The Facilitated Transport of Carbon Monoxide Through Cuprous Chloride Solutions

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The facilitated transport of carbon monoxide through thin, immobilized films of cuprous chloride solutions is investigated, using a tracer $C^{14}O$ technique. Steady-state tracer flux measurements are used to determine the second-order forward rate constant and equilibrium constant for the reversible reaction of CO with cuprous ion. The enhanced results at low CO partial pressures can be interpreted in terms of a consecutive reaction model. The cuprous ion is remarkably effective as a carrier for CO. The CO permeation rate in the presence of cuprous ion can be increased by two orders of magnitude over the nonfacilitated flux. As such, the cuprous ion is an attractive facilitating agent for use in a membrane separation system.

SCOPE

Immobilized liquid membranes which contain a mobile reactive carrier have been used to separate mixtures containing acid gases, for example, CO_2 and H_2S (Ward and Robb 1967, Winnick et al. 1974, Matson et al. 1977). Due to the reversible chemical reaction which occurs in the liquid layer, high membrane permeability and selectivity for a specific permeant can be achieved at atmospheric pressure. In addition, since the complex formed near the upstream (high concentration) boundary dissociates near the downstream (low concentration) boundary, no net reaction occurs in the membrane, eliminating the need for a regeneration step in this type of separation scheme.

The complexation reaction of CO with cuprous ion has been widely used for CO removal in industrial absorbers (Kohl and Riesenfeld 1960). In our study, the reaction has been adapted for use in a membrane geometry. Two complementary experiments were conducted to evaluate this reaction system. Using the tracer technique of Donaldson and Quinn (1975), the reaction kinetics are explored by measuring the steady-state flux of $C^{14}O$ through cuprous chloride solutions equilibrated with equal partial pressures of untagged CO. The transport data are compared to an analytical model for simultaneous reaction and diffusion. The net flux of CO through these membranes was also monitored, by the parallel flux of tracer $C^{14}O$. The extent of flux enhancement was measured as a function of CO partial pressure, total copper concentration, and membrane thickness.

CONCLUSIONS AND SIGNIFICANCE

The carrier-mediated transport of CO by cuprous chloride anion, $Cu(Cl)_3^{-2}$, through thin (190 μm) liquid membranes lies intermediate between the two limiting regimes of very fast and very slow reaction rates. At high CO partial pressures (100% CO), the CO flux is well described by a simple bimolecular reaction model, with an equilibrium constant of 1,600 M^{-1} and a second-order forward rate constant of 8,400 M^{-1} s^{-1} at 25°C. As the CO partial pressure is reduced, the measured enhancement is higher than anticipated. This additional facilitation is discussed in terms of a consecutive reaction model, where the product of the primary reaction can further react with the carrier, forming a second CO-containing species.

Carbon monoxide transport with a 5% CO upstream concentration is multiplied more than 100 times by having a modest copper concentration of 0.2M in the liquid layer. These values translate to a respectable membrane permeability on the order of 100 × 10^{-9} cm^3 (STP)—cm/sec-cm^2—cmHg. Since the carrier solubility can be increased by at least a factor of ten in concentrated potassium chloride solution, the reaction of CO with cuprous ion offers considerable potential for use in a reactive membrane separation system.

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There have been many studies recently of the application of synthetic reactive membranes in separation processes. In these so-called "facilitated transport" membranes, the flux of a permeant through a thin liquid layer or membrane can be substantially enhanced by reversible reaction with a mobile carrier species within the membrane

$$\text{permeant} + \text{carrier} \rightleftarrows \text{complex} \qquad \text{(I)}$$

Recent review articles by Schultz et al. (1974), Smith et al. (1977), and Schultz (1977b) summarize the chemical engineering of carrier-mediated transport in synthetic membranes and discuss the pertinent literature for both gas and liquid phase separations.

Unlike the wide variety of possible liquid phase reactions, the number of gas phase experimental systems suitable for use in a facilitated transport context is relatively small. Early investigators were interested in the transport of the respiratory gases CO_2 and O_2 in physiological systems (Roughton 1959, Scholander 1960, Wittenberg 1966). In an engineering context, Ward and Robb (1967) and later Winnick et al. (1974) employed the CO_2 reactions in basic solution in developing facilitated transport membranes for CO_2 removal from confined environments such as spacecraft or submarines. Immobilized liquid membranes have also been used in the selective removal of H_2S to treat low heat content gasified coal (Matson et al. 1977).

Here we investigate a new facilitated transport system, involving the transport of CO in aqueous cuprous chloride solution. Carbon monoxide reacts with cuprous ion to form a cuprous carbonyl complex

$$CO + Cu^+ \rightleftarrows Cu(CO)^+ \qquad \text{(II)}$$

The viability of this reaction in a facilitated transport sense is demonstrated by measuring the enhanced CO flux through a thin layer of immobilized cuprous chloride solution as a function of copper concentration, membrane thickness, and CO partial pressure.

BACKGROUND

The choice of candidate reactions involving CO which are sufficiently reversible to use in a facilitated transport membrane is limited. Mochizuki and Forster (1962) measured the enhanced transport of CO through thin films of hemoglobin solution, where the CO binds reversibly with the heme groups of hemoglobin

$$CO + Hb \rightleftarrows Hb(CO) \qquad \text{(III)}$$

Schultz (1977a) took advantage of the photosensitivity of this binding to concentrate CO against its gradient by differentially illuminating a hemoglobin membrane. Transport rates through these hemoglobin membranes are small, however, since the carrier (Hb) concentration is necessarily low, due to its high molecular weight.

The high pressure absorption of CO in ammoniacal copper solution is important industrially in removing CO from ammonia-synthesis gas streams. In this copper liquor process, described in great detail by Kohl and Riesenfeld (1960), CO reacts reversibly with the cuprous ion complex, $Cu(NH_3)_2{}^+$ (Randles 1941)

$$CO + Cu(NH_3)_2{}^+ \rightleftarrows Cu(NH_3)_2\,(CO)^+ \qquad \text{(IV)}$$

Hughes and Steigelmann (1974) conducted preliminary facilitated transport experiments involving reaction (IV), measuring enhanced CO fluxes through polymer-supported liquid layers containing ammoniated cuprous chloride solution. We cannot draw quantitative conclusions from their results, since the semi-permeable supports formed the limiting mass transfer resistances.

Other CO complexing reactions involving cuprous ion-containing active agents are summarized in Smith (1978).

CUPROUS ION CHEMISTRY

While the solubility of CuCl (the most commonly used cuprous salt) in water in only 1.1×10^{-3} *M*, it can be increased dramatically by forming cationic complexes with ammonia, amines, and other basic ligands, as in the copper liquor process (Randles 1941, Bailar et al. 1973). Cuprous salts also dissolve readily in acidified solutions of various electrolytes with the formation of anionic complexes. Of these, the solubility of CuCl in aqueous solutions of KCl and HCl has been the most extensively studied (see Chaltykyan 1966). The ligand complex in these solutions is of the form $Cu(Cl)_x{}^{1-x}$, where x is determined by the ratio of the salt concentrations (Randles 1941, Chaltykyan 1966).

The use of chloride ions as stabilizing ligands for the cuprous ion (as opposed to, for example, ammonia) has several advantages. The chloride electrolytes, unlike ammonia, have a negligible vapor pressure, *minimizing the* loss of solution components. Also, cuprous solutions are oxidized to the inactive cupric state when exposed to air (Jhaveri and Sharma 1967)

$$4Cu^+ + 4H^+ + O_2 \rightleftarrows 4Cu^{+2} + 2H_2O \qquad \text{(V)}$$

Ammoniacal cuprous chloride solutions are much more readily oxidized by oxygen than cuprous chloride solutions (Jhaveri and Sharma 1967, Chhabria and Sharma 1974).

In addition to sharply increasing the solubility of Cu^+ in solution, the formation of the ligand complex, $Cu(Cl)_x{}^{1-x}$, has the additional benefit of retarding the disproportionation reaction of Cu^+

$$2Cu^+ \rightleftarrows Cu + Cu^{+2} \qquad \text{(VI)}$$

which otherwise occurs readily in water.

For the range of CuCl (0.02*M*-0.20*M*) and KCl (1*M*) concentrations used in this study, the predominant species

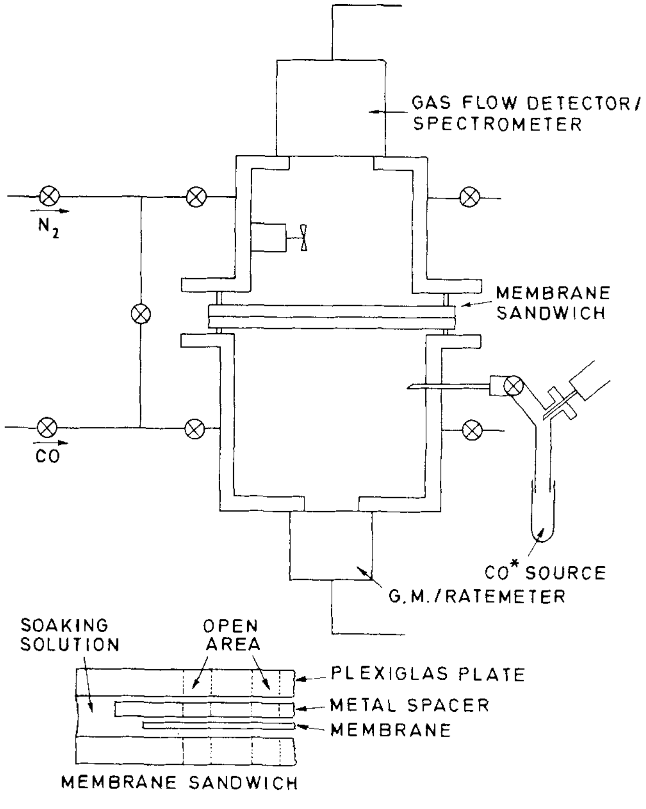

Figure 1. Schematic drawing of diffusion cell and membrane assembly.

in solutions is $Cu(Cl)_3^{-2}$ (Chaltykyan 1966). The solutions were also acidified ($pH = 1$) to prevent precipitation of copper oxides. Thus, the reversible reaction occurring in solution can be written as

$$CO + Cu(Cl)_3^{-2} \overset{k_1}{\rightleftarrows} Cu(CO)(Cl)_3^{-2} \qquad \text{(VII)}$$

Reaction (VII) is analogous to the NO/Fe^{+2} prototype facilitated transport system of Ward (1970a, 1970b)

$$NO + Fe^{+2} \rightleftarrows Fe(NO)^{+2} \qquad \text{(VIII)}$$

EXPERIMENTAL PROCEDURE

Two complementary types of mass transfer experiments were conducted. First, we monitored the flux of a small quantity of tracer $C^{14}O$ through a reactive, immobilized liquid layer, which had been equilibrated with equal partial pressures of background permeant (untagged CO). The experimental arrangement was such that all the untagged species in solution were at their equilibrium values. As a result, the governing equations for this "tracer transport" experiment are linear, and solutions are readily obtained. This tracer technique has been used by Donaldson and Quinn (1975) and Lander and Quinn (1978) in their kinetic studies of CO_2 hydration reaction catalysts. The tracer $C^{14}O$ was also used to monitor the more conventional "net transport" of untagged CO, where there was a net concentration difference of CO across the membrane.

The apparatus for these experiments, shown in Figure 1, is similar to that used by Donaldson and Quinn (1975) and is described in Smith (1978). The tracer, purchased from ICN Chemical and Radioisotope Division in a break-seal ampoule, was introduced into the upstream cell chamber from an external holder by displacing a small volume in the holder with water. To detect the tracer, the downstream and upstream chambers of the diffusion cell were fitted with a gas flow proportional detector and a Geiger-Müller (GM) tube, respectively. Stirring was necessary in the downstream chamber to insure adequate mixing. The experiments were conducted at ambient temperatures (25 ± 1°C).

The reactive cuprous chloride solutions were immobilized in a relatively inert, porous polyvinyl chloride filter (Polyvic®, BDWP 142, Millipore Corp.), sandwiched between supporting Plexiglas plates and metal spacer. We chose this configuration as opposed to supporting permeable polymer films, since the resistances of the latter would be limiting for the high degree of enhancement shown by this system. As shown by Donaldson and Quinn (1975), these filters are sufficiently porous so that the liquid phase can be treated as a homogeneous medium with only a porosity correction for the cross-sectional area for gas transfer. The diffusional path length was determined experimentally from a diffusion experiment through water alone.

To initiate a transport experiment, the membrane assembly was placed between the two half-cells, which were then bolted together. Both half-cells were flushed with a humidified background gas, either 5% CO (in N_2) or 100% CO, for a sufficient time to completely flush the gas spaces and to equilibrate with the liquid layer. In addition, cupric ions in the solution were reduced to the cuprous state by the reducing atmosphere provided by the CO flush

$$CO + 2Cu^{+2} + H_2O \rightleftarrows CO_2 + 2Cu^+ + 2H^+ \qquad \text{(IX)}$$

The cupric ions were formed during the soaking period of the membrane prior to assembly, where the solution was unavoidably partially oxidized. From Latimer (1952), the emf value for Reaction (IX) is favorable not only for this step, but also for further reduction of copper to the elemental state, although the latter did not occur.

After flushing both chambers, a small quantity of isotopic CO was introduced while flushing was continued in the downstream chamber. The amount of tracer was negligibly small compared to the non-radioactive background CO. The cell was then isolated, and the $C^{14}O$ flux during the initial steady-state period was measured. The amount of $C^{14}O$ accumulation in the downstream chamber remained negligibly small with respect to the upstream chamber. After the tracer transport experiment, the downstream chamber was flushed with nitrogen to completely remove the accumulated tracer and the background CO. The cell was again isolated and the buildup of $C^{14}O$ recorded. In this net transport experiment, the $C^{14}O$ monitored the net bulk flow of non-radioactive CO through the membrane.

DATA REDUCTION

The experimental measurements for both the tracer transport and net transport experiments were reduced to a facilitation or enhancement factor, i.e., the ratio of the total flux of a permeant through the reactive membrane (J_T^*) to the molecular diffusive flux through a solution of comparable (but unreactive) composition (J_0^*).

Because the quantity of tracer introduced was not exactly reproducible, the experimental fluxes had to be normalized by the appropriate concentration driving force. This can be accomplished by using an initial steady-state material balance (without reaction) for the diffusion cell, wherein the downstream accumulation can be expressed as (Smith 1978)

$$\left(\frac{dN_2^*}{dt}\right)_0 = \left(\frac{\epsilon ADHR_GT}{LV_1}\right)N_1^* \qquad (1)$$

so that the membrane resistance is defined as

$$R_0 = \frac{LV_1}{\epsilon ADHR_GT} = \left(\frac{N_1^*}{dN_2^*/dt}\right)_0 \qquad (2)$$

The apparent membrane resistance with a reactive solution can be defined analogously

$$R = \left(\frac{N_1^*}{dN_2^*/dt}\right) \qquad (3)$$

Thus, the facilitation factor, ψ, is the ratio of Equations (2) and (3)

$$\psi = \frac{R_0}{R} \qquad (4)$$

Since the two chambers were monitored by different counting instruments, we had to construct an experimental calibration curve so that the GM tube reading could be translated to an equivalent value (in terms of the gas flow detector), before forming the ratios in Equations (2) and (3).

The effective length in Equation (2) was determined for each membrane from a flux measurement through water alone, assuming a value for the CO diffusivity and Henry's law constant

$$L = \left(\frac{\epsilon ADHR_GT}{V_1}\right)\left(\frac{N_1^*}{dN_2^*/dt}\right) \qquad (5)$$

MATHEMATICAL MODEL

The reaction of carbon monoxide with chloride-stabilized cuprous ion

$$CO + Cu(Cl)_x{}^{1-x} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} Cu(CO)(Cl)_x{}^{1-x} \qquad (X)$$

is of the general form

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} AB$$

where

$$A = CO, \quad B = Cu(Cl)_x{}^{1-x}, \quad C = Cu(CO)(Cl)_x{}^{1-x}$$

The reaction is assumed first-order with respect to each of the species. The analysis of the complementary tracer transport and net transport experiments for this reaction are different as a result of the different experimental conditions.

Tracer Transport

The tracer transport experiments are designed such that the sum of the C^{14}O and CO concentrations is the same on both sides of the membrane. The flux of C^{14}O in one direction is countered by the flux of CO in the opposite direction. The concentration of tracer throughout the diffusion cell, however, is always much less than the untagged CO concentration.

At steady-state, the transport of the species A^*, B, and A^*B in solution is governed by an equation of the form

$$D_i \frac{d^2[i]}{dx^2} = R_i \quad (i = A^*, B, A^*B) \qquad (6\text{-}8)$$

where R_i is the local reaction rate. The remaining two species, A and AB, can be related through the constraints ($C_{A*} << C_A$)

$$C_A + C_{A*} = \text{constant} \qquad (9)$$

and

$$K_1 = \frac{C_{AB}}{C_A A_B} \qquad (10)$$

With the assumption $D_B = D_{AB}$, the three differential equations can be reduced to (Smith 1978)

$$D_A \frac{d^2C_{A*}}{dx^2} = k_1 C_{A*} C_B - k_{-1} C_{A*B} \qquad (11)$$

$$J_T = -D_A \frac{dC_{A*}}{dx} - D_{AB} \frac{dC_{A*B}}{dx} = \text{constant} \qquad (12)$$

$$C_T = C_B + C_{AB} \qquad (13)$$

Equation (12) results from an integrated linear combination of Equations (6) and (7). Equation (13) represents a material balance on the total amount of carrier in the membrane. Since C_B is constant throughout the membrane, Equation (11) is a linear second-order differential equation. Equations (10)-(13) can be solved with the aid of the boundary conditions on the permeant

$$x = 0, \quad C_{A*} = C_{A*}{}^0 = HP_{A*}{}^0 \qquad (14)$$

$$x = L, \quad C_{A*} = C_{A*}{}^L = HP_{A*}{}^L \qquad (15)$$

and the constraint that neither the carrier nor the complex can penetrate the membrane-gas boundary (not all of which are independent)

$$x = 0, \quad \frac{dC_{A*B}}{dx} = \frac{dC_B}{dx} = 0 \qquad (16)$$

$$x = L,$$

The solution, expressed in terms of the facilitation factor, ψ, is

$$\psi = \frac{J_T{}^*}{J_0{}^*} = \frac{1 + F}{1 + \dfrac{F}{\phi}(\tanh \phi)} \qquad (17)$$

where

$$F = \frac{D_{AB} K_1 C_T}{D_A (1 + K_1 C_A)},$$

$$\phi = \frac{1}{2} \sqrt{\frac{k_1 C_T L^2}{D_A (1 + K_1 C_A)} \left(\frac{1 + F}{F} \right)}$$

Equation (17) has two asymptotic limits. For very fast reactions or for very thick membranes (i.e. $\phi > F$), Equation (17) approaches an upper, thermodynamic limit termed reaction equilibrium

$$\psi = 1 + F \qquad (18)$$

In the opposite regime where $F >> \phi/\tanh \phi$, the facilitation is reaction rate-limited

$$\psi = \phi/\tanh \phi \qquad (19)$$

Net Transport

In the net transport experiments, there is a net flux of CO from the high partial pressure side to the low partial pressure side. The total amount of CO which is transferred is small, however, relative to the upstream CO concentration, so the experiments are again conducted at steady-state. The net flux is monitored by the parallel flux of tracer C^{14}O. The modeling equations, here written for the untagged species, are identical for each—since the specific activity of the tracer is constant in this experiment.

The differential balances on the species in solution, with the assumption $D_B = D_{AB}$, lead to

$$D_A = \frac{d^2C_A}{dx^2} = k_1 C_A C_B - k_{-1} C_{AB} \qquad (20)$$

$$N_T = -D_A \frac{dC_A}{dx} - D_{AB} \frac{dC_{AB}}{dx} = \text{constant} \qquad (21)$$

$$C_T = C_B + C_{AB} \qquad (22)$$

The boundary conditions are analogous to the tracer transport case. Unlike the tracer transport case, the reaction rate expression in Equation (20) is no longer linear, which precludes a closed form solution. A number of numerical solutions to Equations (20)-(22) have been published (e.g. Ward 1970, Kutchai et al. 1970, Smith and Quinn 1978). In addition, Smith et al. (1973) have developed solutions for the asymptotic regime, near the reaction equilibrium limit and the opposite regime, where the facilitation is reaction rate-limited.

RESULTS AND DISCUSSION

Membrane Permeation Experiments

The effective thickness of each membrane was determined from a transport experiment through deionized water. Values of 2.1 × 10^{-5} cm^2/s and 9.3 × 10^{-4} M atm^{-1} were assumed for the CO diffusivity and solubility in water (Wise and Houghton 1968, Pfeiffer and Krieger 1974, Seidell 1940). An average path length of 190 μm for a PVC filter with 73% porosity was obtained. The tortuosity for filters with a nominal thickness of 135 μm was 1.41, which compares favorably with similar cellulose acetate filters (Keller and Friedlander 1966, Wittenberg

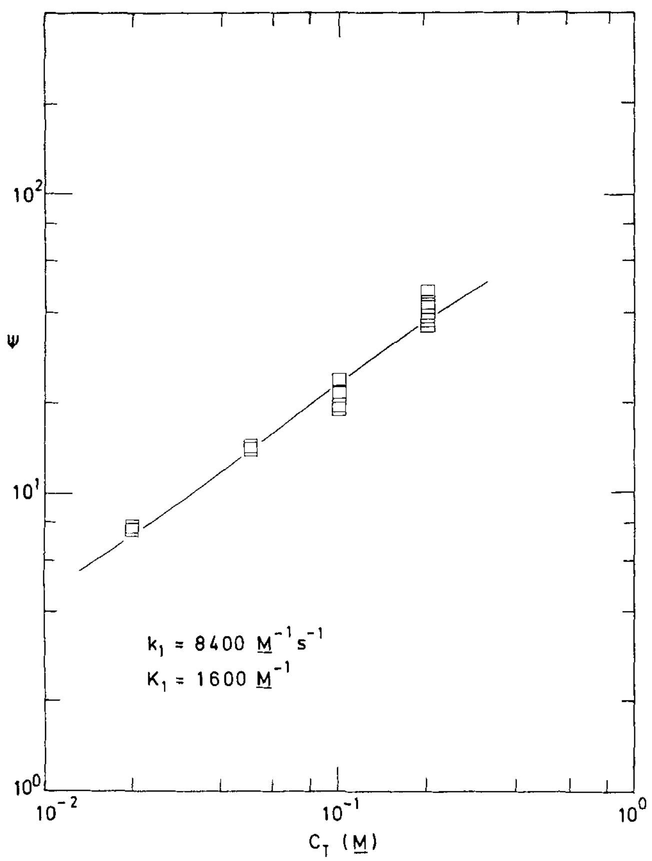

Figure 2. Tracer transport results with 100% CO: facilitation factor vs. total copper concentration. Solid line represents Equation (17), using physical constants discussed in text.

1970, Colton et al. 1973, Donaldson and Quinn 1975). In comparing results from filters of different thicknesses, the facilitation results were first corrected to a common thickness value (see below).

In addition to the thickness measurements, for every facilitation experiment, a complementary trial to determine R_0 was performed with the same membrane and background salt solution. For example, to determine R_0 for a solution consisting of 0.2*M* CuCl, 0.2*M* HCl, and 1.0*M* KCl, the membrane was first soaked in a solution composed of 1.2*M* KCl and 0.2*M* HCl. The replacement of K^+ for Cu^+ is a good assumption, since monovalent ions have similar activity coefficients in solution (Robinson and Stokes 1970). The R_0 values obtained experimentally were in good agreement with the transport results for pure water (when corrected for salting-out effects), using the values for D_{O_2} (Goldstick 1966) and for H_{O_2} (Seidell 1940) as a function of KCl concentration. These salting-out effects increased the membrane resistance by roughly a factor of two.

Tracer Facilitation: 100% CO Background

A series of tracer transport experiments involving cuprous ion concentrations ranging from 0.02*M* to 0.20*M* were performed with 100% CO as the bulk gas concentration in both chambers. For these experiments, the KCl concentration was maintained at 1.0*M* to provide a high excess chloride concentration. This was done so that the cuprous-cupric ion equilibrium (reaction VI) lay overwhelmingly with the cuprous state (Randles 1941). Also, with the high KCl background concentration, the nominal ionic strength remained relatively constant as the total copper concentration was varied. No attempt was made to account for the formation of the cuprous chloride complex. Likewise, the HCl concentration was kept constant at 0.2*M*.

While the membranes were soaking in the cuprous chloride solution, a portion of the copper was unavoidably oxidized to the inactive cupric state (reaction V). Preliminary experiments were designed then to insure that all the copper was reduced by CO to the active cuprous state via reaction (IX) by the time the tracer $C^{14}O$ was introduced to start the experiment. A flushing period of two hours was more than sufficient to yield a constant facilitation factor, regardless of the length of the soaking period. In fact, the measured facilitation factor was identical when the copper was introduced into the soaking solution as the inactive cupric chloride, $CuCl_2$.

Several tracer transport experiments were also conducted where the excess chloride concentration was reduced by 30%. The measured facilitation factors for 0.2*M* CuCl solutions were insensitive to this reduction in chloride content. Thus, small variations in chloride content when varying the copper concentration did not influence the extent of facilitation.

The results of the tracer transport experiments with 100% CO background gas concentration are shown in Figure 2 in terms of the facilitation factor versus total copper concentration. A very high degree of enhancement is shown for the relatively low carrier concentrations and high CO gas concentration used. The facilitation ψ varies with C_T as

$$\psi \sim C_T^{0.73} \tag{23}$$

From Equation (18), ψ varies with C_T at reaction equilibrium as

$$\psi \sim C_T^{1.0} \quad (F > 1) \tag{24}$$

If the facilitation were reaction rate-limited (Equation 19) the factor would vary as

$$\psi \sim C_T^{0.5} \tag{25}$$

The exponent indicates that the mode of transport is intermediate between the two limiting regimes. As a result, the full solution, Equation (17), must be used for comparison with the experimental results.

The line drawn in Figure 2 is a plot of Equation (17) for values of the second-order rate constant, k_1, and the equilibrium constant, K_1, of

$$k_1 = 8{,}400\, M^{-1}\, s^{-1}$$

$$K_1 = 1{,}600\, M^{-1}$$

Note that Equation (17) is almost, but not quite, linear on this logarithmic plot. Thus, the exponential relationship in Equation (23) is only an approximation.

These two values were determined by a least square minimization between the calculated and experimental results. In the calculation of Equation (17), the CO diffusivity and Henry's law value used were 1.9×10^{-5} cm²/s and 6.5×10^{-4} *M* atm^{-1} respectively. The carrier diffusivity, $D_{Cu(Cl)_3^{-2}}$ was estimated to be 1.1×10^{-5} cm²/s from values for electrolytes of comparable molecular size and similar ionic strength (Robinson and Stokes 1970). A confidence interval for this value is judged to be ± 0.2 cm²/s. Thus, the values of k_1 and K_1 extracted from Figure 2 may be in error by 25%, as a result of the uncertainty in the carrier diffusivity.

The second-order rate constant for the reaction of CO with $Cu(Cl)_3^{-2}$ has evidently not been previously determined. Van Krevelen and Baans (1950) developed correlating equations for the equilibrium constant K_1 for cuprous-ammonium chloride and cuprous-ammonium formate solutions. Their predicted values are in excellent agreement with the value obtained here.

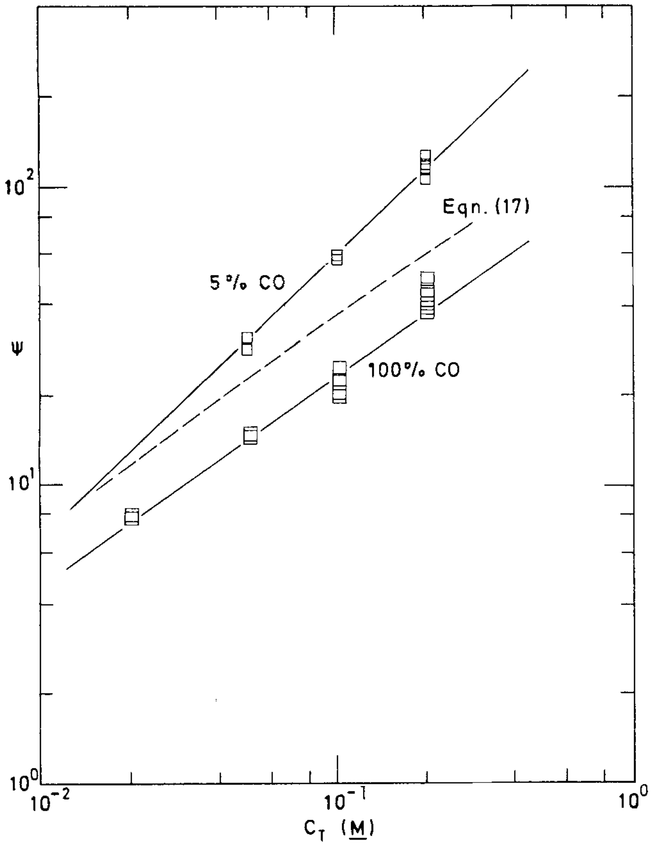

Figure 3. Tracer transport results with 5% and 100% CO: facilitation factor vs. total copper concentration. Dashed line represents Equation (17) for 5% CO using $k_1 = 8400\ M^{-1}s^{-1}$ and $K_1 = 1600\ M^{-1}$. Solid lines are least-squares fit of data.

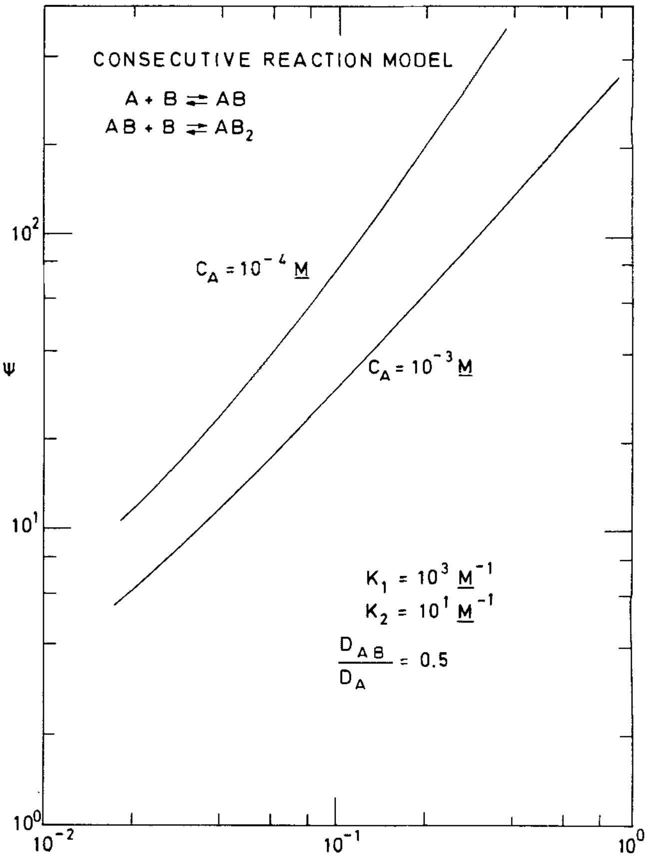

Figure 4. Calculated facilitation factors for the consecutive reaction model.

Tracer transport experiments with 100% background were also performed with twice the usual membrane thickness. This was done by stacking two membranes, soaked in the same $0.2M$ CuCl solution, on top of each other. The facilitation factor increased with the effective length as

$$\psi \sim L^{0.43} \tag{26}$$

The exponent was the same for the net transport trials. This exponent is intermediate (between the limiting regimes of fast and slow reaction rates), confirming the conclusion reached by varying C_T. Also, since these two experiments, varying C_T and L, are entirely independent experiments, the results of the latter can also be used to predict k_1 and K_1, yielding

$$k_1 = 9{,}600\ M^{-1}\,s^{-1}$$

$$K_1 = 1{,}100\ M^{-1}$$

The agreement is good considering only two experimental points are fitted and, that in doubling the membrane thickness, the facilitation factor is made more uncertain. This results because the accumulation rate in the downstream chamber in the R_0 determination for the doubled thickness was typically of the magnitude of the background signal fluctuation, introducing appreciable statistical uncertainty. Thus, the values of k_1 and K_1 taken from Figure 2 are the more accurate.

As mentioned previously, the effective lengths of the PVC filters varied somewhat (± 30 μm). When comparing transport experiments, all the results were corrected to a common length using Equation (26). The correction was small, usually 5% or less.

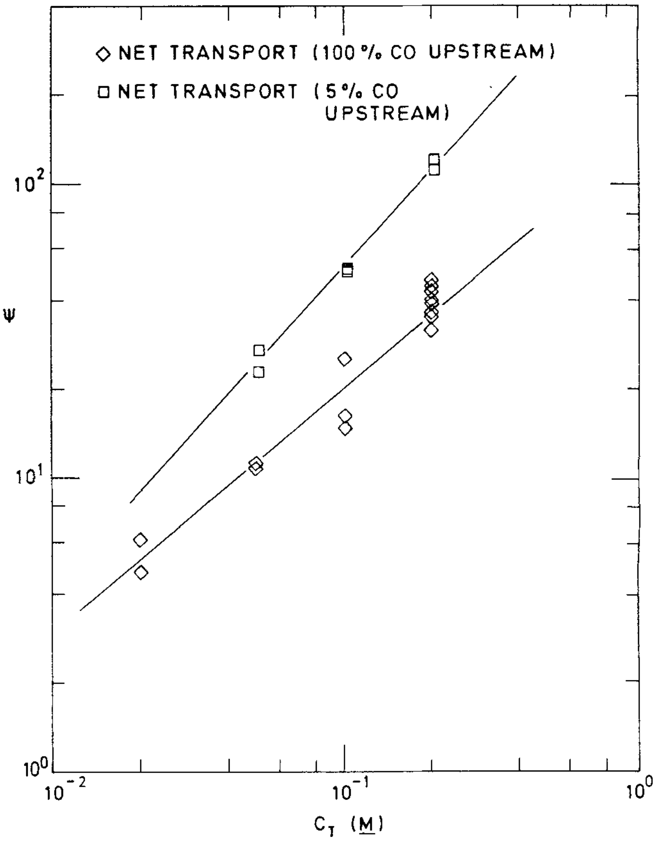

Figure 5. Facilitation factors for net transport with 5% or 100% CO upstream. Solid lines represents least-squares fit of data.

TABLE 1. COMPARISON OF METAL ION CARRIERS. FACILITATION FACTOR MEASURED AT CONSTANT METAL ION CONCENTRATION

$$CO + \text{Carrier} \rightleftarrows \text{Complex}$$

Carrier	ψ
Cu^{+} (0.2M)	41.5
CO^{+2} (0.2M)	2.1
Fe^{+2} (0.2M)	1.9

Tracer Transport: 5% CO Background

Transport trials were also conducted with 5% CO (in N_2) as background gas. We ran preliminary experiments with a two-hour flush of 5% CO and with a one-hour flush of 100% CO, followed immediately by one hour of 5% CO. These tests gave identical results for a 0.20M CuCl solution, indicating that the former arrangement was sufficient to reduce all the copper.

The tracer transport results for 5% CO are shown in Figure 3, along with the corresponding logarithmic plot of Equation (17)—which is again nearly linear in the range of variables studied. The dependence of the facilitation factor on the total carrier concentration is unexpectedly higher than before. A possible explanation for this may be the formation of a second carrier species in solution. In this consecutive reaction model, the product of the primary reaction can undergo further reaction

$$B + AB \rightleftarrows AB_2 \qquad \text{(XI)}$$

or written in terms of the species in solution

$$Cu(CO)(Cl)_3^{-2} + Cu(Cl)_3^{-2} \overset{k_2}{\rightleftarrows} (Cu(Cl)_3)_2(CO)^{-4} \qquad \text{(XII)}$$

The model is suggested by reports in the literature of non-stoichiometric compounds formed in reactions similar to the CO/Cu^{+} system. Jones (1899) reported evidence of a compound $3CO \cdot 4CuCl$, when CO was passed into a pyridine solution of cuprous chloride. Manchot et al. (1912) passed acetylene into an acidified solution of cuprous chloride; two types of compounds were formed, $C_2H_2 \cdot CuCl$ and $C_2H_2 \cdot 2CuCl$. In his comprehensive book on ethylene chemistry, Miller (1969) reviewed reports of nonstoichiometric silver compounds with ethylene. Thus, addition reactions of compounds containing double or triple bonds with cuprous or silver salts are not uncommon.

If this second reaction were to occur in the copper chloride solution, the facilitation would be augmented, due to the formation of the second permeant-containing species. This second carrier is formed at the expense of not only the primary carrier but also the free cuprous ion, so that the total concentration of permeant-containing species is increased. This can be demonstrated by calculating ψ as a function of C_T, incorporating the influence of the second reaction. This can be done directly if the the reactions are assumed to be very fast. The facilitation can then be expressed simply as

$$\psi = 1 + \frac{D_B}{D_A}\left(\frac{C_{A*B}}{C_{A*}} + \frac{C_{A*B_2}}{C_{A*}}\right) \qquad (29)$$

with the following mass balance and equilibrium constraints ($C_{A*} << C_A$)

$$C_T = C_B + C_{AB} + C_{AB_2} \qquad (30)$$

$$K_1 = \frac{C_{A*B}}{C_{A*}C_B} = \frac{C_{AB}}{C_A C_B} \qquad (31)$$

$$K_2 = \frac{C_{A*B_2}}{C_B C_{A*B}} = \frac{C_{AB_2}}{C_B C_{AB}} \qquad (32)$$

The carrier and complex diffusivities have been assumed equal. Curves calculated from Equation (29) are shown in Figure 4 for values corresponding roughly to those of the CO/Cu^{+} system. The equilibrium constant, K_2, was chosen arbitrarily. The results are qualitatively similar to the experimental results with 100% and 5% CO. The dependence of the facilitation factor on the total copper concentration increases at higher values of C_T at reduced permeant partial pressures, as a result of an appreciable concentration of AB_2, the second carrier. The qualitative agreement lends support to the consecutive reaction model. In addition, the results of net transport experiments also indicate that the simple bimolecular reaction model does not describe the results at low CO partial pressures (see below).

Net Transport—100%, 5% CO

The series of tracer transport experiments were conducted along with corresponding net transport trials, using 100% and 5% CO as the upstream concentrations. The experimental facilitation factors are shown in Figure 5. A very high degree of enhancement, over two orders of magnitude with 5% CO, is demonstrated for the relatively low copper concentrations and high permeant partial pressures used. These copper concentrations can be increased by an order of magnitude or more in the presence of a high KCl background concentration (Chaltykyan 1966). Thus, the enhancement data in Figure 5 indicate that the reaction of CO with Cu^{+} is very effective in a facilitated transport context for use in a membrane separation system.

The influence of the secondary reaction forming AB_2 is in evidence in Figure 5. The net transport results for 100% CO for the range of copper concentrations of 0.02M-0.20M CuCl are well fit by the equation (95% confidence interval)

$$\psi = 157\, C_T^{0.88(\pm 0.12)} \qquad (33)$$

From the first-order matched asymptotic solution of Smith et al. (1973) near the reaction equilibrium limit, the dependence of ψ on C_T is expected to decrease slightly for this concentration range, as the upstream CO concentration is decreased twenty-fold. However, the experimental data for 5% CO has a higher functional dependence

$$\psi \sim C_T^{1.1(\pm 0.1)} \qquad (34)$$

The exponent is, in fact, higher than the maximum value of 1.0 for the bimolecular reaction model (Smith et al. 1973). If the product of the primary reaction were to undergo further reaction to form AB_2, however, facilitation would again be augmented at the higher copper concentration, as in Figure 4. Thus, the results of the net transport experiments reinforce the idea of a consecutive reaction model, where the concentration of the product of the second reaction, AB_2, becomes appreciable only at lower CO partial pressures (e.g. 5%).

Other Metal Carriers

A wide variety of other metal ions in addition to cuprous ion react with carbon monoxide. Two were investigated experimentally, cobaltous ion (Co^{+2}) and ferrous ion (Fe^{+2}). Their chloride salts were dissolved in acidified 1.0M KCl solution. In Table I, the relative effectiveness of cobaltous and ferrous ions as carriers for carbon monoxide are compared to the tracer transport results with cuprous ion. The cuprous ion is remarkably effective as a carrier agent for CO, as a result of its much larger forward rate of reaction (Ward 1970a).

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NOTATION

A = area for gas transfer, cm^2
C = concentration, mol/l or mol/cm^3
C_T = overall carrier concentration based on the total amount of carrier added to the membrane divided by the membrane volume, mol/l
D = diffusion coefficient, cm^2/s
F = see Equation (17)
H = Henry's law constant, mol/l/atm
J_0^* = flux of tracer through membrane without chemical reaction, mol/cm^2/s
J_T^* = total flux of tracer through the membrane – sum of permeant and carrier fluxes, mol/cm^2/s
k_1 = second-order forward reaction rate constant for reaction (X), (mol/l)$^{-1}$s^{-1}
k_{-1} = reverse reaction rate constant for reaction (X), s^{-1}
K_1 = equilibrium constant for reaction (X), (mol/l)$^{-1}$
K_2 = equilibrium constant for reaction (XII), (mol/l)$^{-1}$
L = diffusional path length, cm
N^* = extensive quantity of tracer in diffusion cell chamber, mol
P = bulk phase partial pressure, atm
R = apparent membrane resistance (Equation 3), time
R_0 = membrane resistance without chemical reaction (Equation 2), time
R_A = gas law constant
R_i = local reaction rate of species i
T = absolute temperature, °K
V = volume of chamber, cm^3
x = coordinate in direction of transport, cm

Greek Letters

ϵ = membrane porosity
ϕ = see Equation (17)
ψ = facilitation factor, i.e. ratio of permeant flux through membrane with reaction to that without reaction

Superscripts

0 = upstream boundary
L = downstream boundary
$*$ = tracer species

Subscripts

1 = upstream chamber
2 = downstream chamber

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Equilibrium Staged Parametric Pumping:

Part III. Open Systems at Steady-State-McCabe-Thiele Diagrams

The theory of equilibrium staged parametric pumps with discrete fluid transfers has been presented in previous papers for total reflux. Here, it is extended to open, fractionating systems, operating in cyclic steady state. The cases of an enriching section, a stripping section, and a complete fractionating apparatus are successively considered. Providing adequate variables are defined, the result is a diagram which plays the same role as the McCabe-Thiele diagram in distillation. The optimal feed stage location, the minimum reflux, and the separation factor for given operating conditions are determined analytically and graphically in the case of linear equilibrium isotherms. The method is then generalized to non-linear equilibria, particularly of constant relative volatility type.

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SCOPE

In two previous papers of this series, (Grevillot and Tondeur 1976, 1977), parametric pumps were studied in which the usual packed adsorbent bed is replaced by a cascade of discrete equilibrium stages, and the usual continuous flow by discrete transfers of fluid fractions. The study dealt with the steady limit regime (or cyclic steady state) of these pumps at total reflux. Striking analogies *with binary distillation theory are found, in particular with* respect to graphical, McCabe-Thiele-like, constructions. Here, we extend this approach to open pumps at cyclic steady-state, that is pumps with feed introduction, and withdrawal of products. The study is restricted to single-transfer per half-cycle, as was the first article of this series. We present the complete treatment in the case of linear isotherms, as this leads to analytical solutions for the separation factor and the minimum reflux ratio. The treatment is next generalized to Langmuir-type isotherms and to experimental equilibrium data.

CONCLUSIONS AND SIGNIFICANCE

Open equilibrium, staged parametric pumps at cyclic steady state can be analyzed graphically, in a manner analogous to distillation columns. The following concepts must be employed:

1. The fluid fractions of composition x', undergoing transfer upward at temperature T', play the same role as the ascending vapor phase in distillation. The fluid fractions of composition x, undergoing transfer downward at temperature T, play the same role as the descending liquid phase in distillation. Accordingly, a McCabe-Thiele-like diagram will plot x' as a function of x.

2. The linear operating lines relate the compositions that cross each other between stages. They are obtained by a component balance on the end of the enriching or of the stripping section, *over a complete cycle*. The curves relating the compositions x' and x exiting from a given stage are not equilibrium curves as in distillation. They are obtained by component balances on a stage of the enriching section, a stage of the stripping section, and the feed stage, *over a half-cycle*. There are thus three different "partition curves," each depending on the reflux ratio.

Using these concepts, the classical McCabe-Thiele construction of binary distillation in transposed to parametric pumping: stepping off stages between operating and partition lines, optimal location of feed stage, determination of minimum reflux.

For linear equilibrium isotherms, the partitions are also linear. The separation factor may be expressed explicitly as a function of the operating parameters and the number of stages N_e and N_s of each section in the form

$$SF = \frac{x_{\text{top}}}{x_{\text{bottom}}} = \frac{(a_1)^{N_e} a_2 + a_3}{(b_1)^{N_s} b_2 + b_3}$$

The minimum reflux ratio is obtained as the solution of a 4th degree equation.

For arbitrary, non-linear isotherms, (using experimental data for instance) the partition lines are curved, but can still be easily constructed, and the graphical properties still hold. The separation factor and minimum reflux must

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