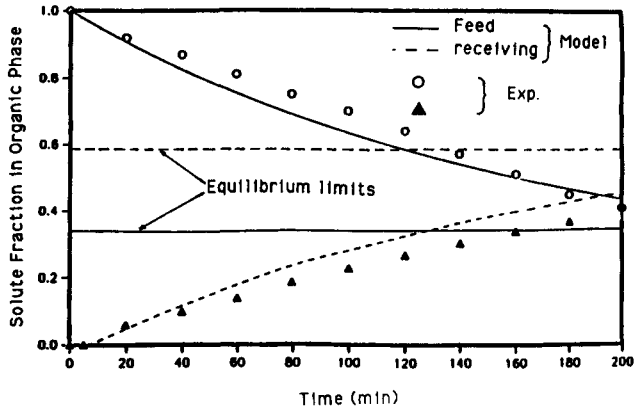


Figure 6. Extraction and concentration of acridine.

$K_r = 0.47$, $K_o = 0.20$, $Q_a = 16.5$ mL/min, $Q_f = 19.0$ mL/min, and $Q_r = 19.0$ mL/min.

Results and Discussion

Extraction and concentration of individual compounds

The extraction and concentration of the nitrogen compounds were performed according to the procedure described earlier. Figures 4 through 8 show the experimental results for isoquinoline, indole, acridine, benzothiazole, and 2-aminonaphthalene. In all these runs, the feed-, aqueous- and receiving-phase volumes were set to 225 mL. The values of the distribution coefficients were measured at the same solute and complexing agent concentrations according to the procedure described by Drew (1989).

For these solutes, the extraction and concentration steps were successful to various degrees. Isoquinoline, which has the largest distribution coefficient K_r, has a high fraction removal and a high fraction concentrated in the receiving phase. The 2-aminonaphthalene has the lowest K_r at these experimental conditions and shows poor results in the extraction and concentration steps. Indole, acridine, and benzothiazole have intermediate distribution coefficients between isoquinoline and 2-aminonaphthalene and show intermediate results in both steps.

The solute diffusion coefficients in water and in the isooctane phase are comparable. The different results shown in the previous figures are due mainly to the difference in the distribution coefficient magnitudes (K_r and K_o). The magnitude of these coefficients depend on the solute concentration in feed and complexing agent concentration in the contacting phase (besides physical and chemical solubilities). A higher value of K_r means more solute is extracted. As the value of K_o decreases, more solute is concentrated in the organic receiving phase. Performing these experiments at different conditions (different solute and carrier concentrations) could yield different results.

In an equilibrium stage analysis (Jemaa et al., 1991), analytical expressions for the limits of this separation process, based on the magnitude of the distribution coefficients K_r and K_o, were derived. The maximum fraction of solute that can be removed from the feed phase (F_r) and the maximum fraction that can be concentrated in the receiving phase (F_c) are expressed, respectively, as:

$$F_r = \frac{1 + \frac{V_r}{V_a}\frac{1}{K_o}}{1 + \frac{V_r}{V_a}\frac{1}{K_o} + \frac{V_f}{V_a}\frac{1}{K_r}} \tag{13}$$

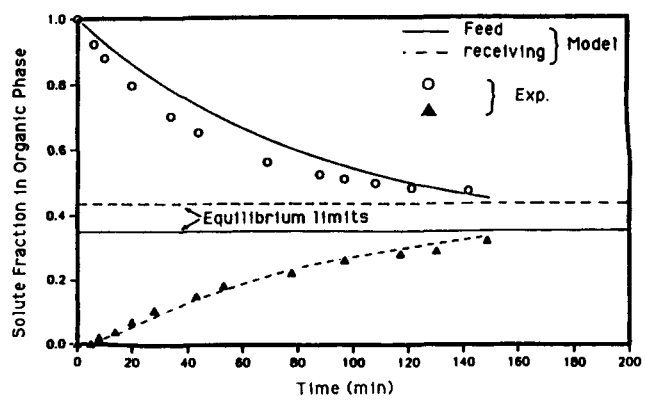


Figure 5. Extraction and concentration of indole.

$K_r = 0.42$, $K_o = 0.42$, $Q_a = 25.0$ mL/min, $Q_f = 20.0$ mL/min, and $Q_r = 19.5$ mL/min.

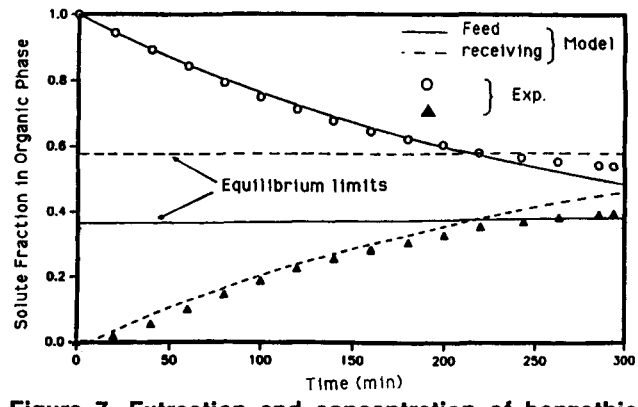


Figure 7. Extraction and concentration of benzothiazole.

$K_r = 0.35$, $K_o = 0.15$, $Q_a = 16.0$ mL/min, $Q_f = 19.0$ mL/min, and $Q_r = 20.0$ mL/min.

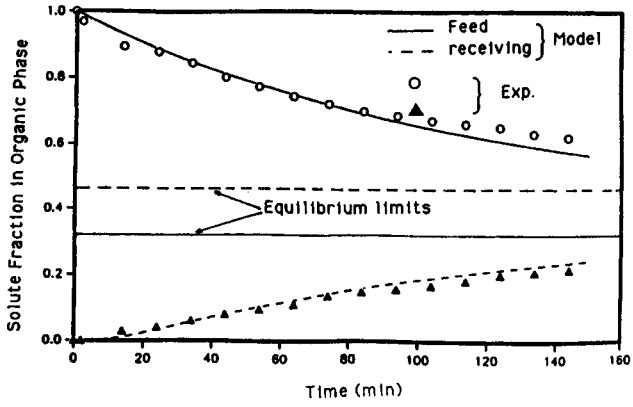


Figure 8. Extraction and concentration of 2-aminonaphthalene.

$K_r = 0.47$, $K_o = 0.40$, $Q_a = 24.5$ mL/min, $Q_f = 19.5$ mL/min, and $Q_r = 19.5$ mL/min.

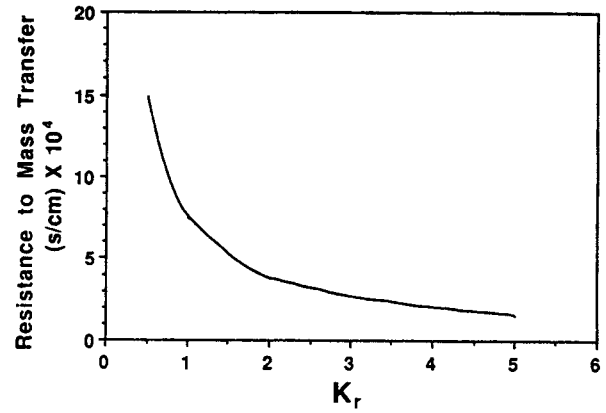


Figure 9. Dependency of the overall mass-transfer resistance in the extraction module on K_r.

$$F_c = \frac{\frac{V_r}{V_a}\frac{1}{K_o}}{1 + \frac{V_r}{V_a}\frac{1}{K_o} + \frac{V_f}{V_a}\frac{1}{K_r}} \tag{14}$$

V_a is the volume of the aqueous phase. In Figures 4–8 these limits are obeyed. In the continuous process, when t (time) is large the fraction extracted from feed approaches F_r and the fraction concentrated in the waste tends to F_c. The two maximum fractions are obtained after assuming an infinite number of stages. A large value of K_r is important for reaching these limits in relatively short times. These limits are shown on the figures as horizontal lines (the solid line indicates $1 - F_r$ which is the fraction in the feed phase and the dashed line shows F_c). Isoquinoline was the only compound to reach these limits during the experimental time. The other solutes, having a lower value of K_r, require more time to approach these limits. Benzothiazole has the lowest K_o value, and hence only a very small amount remained in the contacting phase (most of what has been extracted from the feed phase was concentrated in the receiving phase: at the end of the run about 43% was removed and about 38% was concentrated).

Dependency on distribution coefficients and flow rates

In previous analysis, investigators have varied the different parameters in Eqs. 1 and 2 to see the effect on the mass-transfer coefficient (such as velocities and membrane thickness). However, the ability to vary m (which corresponds to K_r or K_o) without changing the solvent has not been investigated. In this work, the distribution coefficient of a particular solute can be altered.

The overall mass-transfer coefficient in both hollow-fiber modules depends highly on the values of the distribution coefficients K_r and K_o. Figures 9 and 10 demonstrate this behavior. In each figure, there are two limits. As K_r approaches zero, the overall resistance increases tremendously preventing the solute from dissolving in the aqueous phase. As K_r increases, the curve approaches a constant value equal to the magnitude of the organic film resistance. Figure 10 shows that at one end of the curve, the aqueous-phase resistance is dominant (low K_o), while at the other end of the organic-phase resistance is governing (large K_o).

The solutes employed in these experiments have comparable diffusion coefficients, hence the results in Figures 9 and 10 are applicable to any of these solutes if the magnitude of K_r and K_o are within that range. The larger the value of K_r, the lower the resistance in the extraction module and the lower the value of K_o, the lower the resistance in the stripping module. The same observation was noticed during the equilibrium-stage analysis of this electrochemical process. These distribution coefficients depend highly on the reaction equilibrium constants which are responsible for the rapid uptake and release steps of the nitrogen compounds. An increase in the complexing agent concentration increases the distribution coefficients, mainly K_r, which reflects the high complexing agent affinity for the solute. However, K_o undergoes a small increase in magnitude (low complexing agent affinity toward the solute). As an overall result, the extraction and stripping steps are accelerated. The amount concentrated in the receiving phase would be larger at any given time. At a constant aqueous-phase flow rate and at variable K_r and K_o, the extraction and concentration of isoquinoline and 2-aminonaphthalene are presented in Figures 11 and 12, respectively. The larger fraction removed is due to the increase in K_r. The larger amount concentrated in the receiving phase is not due to an increase in K_o, but as result of extracting more solute from the feed phase.

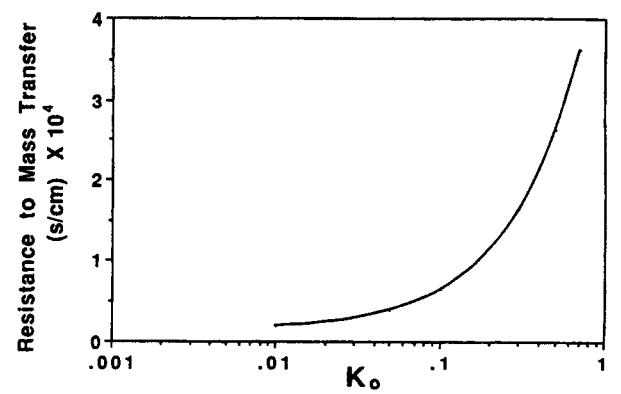


Figure 10. Dependency of the overall mass-transfer resistance in the extraction module on K_o.

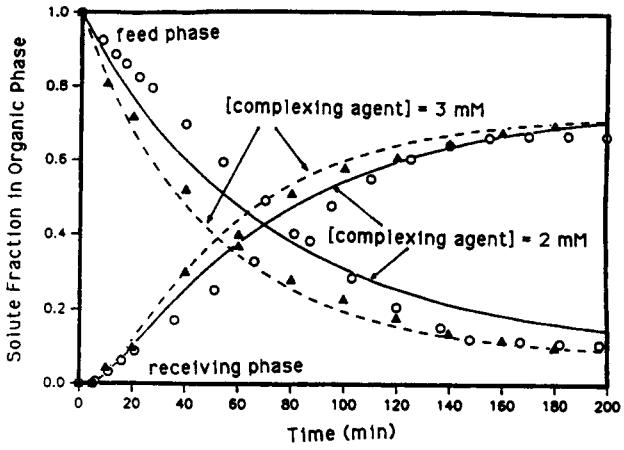


Figure 11. Extraction and concentration of isoquinoline at two different concentrations of FeTPPS.

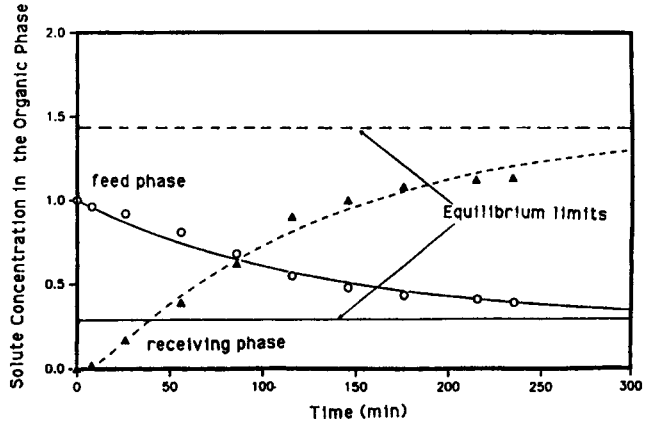


Figure 13. Extraction and concentration of isoquinoline $V_r = 3/8\ V_f$.

Symbols are experimental data and lines are model predictions.

Varying the aqueous-phase flow rate normally increases the mass-transfer coefficient. In this process, an increase in the contacting-phase flow rate can lower the magnitude of the distribution coefficient K_r, if the electrolysis becomes much less than 100% efficient (Figure 3). The overall effect cannot be predicted. One way of increasing K_{or} without altering K_r is to lengthen the porous electrodes. In this work, the electrode length was kept constant, and this restricted the range of the aqueous-phase flow rate.

Figures 13 and 14 show some additional results for isoquinoline. In these experiments, the volume of the receiving phase was reduced to demonstrate that the solute can be concentrated in a small volume. In Figure 13, starting with a 400-mL feed phase having a concentration of 1.0 mM of isoquinoline, a concentration of 1.15 mM in a 150-mL receiving phase was reached. The distribution coefficients for this case are $K_r = 1.17$ and $K_o = 0.22$. In Figure 14, isoquinoline was concentrated in much smaller receiving phase (100 mL or one fourth of the feed volume). The concentration of iron porphyrin was increased to yield $K_r = 3.26$ and $K_o = 0.35$. As long as K_r is made larger (increasing complexing agent concentration), a further reduction in volume is possible. This reduction of volume is important so that handling and further processing, if any, become easier to accomplish.

For this EMC process, the electrolysis step is certainly not the limiting step. The amount of the complexing agent reduced or oxidized was constant during the course of each experiment. Mass transfer ceased mainly because of the saturation of the receiving phase with the solute. As a result, the contacting phase is equilibrated with the receiving phase, and hence all the phases are equilibrated. To further reduce the solute level in the feed phase, a larger complexing agent concentration is needed (this may require searching for a more soluble complexing agent in the contacting phase). For the extraction and concentration of individual compounds, the model was able to predict the behavior of this EMC process.

Experiments and Analysis of a Mixture

The extraction and concentration of a mixture of 2-aminonaphthalene, indole, and isoquinoline were performed. These compounds span a wide range of distribution coefficients. The experiment conditions were: $Q_a = 25.0$ mL/min, $Q_f = 40.0$ mL/

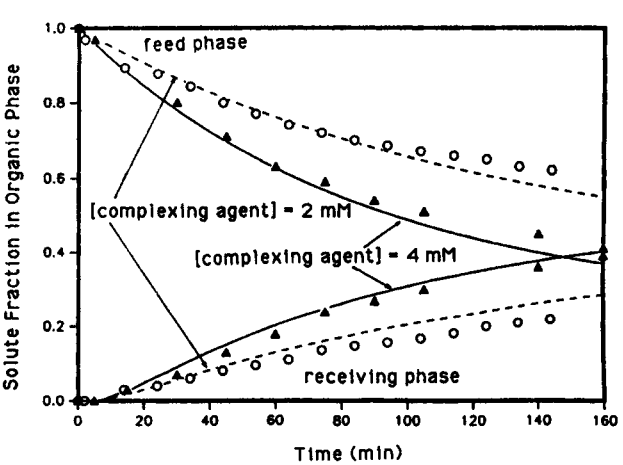


Figure 12. Extraction and concentration of 2-aminonaphthalene at two different concentrations of FeTPPS.

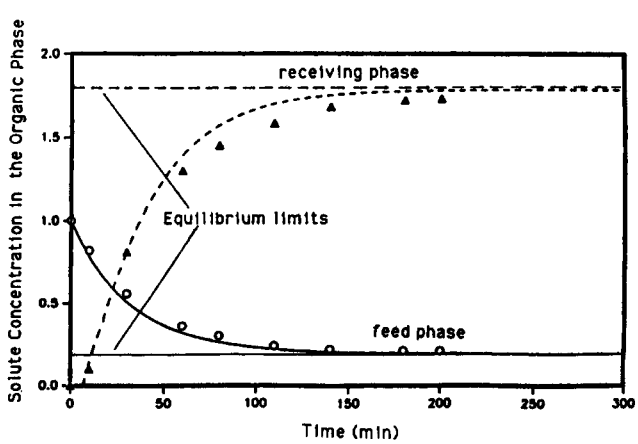


Figure 14. Extraction and concentration of isoquinoline $V_r = 1/4\ V_f$.

Symbols are experimental data and lines are model predictions.

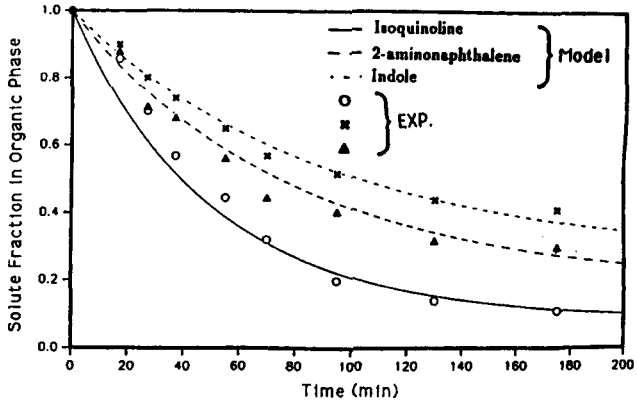


Figure 15. Fraction of solute in the feed phase for the extraction of a mixture of nitrogen compounds.

Symbols are experimental data and lines are model predictions.

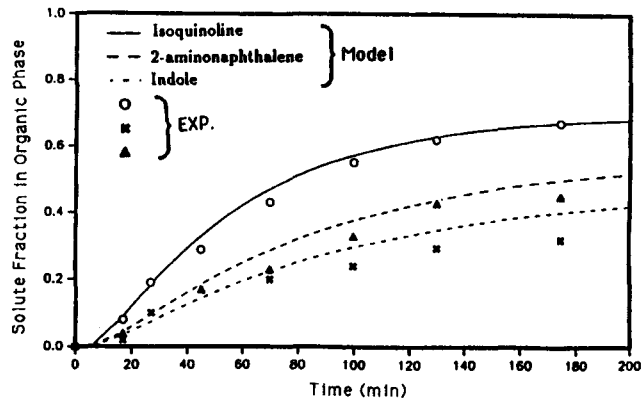


Figure 16. Fraction of solute in the receiving phase for the extraction of a mixture of nitrogen compounds.

Symbols are experimental data and lines are model predictions.

min, $Q_r = 40.0$ mL/min, [FeTPPS] = 5.0 mM, [Indole] = 0.48 mM, [Isoquinoline] = 0.51 mM, and [2-aminonaphthalene] = 0.45 mM.

The distribution coefficients in a mixture for these three compounds were measured experimentally. Aqueous and organic phases having the same concentrations as above were equilibrated (for both the reduced and oxidized forms of the iron porphyrin) and a sample of the organic phase was withdrawn. The concentration of the nitrogen compounds was determined. The distribution coefficients calculated were used to model the experimental results. Under these conditions, isoquinoline has the highest affinity to bind with the iron porphyrin. Indole has the lowest distribution coefficient K_r and will be the least extracted and concentrated. The 2-aminonaphthalene has intermediate K_r and is expected to exhibit behavior between the other two solutes.

Figures 15 and 16 show the results of these experiments. The amounts extracted and concentrated in the receiving phase are consistent with the magnitudes of the distribution coefficients. These compounds have similar physical solubilities and diffusion coefficients. The only factor responsible for the results in Figures 15 and 16 is the chemical solubilities due to the complexing agent.

Conclusion and Potential Applications

A continuous, electrochemically modulated complexation process for the removal and concentration of heterocyclic compounds containing nitrogen has been investigated. Such a process is important since it offers a new separation scheme, and the removal of such solutes is a critical environmental concern. A mass operating agent has been employed to accomplish this purpose. It is regenerated electrochemically with the aid of an electrode placed in the system.

The extraction of some organonitrogen compounds have been demonstrated successfully. These compounds have different values of distribution coefficients, K_r and K_o, and the extent of their extraction and concentration in the receiving phase behaved accordingly. A large value of K_r yielded large fraction extracted, and a small value of K_o gave high fraction concentrated in the waste phase. The difference of the distribution coefficient from one solute to another is due mainly to the chemical solubility. These coefficients can be altered to improve the separation by increasing the complexing agent concentration in the system. A model has been developed which successfully predicts single-component and mixture results.

The importance of this continuous, electrochemically modulated complexation process does not lie in the removal and concentration of heterocyclic nitrogen compounds; instead, the process provides a novel separation technique that can potentially be applied to segregate and concentrate other solutes. The primary task involved in applying the process to other systems is the search for a complexing agent that satisfies the stated requirement. This search for a highly selective mass separating agent that satisfies the stated requirement. T' is search for a highly selective mass separating agent should be initiated from the fundamental interactions at the atomic or molecular level. This calls for the cooperation of engineers with chemists who have the ability to synthesize the required agent based on the necessary characteristics. This fruitful interaction is the foundation of a successful electrochemically modulated process.

This electrochemical process can potentially be used to transport such gases as CO_2, CO, and H_2S, once the appropriate complexing agent is found. These compounds are known to be major pollutants and/or serious industrial problems. No major modification, for a bench scale, is required to perform gas transport. Water and many waste streams contain dissolved metals such as copper, zinc, cobalt, and nickel. The reduction of their levels is often required, and it could be achieved by this electrochemically modulated process. The segregation of olefins from paraffins is another example where use of this process could be explored.

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Notation

a = time lag, s
C_a = solute concentration in the aqueous phase, mM
C_f = solute concentration in the feed phase, mM

C_r = solute concentration in the receiving phase, mM
C_x^0 = solute concentration in phase x at the entrance of the module, mM
C_x^l = solute concentration in phase x at the exit of the module, mM
d_i = fiber inside diameter, cm
d_{lm} = fiber log mean diameter, cm
d_o = fiber outside diameter, cm
D_o = solute diffusion coefficient in the organic film, cm^2/s
D_w = solute diffusion coefficient in the aqueous film, cm^2/s
h = thickness of the membrane, cm
k_m = membrane mass transfer coefficient, cm/s
K_o = distribution coefficient (when carrier is in the oxidized state)
k_{of} = organic film mass transfer coefficient, cm/s
K_{or} = overall mass transfer coefficient (based on the organic phase), cm/s
K_r = distribution coefficient (when carrier is in the reduced state)
K_w = overall mass transfer coefficient (based on the aqueous phase), cm/s
k_{wf} = aqueous film mass transfer coefficient, cm/s
l = length of the fibers, cm
m = distribution coefficient (no carrier is present)
Q_a = flow rate of the aqueous phase, cm^3/min
Q_f = flow rate of the feed phase, cm^3/min
Q_r = flow rate of the receiving phase, cm^3/min
Sh = Sherwood number
t = time, s
v_{aq} = velocity of the aqueous phase in fibers, cm/s
v_f = velocity of the feed phase in fibers, cm/s
V_a = volume of the aqueous phase, cm^3
V_f = volume of the feed phase, cm^3
V_r = volume of the receiving phase, cm^3

Greek letters

τ = membrane tortuosity factor
ϵ = membrane porosity
ν = kinematic viscosity, cm^2/s

Subscripts

a = aqueous phase
f = feed phase
o = organic phase
r = receiving phase

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