Electrochemically Modulated Complexation Process for Ethylene/ Ethane Separation

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An electrochemically modulated complexation (EMC) process was designed to selectively extract and concentrate ethylene from a feed-phase mixture with ethane. Unlike previous EMC processes, where the separation was based on equilibrium solubility differences, this separation was based on differences in the rate of complexing with copper(I) solution between the two gases. The EMC process employed flowthrough electrolysis cells that electrochemically modulate aqueous-phase copper chlorides between high, copper(I), and low, copper(II), affinity states. The liquid phase in the high affinity form contracts a feed gas phase in a hollow-fiber membrane module for selective extraction and contacts the receiving gas phase in the low affinity form for concentration. Experimental results and modeling of the process are reported.

Introduction

Separation and concentration of gases into individual components is an important issue for the chemical industry. Any separation process divides a feed stream into at least two products with different compositions. Conventional mass-transfer techniques typically use differences in the physical properties of the gases to be separated, such as vapor pressure or physical solubility. These methods are often energy-intensive in terms of heat input duties and solvent recovery.

The National Research Council (NRC, 1987) targeted high-priority research needs and opportunities in chemical separations. Their report stated that the development of techniques that use mass-separating agents or external fields to selectively remove solutes from a mixture was a promising area of research. In addition, they recommended processes that use electrical energy because of the fact that conversion of electrical energy to chemical energy is quite efficient. Processes that exploit this approach can be used for various chemical separations. Ward (1970) first demonstrated that by electrochemically cycling Fe(II) and Fe(III) within a liquid membrane, nitrogen oxide transport could be improved. Winnick (1990) has shown that an electric field can replace a concentration gradient in some separations. Jenna et al. (1993) designed a continuous process to concentrate organonitrogen compounds by controlling the oxidation state of iron metalloporphyrins in aqueous solution. Terry et al. (1995) extended this process to gas separations by using a copper chloride complexing agent in aqueous solution to selectively separate and concentrate carbon monoxide from a feed-phase mixture with nitrogen.

One gas separation problem that has received considerable attention is that of separating unsaturated aliphatic hydrocarbons, such as olefins, from their corresponding saturated paraffins in cracked-petroleum refinery gases (Long, 1972). Of particular interest is the separation of ethylene from its mixture with ethane and of butylene or butadiene from their mixture with butane. The similarities in boiling points and other physical properties renders these separations both difficult and energy intensive. Many processes have been used

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for such separations, including extraction, distillation, and complex formation. However, difficulties exist in these systems with respect to stability issues, solvent requirements, and energy inputs. There exists, then, the need for a separations method that has high olefin complexing capacity, adequate stability, and reasonable material and energy usage.

This research presents an electrochemically modulated complexation process to selectively separate and concentrate ethylene from a feed mixture with ethane. Unlike the carbon monoxide electrochemically modulated complexation (EMC) study, where the separation was due to equilibrium solubility differences in copper(I) solution, this separation was found to be based on a significant difference in forward reaction rates between the two gases for complexing with copper(I). In this article, we report a continuous electrochemical process for regeneration of a copper chloride mass-separating agent. The process employs hollow-fiber membrane modules for phase contacting and flowthrough electrolysis cells for redox cycling of the mass-separating agent. The system is analyzed in terms of the driving forces for separation and concentration. A copper(I,II)/aqueous HCl/KCl complexing system is used to selectively separate and concentrate ethylene. A mathematical model is developed to characterized mass transfer in the system.

Process Description

An electrochemically modulated complexation process is shown in Figure 1. A complexing-agent carrier, dissolved in an aqueous electrolyte phase, is electrolyzed to its high solute affinity state in step 1. This solution is contacted with the feed-gas phase to extract the solute into the electrolyte phase via reaction with the carrier in step 2. In step 3, the carrier is electrolyzed to its low affinity state. Following dissociation of the solute-carrier complex, the solute is concentrated into the receiving gas phase in step 4. The contacting phase is continuously cycled through the anode and cathode compartments of an electrolysis cell.

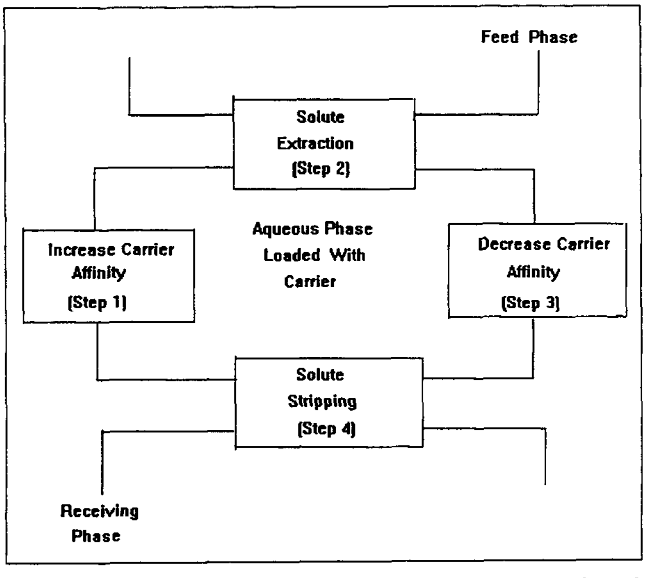

Figure 1. Continuous electrochemically modulated complexation process.

The carrier must meet several requirements for an EMC process to be successful (Terry et al., 1995). Previous work suggests that a considerable difference must exist between the carrier's affinity toward the solute of interest in its two oxidation states. Solute is transferred by dissolving and binding to the complexing agent according to the following reactions:

$$C_{\text{red}} + P \overset{K_1}{\longleftrightarrow} C_{\text{red}}P$$

$$C_{\text{ox}} + P \overset{K_2}{\longleftrightarrow} C_{\text{ox}}P$$

where C_{red} and C_{ox} are the complexing agent concentrations in the reduced and oxidized forms and P is the free solute in solution; and K_1 and K_2 are the reaction equilibrium constants. The kinetics of the reactions of the solute of interest with the complexing agent should be rapid enough to reach equilibrium in times that are short with respect to mass transfer. In addition, if the solute of interest is present in the feed as a mixture, the carrier should have no affinity for the other components of the mixture in either oxidation state.

We are investigating the use of water-soluble copper chloride ions as the complexing agent for removing ethylene gas from a feed phase and concentrating it into a receiving phase. Previous literature has shown that copper(I) will complex with the double bond in olefins, but not with their corresponding saturated alkanes (Francis, 1956). In aqueous chloride solutions, copper possesses the desirable characteristic of chemical reversibility between the cupric, Cu(II), and cuprous, Cu(I), states. The use of Cu(I) in chloride media for facilitated transport of ethylene has been reported by several groups (Smith and Quinn, 1980; Long, 1972). In this electrolyte, Cu(II) exists as a mixture of Cu^{2+}, $CuCl^{+}$, and $CuCl_2$ (McConnell and Davidson, 1950). These species have no appreciable affinity for ethylene or ethane. Because ethylene has a high binding affinity reduced Cu(I) state and low affinity oxidized Cu(II) state, modulating the oxidation state of this copper complexing agent can significantly alter the degree to which the electrolyte solution stores ethylene.

Two distribution coefficients define the electrochemically modulated complexation process. K_r is the ratio of the solute concentration in the contacting phase to that in the feed phase when the complexing agent is in the reduced state. Similarly, K_o is the ratio of the contacting phase solute concentration to the receiving phase when the complexing agent is in the oxidized state. Both K_r and K_o are functions of the chemical and physical solubilities of the solute, the complexing agent concentration, and the degree of oxidation or reduction achieved in the flow cells. In addition, unlike the previous equilibrium-based EMC separations, K_r and K_o also depend on the kinetic binding rates of the solute with the complexing agent for this kinetic-driven separation.

Experimental Studies

Chemicals

Copper(I) and copper(II) chlorides (Mallinckrodt Specialty Chemicals and Sigma Chemicals) dissolved in an aqueous solution to a concentration of 0.05 M in copper were used as the contacting solution. This solution also contained 1.0-M potassium chloride (Mallinckrodt) and 0.1-M hydrogen chloride (Mallinckrodt) as supporting electrolytes. Ethylene and ethane (Matheson Gas Products) were the feed- and receiving-phase gases.

Apparatus

A diagram of the experimental apparatus is shown in a previous publication (Terry et al., 1995). An aqueous copper(II) solution is passed through two porous carbon-flow electrodes in series to produce copper(I). Ethylene (solute) is extracted from the feed phase by binding with copper(I) via contact in a hollow fiber membrane module. The solute-rich contacting phase is then passed through the flow electrodes to produce the low affinity, Cu(II), form of the complexing agent. The dissociated solute is then concentrated in the receiving phase through contact in a second hollow-fiber membrane module.

The experimental apparatus employed contained two flowthrough electrochemical cells used in series for the reduction and oxidation of the copper complexing agent. Characterization of the cells with respect to process operating conditions was performed in prior experiments (Terry et al., 1995). In addition, rotating ring-disk electrode studies were carried out to investigate the processes occurring in the electrolysis cells. Contact between the aqueous and gas phases was carried out in hydrophobic, microporous polypropylene hollow-fiber membrane modules (Hoechst Celanese). These membrane modules offer the advantages of high contact area between the phases per unit volume and independent control of the stream flows. Mass transfer in these modules was also characterized in the prior work (Terry et al., 1995).

The concentrations of copper(II) in the aqueous solution 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 solutions, a Hewlett-Packard 5890 Series II gas chromatograph was employed with an HP 3396 Series II Integrator.

Results and Discussion

Ethylene solubility

Equilibrium solubility measurements were made of ethylene in both copper(I) and copper(II) solutions at a variety of carrier concentrations, a gas partial pressure of approximately 0.69 atm, and a temperature of approximately 33°C. These curves, shown in Figure 2, indicated that a significant difference exists between the solubilities of ethylene in copper(I) and copper(II) that should be sufficient to concentrate ethylene with an electrochemically modulated complexation process. The curves also show that increasing the copper(I) concentration resulted in a corresponding increase in ethylene solubility, while an increase in copper(II) concentration did not significantly alter ethylene solubility. Hence, increasing the complexing-agent concentration should increase the ethylene concentrating ability of the system.

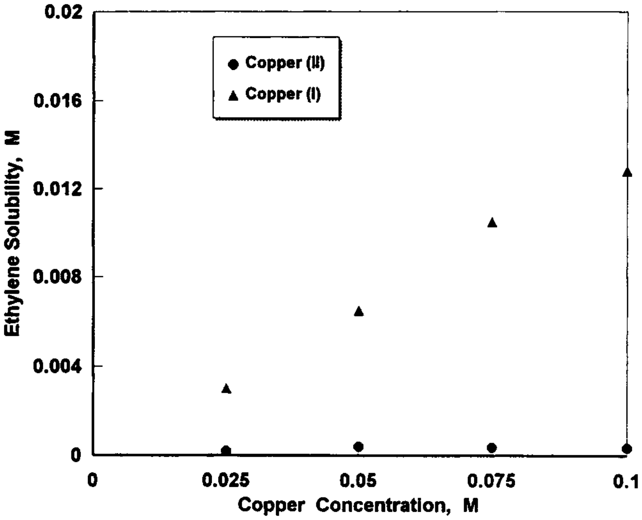

Figure 2. Solubility of ethylene in copper(I) and copper(II) aqueous solutions as a function of carrier concentration at 0.69 atm and 33°C.

EMC ethylene concentration

The extraction and concentration of pure ethylene was performed according to the procedure described in a previous publication (Terry et al., 1995). An electrochemically modulated complexation process to concentrate ethylene was performed with a carrier concentration of 0.05 M copper. The aqueous flow rate was 21 mL/min, and the resulting electrochemical efficiency was 0.93. Experimental and model results are given in Figure 3. The ratio of the feed and receiving phase distribution coefficients was estimated as 7.8. Equilibrium limits for the final feed and receiving phases can be estimated from the distribution coefficients (Jemaa et al., 1991). These limits predict the ability of the process to extract solute from the feed phase and concentrate it into the receiving phase for a given set of feed- and receiving-phase initial conditions, complexing-agent concentration, and electrochemical efficiency. A higher ratio of the high affinity distribution coefficient to the low affinity distribution coefficient

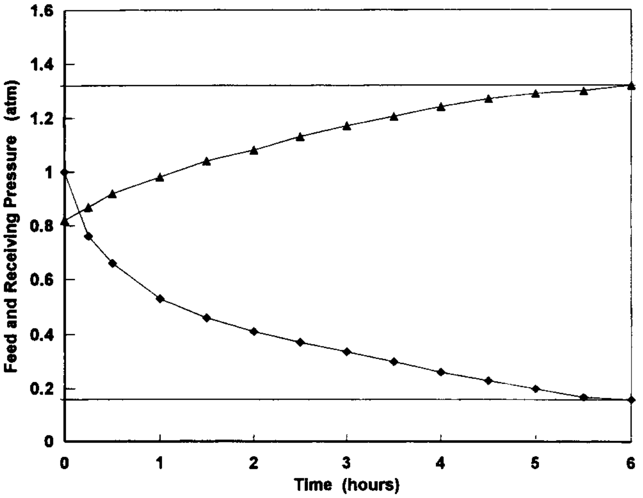

Figure 3. Electrochemically modulated complexation process concentrating ethylene when [Cu] = 0.05 M and aqueous flow rate = 21 mL/min.

Experimental data are represented by individual points and the model is denoted by solid lines.

indicates a greater ability to extract solute from the feed phase and concentrate it into the receiving phase.

The equilibrium limits of 0.17 atm in the feed phase and 1.36 atm in the receiving phase indicate that the process achieved the maximum operating capability of the equilibrium limits. These limits can be predicted for any process given knowledge of the electrochemical-cell efficiency, equilibrium constants for the binding reactions in the reduced and oxidized phases, and complexing-agent concentration (Jemaa et al., 1991). The slope of the feed and receiving pressures vs. time curves in Figure 3 represent the amount of gas that can be concentrated per unit time at a given pressure difference. The absolute value of either slope decreases as equilibrium is approached. Hence, a realistic process using this concentration technique would operate optimally at a point where the slope is high and the gas solute is being concentrated for the highest energy efficiency.

Ethylene/ethane EMC separation

Previous work reported in the literature suggests that the double bond in short-chain olefins will form a reversible chemical complex with copper(I) chloride in an aqueous solution of 1.0-M KCl and 0.1-M HCl, while their corresponding saturated paraffins will not (Long, 1972; Friedman and Stedman, 1949). Solubility measurements were taken for ethylene and ethane in 0.05-M copper(I) chloride solution (1.0-M KCl and 0.1-M HCl) as a function of gas pressure. Surprisingly, the resulting estimated Henry's law coefficients were 33,930 atm for ethylene and 81,600 atm for ethane. As can be seen from these values, there was not a significant difference between the equilibrium solubilities for the two gases. Based purely on these equilibrium solubilities, an EMC separation process would not be feasible.

Despite the indication that a reasonable ethylene/ethane separation could not be achieved based on differences in equilibrium solubility, an EMC experiment was performed. Copper carrier concentration for the experiment was 0.05 M, and the aqueous flow rate was 8.5 mL/min. The resulting electrochemical efficiency was 0.96. Results are presented in Table 1. A feed-phase mixture of 0.46-atm ethylene (52 mol %) and 0.42-atm ethane (48%) and a receiving phase of 0.83-atm ethylene (100%) were the initial conditions. After two hours of experimental time, the feed phase had been reduced to 0.046-atm ethylene (10%) and 0.40-atm ethane (90%), and the receiving phase had been concentrated to 1.12-atm ethylene (> 99%) and 0.01-atm ethane (< 1%). Thus, in spite of similar solubilities, ethylene was both selectively separated and concentrated from a mixture with ethane using the EMC process.

Table 1. Experimental Results vs. Equilibrium-Model-Predicted Results for an Electrochemically Modulated Complexation Process Separating and Concentrating Ethylene from Ethane when [Cu] = 0.05 M and Aqueous Flow Rate = 8.5 mL/min*

	Initial Cond. atm	Final Equil. Model atm	Final Exp. Results atm
Feed			
Ethylene	0.46	0.058	0.046
Ethane	0.42	0.13	0.40
Receiving			
Ethylene	0.83	1.03	1.12
Ethane	0.00	0.33	0.01

*Overall experimental time was 2 h.

Data for the system were also taken after 1.5 and 2.25 hours to trace ethylene and ethane concentrations in the feed and receiving phases as a function of time. After 1.5 hours, the feed-phase reservoir was reduced to 0.08-atm ethylene (15%) and 0.45-atm ethane (85%). The receiving reservoir was concentrated to 1.01-atm pure ethylene. Thus, if the process goal was to obtain pure ethylene, this operating time was preferable to two hours, despite the fact that less ethylene was concentrated. After 2.25 hours, the feed-phase reservoir contained 0.044-atm ethylene (12%) and 0.32-atm ethane (88%), and the receiving reservoir held 1.10-atm ethylene (96%) and 0.04-atm ethane (4%). Hence, after two hours of operation, ethane was the primary component being transferred from the feed to the receiving phase and the ethylene product purity decreased.

The equilibrium limits of the ethylene/ethane process were calculated based on a purely equilibrium model and contrasted with those obtained experimentally. Results are also presented in Table 1. The equilibrium model formulated by Jemaa et al. (1991) predicts a final feed phase of 0.058-atm ethylene in 0.13-atm ethane and a final receiving phase of 0.13-atm ethylene in 0.33-atm ethane. Thus, the receiving-phase ethylene purity predicted by the equilibrium model, 76%, is far less than that obtained experimentally, 99%, confirming that the process is not equilibrium based.

Since the success of the EMC separation contradicted results predicted by the solubility measurements, further investigation was warranted. Kinetic uptake experiments were performed by contacting fresh 0.05-M copper(I) solution with either ethylene or ethane gas in a nonrecirculated fashion. Initial uptake rates, measured as dP/dt of the gas over a 20-min period, were recorded as a function of aqueous flow rate. Flow rates ranged from 3.5 to 57 mL/min. Ethylene reached a maximum initial uptake rate of 0.013 atm/min at a flow rate of 21 mL/min, while ethane reached its maximum value of 1.7×10^{-3} atm/min at 35.5 mL/min. Both gases showed an increase in initial uptake rate with increasing flow rate until a maximum, after which the residence time of the aqueous solution in the contactors became too short for adequate contacting and the uptake rate began to decrease. Unlike the equilibrium solubilities, these initial uptake rates demonstrated a significant difference for the affinity of copper(I) solution between ethylene and ethane. This suggested that the separation process was kinetically limited, as opposed to equilibrium limited.

The initial facilitation factor, defined as the ratio of the initial uptake rate for ethylene to that of ethane at a given aqueous flow rate, was plotted as a function of flow rate for the preceding uptake experiments. Results are presented in Figure 4. The initial facilitation factor increased from 9.1 at 3.5 mL/min to a maximum value of 18.4 at 8.5 mL/min, then decreased to 6.7 at 57 mL/min. The maximum initial facilitation factor of 18.4 suggested that the electrochemically modulated complexation process could be used to separate ethylene from ethane. In addition, since this analysis showed the

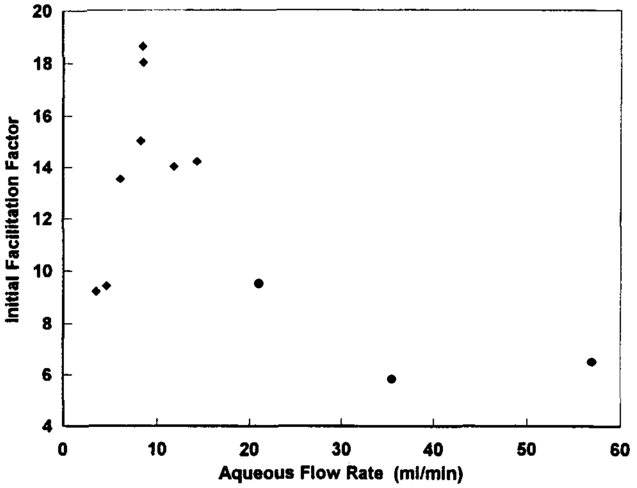

Figure 4. Initial facilitation factor for ethylene/ethane separation in 0.05-M copper(I) solution as a function of aqueous flow rate.

process to be kinetically driven, there was an optimal aqueous flow rate, or gas/liquid contact time, for the highest possible facilitation factor.

For each of the aqueous flow rates just given, the mass-transfer coefficients for both ethylene and ethane were estimated. Figure 5 contains these values. As with the initial uptake rates, the highest mass-transfer coefficient for ethylene, 1.2×10^{-3} cm/min, was achieved at approximately 21 mL/min. For ethane the peak value of 3.4×10^{-4} cm/min was reached at approximately 35.5 mL/min. The shapes of the two curves explained the maximum value of the initial facilitation factor at 8.5 mL/min in Figure 4. The ethylene mass-transfer coefficient curve rose rapidly to its maximum and, hence, was at a reasonably high value of 1.0×10^{-3} cm/min at 8.5 mL/min. Ethane, on the other hand, remained fairly constant and close to its minimum value of 1.65×10^{-4} cm/min at 8.5 mL/min. After this flow rate, the ethane mass-transfer coefficient began to rise toward its maximum. These maxima occur as a result of the competing effects of increased aqueous-phase velocity producing both improved mixing rates and reduced contact time. At velocities below those corresponding to the maximum, contact time is high, but mixing is below optimal. The opposite is true for aqueous velocities greater than those corresponding to the maximum. Thus, since the initial facilitation factor is the ratio of these uptake rates, its maximum will be where the ethylene uptake rate is close to its maximum and that of ethylene is still close to its minimum. This occurred at 8.5 mL/min aqueous flow rate.

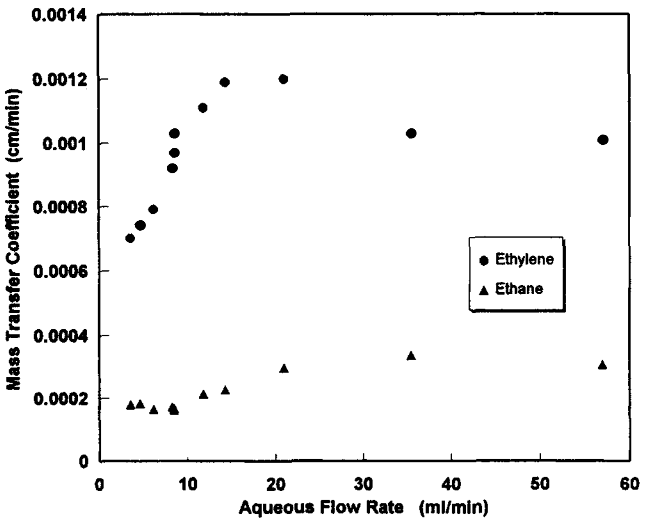

Figure 5. Initial mass-transfer coefficients for ethylene and ethane in 0.05-M copper(I) solution as a function of aqueous flow rate.

The system characterization has thus far shown that the ethylene/ethane separation is feasible with an electrochemically modulated complexation process due to kinetic differences in the uptake rates. In addition to an optimal aqueous flow rate, there should also be an optimal overall EMC experimental time associated with this flow rate for the best gas separation. If the experiment is allowed to run until it has reached equilibrium, then the separating ability of the system will only be equivalent to the equilibrium solubility difference. On the other hand, if experimental time is too short, the ethylene transfer from the feed to the receiving phase will be less than optimal. To determine the best overall experimental time, uptake experiments were done for both ethylene and ethane as a function of time. As with the initial uptake-rate experiments, each gas was contacted with unrecirculated 0.05 M copper(I) solution. However, the experiments were continued until gas mass transfer had ceased. These characterizations were performed at the optimal aqueous flow rate of 8.5 mL/min. Mass-transfer coefficients were estimated for each gas as a function of time. Results are presented in Figure 6. The ethylene experiment reached equilibrium and gas mass transfer ceased after 4.5 hours. For ethane, equilibrium was not reached until over 10 hours of contact had occurred. The best overall experimental time will be in

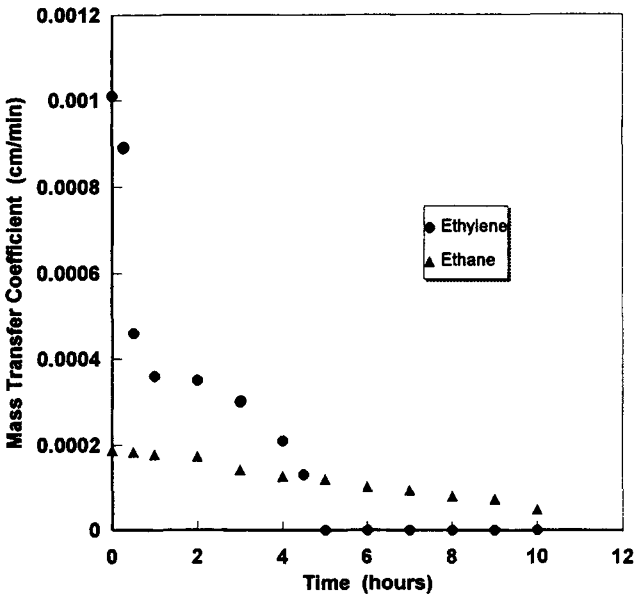

Figure 6. Mass-transfer coefficients for ethylene/ethane in 0.05-M copper(I) solution as a function of time when aqueous flow rate = 8.5 mL/min.

the region where a significant difference exists between the two mass-transfer coefficients and the ethylene mass-transfer coefficient is greater than that of ethane. From Figure 6 this is at approximately 1.5 hours. At lower times, the total ethylene transferred from the feed to the receiving phase was too low for a reasonable process. At times over about 4 hours, ethylene mass transfer became very low and eventually ceased. Ethane became the dominant gas being transported from the feed to the receiving phase and, hence, the final ethylene product purity decreased.

To confirm that 8.5 mL/min is the optimal aqueous flow rate for this system in producing the purest ethylene product, two additional electrochemically modulated complexation experiments were performed. For each, data were taken at a variety of overall experimental times, with only the optimal being reported here. The two flow rates were chosen to lie on either side of 8.5 mL/min and correspond to approximately the same initial facilitation factor. The first of these experiments was done at an aqueous flow rate of 20 mL/min. From Figure 4, the estimated initial facilitation factor was 9.3. The measured initial facilitation factor for this experiment was 7.0. After 2 hours of experimental time, the feed phase of 0.47-atm ethylene (52 mol %) and 0.43-atm (48%) ethane had been reduced to 0.042-atm ethylene (10%) and 0.366-atm ethane (90%). The receiving phase was concentrated from 0.83-atm pure ethylene to a mixture of 1.19-atm ethylene (97%) and 0.035-atm ethane (3%). Comparing these results to those obtained from the first experiment, it was seen that the ethylene product purity was overall lower in the concentrated receiving phase and, hence, results were less than optimal.

The third experiment was performed at an aqueous flow rate of 4.8 mL/min. The facilitation factor measured in Figure 4 at this flow rate was 9.3, while that obtained from this experiment was 6.5. Because the ethylene mass-transfer coefficient was lower than in the previous two processes, it was anticipated that a longer operating time would be required. After 2.5 hours of experimentation, the feed-phase reservoir was reduced from a mixture of 0.48-atm ethylene (52 mol %) and 0.44-atm ethane (48%) to 0.07-atm ethylene (16%) and 0.38-atm ethane (84%). The receiving phase was concentrated from 0.83-atm pure ethylene to a mixture of 1.16-atm ethylene (97%) and 0.04-atm ethane (3%). As in the previous experiment, the final ethylene purity obtained was not as high as that obtained with an aqueous flow rate of 8.5 mL/min. These results demonstrated that both an optimal aqueous flow rate and overall experimental time exists for this process. Under these conditions, ethylene purities in the concentrated receiving phase could exceed 99%.

Model

The continuous EMC process was modeled by a mass-transfer mechanism that is a function of three resistances in the hollow-fiber membrane contactors: diffusion of the solute in the gas phase, mass transfer of the solute across the membrane, and diffusion through the aqueous solution to a molecule of complexing agent. In both modules, the aqueous solution flows inside the hollow fibers and the solute gas flows in the shell.

Hydrophobic membranes were used throughout this research to have gas-phase diffusion in the membrane. Prasad and Sirkar (1987) derived expressions for these resistances for hydrophobic membranes. For the aqueous phase flowing inside the fibers and the organic (gas) phase outside,

$$K_{or}^{-1} = d_i\left[(d_o k_{of})^{-1} + (d_{lm} k_{mo})^{-1} + (m d_i k_{wf})^{-1}\right] \qquad (1)$$

$$K_{w}^{-1} = d_i\left[(m d_o k_{of})^{-1} + (m d_{lm} k_{mo})^{-1} + (d_i k_{wf})^{-1}\right], \qquad (2)$$

where d_i and d_o are the inside and outside fiber diameters; d_{lm} is the log mean fiber diameter; k_{of} and k_{wf} are the gas- and aqueous-phase film mass-transfer coefficients; k_{mo} is the membrane mass-transfer coefficient; and m is the distribution coefficient between the two phases. For the feed phase, m is K_r, the reduced phase-distribution coefficient, while for the receiving phase it is K_o, the oxidized phase-distribution coefficient. K_{or} and K_w are the overall mass-transfer coefficients based on the gas and aqueous phases, respectively.

Few correlations relate individual mass-transfer coefficients inside and outside fibers in a hollow-fiber membrane module. A literature review has produced correlations appropriate for this work. For laminar flow inside membrane fibers, Prasad and Sirkar (1987) found for flow inside the fibers

$$Sh = 1.62(Re * Sc * d_e/l)^{1/3}, \qquad (3)$$

where d_e is the effective diameter; l is the length of the fibers; Re is the Reynolds number; Sc is the Schmidt number; and Sh is the Sherwood number defining the film mass-transfer coefficient. For correlations of the mass-transfer coefficient outside the fibers, Prasad and Sirkar (1987) have developed

$$Sh = 5.9(d_e/l)Re^{0.6}Sc^{1/3}. \qquad (4)$$

This model is general and applies to both liquid extraction and gas absorption. Any chemical reaction effects are lumped with the mass-transfer coefficients.

Jemaa (1993) applied the preceding model to an EMC process and performed mass balances on each of the feed and receiving reservoirs to yield a set of equations describing solute concentrations both as a function of time and the length of the hollow-fiber membrane modules. These equations, however, apply to processes that are equilibrium based. Because the ethylene/ethane process was kinetically limited, the model required modification to characterize this situation. Only the feed-phase extraction equations were altered; the receiving phase was still considered to be only a function of resistances to mass transfer in the membrane modules. It was assumed that the kinetic effects in the feed-phase uptake rate did not effect the dissociation rate in the receiving phase and, furthermore, that the dissociation rates for ethylene and ethane in copper(II) solution were equilibrium based. The revised model for the feed phase assumed that the concentration was a function of the resistance to mass transfer, in addition to the forward and reverse reaction rate constants describing ethylene binding with copper(I).

The mass balances along the length of the feed-phase hollow-fiber membrane module for the feed solute and the solute-carrier complex are

$$\frac{d\overline{C}_f}{dz}-\frac{4K_{or}}{d\cdot V_z}\left(1-\frac{Q_f}{Q_aK_r}\right)+\frac{k_2}{V_z}C_L-\frac{k_1}{V_z}C_T\overline{C}_f-\frac{k_1}{V_z}C_TC_f^0=0 \tag{5}$$

$$\frac{dC_c}{dz}-\frac{k_2}{V_z}C_c+\frac{k_1}{V_z}C_T\overline{C}_f+\frac{k_1}{V_z}C_TC_f^0=0, \tag{6}$$

where

$$\overline{C}_f=C_f-C_f^0. \tag{7}$$

Here, C_f is the ethylene gas concentration in the feed phase; C_f^0 is the initial concentration; C_c is the copper(I)–ethylene complex in solution; and C_t is the complexing-agent concentration. Also in these equations, k_1 is the forward rate constant for the binding reaction; K_{or} is the overall mass-transfer coefficient; V_z is the feed-phase volume; Q_f and Q_a are volumetric flow rates of the aqueous and feed phases, respectively; K_r is the reduced-phase distribution coefficient; and k_2 is the reverse rate constant for the binding reaction.

These two equations can be solved simultaneously using Laplace transforms. The resulting equation for C_f as a function of axial location along the hollow-fiber length in Laplace transform format is

$$\overline{C}_f(s)=\frac{mC_f^0}{s^2-ps+q}, \tag{8}$$

where

$$m=\frac{k_1C_t}{V_z} \tag{9}$$

$$p=\frac{4K_{or}}{d\cdot V_z}\left(1-\frac{Q_f}{Q_aK_r}\right)+\frac{k_2}{V_z}+\frac{k_1C_T}{V_z} \tag{10}$$

$$q=\frac{4K_{or}}{d\cdot V_z}\left(1-\frac{Q_f}{Q_aK_r}\right)\frac{k_2}{V_z}. \tag{11}$$

This equation can be inverted into the length domain as

$$\overline{C}_f(z)=\frac{mC_f^0}{x-y}e^{-xz}-\frac{mC_f^0}{x-y}e^{-yz}, \tag{12}$$

where x and y are the roots of s^2-ps+q. This equation can be rewritten as

$$\overline{C}_f(z)=mC_f^0\left[\frac{e^{-pz/2}\sinh(p^2/4-q)^{1/2}z}{(p^2/4-q)^{1/2}}\right]. \tag{13}$$

The Laplace transform describing C_c is given as

$$C_c(s)=\frac{d_1mC_f^0}{s+n}+\frac{d_2mC_f^0}{s-x}+\frac{d_3mC_f^0}{s-y}+\frac{\frac{mC_f^0}{n}}{s}-\frac{\frac{mC_f^0}{n}}{s-n}, \tag{14}$$

where

$$n=k_2/V_z \tag{15}$$

$$d_1=\frac{-1}{xy^2-x^2y+n^2y-ny^2+nx^2-n^2x} \tag{16}$$

$$d_2=\frac{-\left(\frac{n-y}{y-x}\right)}{xy^2-x^2y+n^2y-ny^2+nx^2-n^2x} \tag{17}$$

$$d_3=\frac{-\left(\frac{x-n}{y-x}\right)}{xy^2-x^2y+n^2y-ny^2+nx^2-n^2x}. \tag{18}$$

This form is solved in the length domain to give

$$C_c(z)=mC_f^0\left\{d_1e^{-nz}+d_2e^{-xz}+d_3e^{-yz}+\frac{1}{n}-\frac{1}{n}e^{-nz}\right\}. \tag{19}$$

An analysis of this equation was performed to lend some physical interpretation to the solution. Plots were made of $\overline{C}_f/C_f^0$ as a function of n, the reverse reaction rate term, for various values of m, the forward reaction rate term. Results are given in Figure 7. As can be seen, $\overline{C}_f/C_f^0$ increases with increasing m when n is constant. In turn, when n is increased at constant m, $\overline{C}_f/C_f^0$ decreases. These trends are appropriate for what one would expect for any reaction expression.

The remaining mass balances on the gas reservoirs and on each hollow-fiber membrane module yield the following set of equations as described by Jemaa et al. (1993):

$$V_f\frac{dC_f^1}{dt}=Q_f\left(C_f^0-C_f^1\right) \tag{20}$$

$$Q_a(C_a^1-C_a^0(t-a))=Q_f\left(C_f^1-C_f^0\right) \tag{21}$$

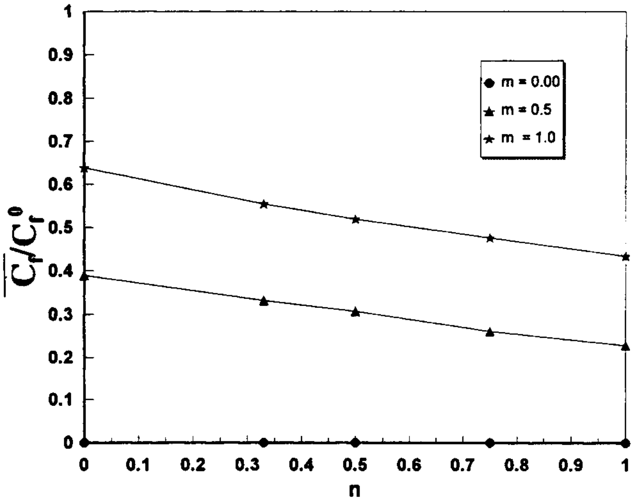

Figure 7. Plots of $\overline{C}_f/C_f^0$ as a function of *m*, the forward complexing reaction rate term, and *n*, the reverse reaction rate term.

Table 2. Experimental Results vs. Kinetic-Model-Predicted Results for an Electrochemically Modulated Complexation Process Separating and Concentrating Ethylene from Ethane when [Cu] = 0.05 M and Aqueous Flow Rate = 8.5 mL/min*

	Initial Cond. atm	Final Kinetic Model atm	Final Exp. Results atm
Feed			
Ethylene	0.46	0.05	0.046
Ethane	0.42	0.41	0.40
Receiving			
Ethylene	0.83	1.14	1.12
Ethane	0.00	0.00	0.01

*Overall experimental time was 2 h.

$$\frac{C_r^1 - C_r^{1*}}{C_r^0 - C_r^{0*}} = \exp\left(\frac{4K_w^l}{dv_{aq}}\left(1 - \frac{K_0 Q_a}{Q_r}\right)\right) \tag{22}$$

$$V_r \frac{dC_r^0}{dt} = Q_r(C_r^1 - C_r^0) \tag{23}$$

$$Q_a(C_a^1(t-a) - C_a^0) = Q_r(C_r^1 - C_r^0), \tag{24}$$

where the subscripts f, a, and r stand for the feed, aqueous, and receiving phases; the superscripts 0 and 1 stand for the entrance and exit of the modules; and C^* denotes the feed- or receiving-phase concentraion that would be in equilibrium with the aqueous-phase concentration. Velocities are denoted by v, and V denotes volume. The constant a is the lag time required for the aqueous phase to reach the second hollow-fiber membrane module after entering the prior one. This set of equations was solved numerically for the concentrations of the feed and receiving reservoirs as a function of time. The main variables of interest are the solute concentrations in the gas-phase reservoirs.

The revised model was applied to the initial EMC ethylene/ethane separation to verify lhow well the experimental results could be predicted. Results are presented in Table 2 As can be seen, this kinetic model predicts the final feed- and receiving-phase pressures to within a few percent; much more closely than the equilibrium model. The kinetic model, as shown in Figure 7, also agrees with experimental data within the margin of error of the measurements.

Conclusions

It has been demonstrated that an electrochemically modulated complexation process can be used to selectively separate ethylene from a mixture with ethane. A mass separating agent has been used to accomplish this purpose. It is electrochemically regenerated using porous electrodes placed in the continuous system. Results have indicated that this separation occurs because of differences in kinetic uptake rates of the gases in copper(I), rather than equilibrium solubility differences. The model described by Jemaa et al. (1993) was modified to characterize this phenomenon.

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