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Chemical Kinetic Approach To The Mechanism Of Coupled Transport Of Cu(II) Ions Through Bulk Liquid Membranes

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Transport of copper(II) ions through bulk liquid membranes is studied in various experimental conditions. The results obtained are analyzed by using the concepts and methods of chemical kinetics. This approach allowed kinetic equations to be established which are sufficiently general to account for a large variety of transport kinetics (steady or nonsteady state, first or zeroth order, diffusion or reaction controlled, reversible or irreversible), to identify clearly the rate-determining steps, and to propose a detailed mechanism at the molecular level. The important role played by the interfaces is also demonstrated.

Introduction

The large number of publications concerning liquid membranes shows their importance in separation science.[1−3] Their optimal application requires detailed knowledge of their mechanism of action. Therefore, it is not surprising that a great number of kinetic studies were carried out to determine the mechanism of transport through liquid membranes. Essentially three types of approaches were used for this purpose.

The irreversible thermodynamic approach is basically phenomenological, and although it shows explicitly the coupling effects, it is not suitable for obtaining information at the molecular level. Furthermore, in its linear form, it is applicable only to systems close to equilibrium which is certainly not the case when the whole transport process is considered.[4,5] However, the intervention of multistep chemical events may render this condition less stringent.[6]

The diffusion−reaction method also shows clearly the coupling effects and yields useful information about diffusion constants and global chemical events in the steady-state approximation.[7,8]

The chemical kinetic approach is the most suitable for establishing the transport mechanism at the molecular level.

In a great many cases, the mechanism of extraction was established, which is in fact the first part of the whole transport process.[9−11] In general, kinetic analyses were realized in the steady-state approximation, which is perfectly suitable for supported (SLM)[12] or emulsion (ELM)[13] liquid membranes. However, in the case of bulk liquid membranes (BLM) nonsteady-state kinetic regimes appear also frequently and a more general kinetic analysis is necessary.[14−18] Since relatively few studies were realized for divalent metals, the purpose of this work is to provide a general chemical kinetic approach to the mechanism of coupled transport of Cu(II) ions through bulk liquid membranes containing Acorga P-50 as carrier. This compound, and in general oximes, are excellent ligands for copper extraction. The mechanism of copper extraction and re-extraction was studied in detail using sophisticated experimental techniques.[9,11] Therefore, it appears interesting to examine whether the conclusions obtained are also valid for the transport systems taken as a whole in conditions closer to the actual industrial procedure.

Theory

It was shown previously that the coupled transport of Cu (II) ions through various liquid membranes obeys formally the kinetic laws of consecutive irreversible first-order reactions:[17−19]

$$\mathrm{Cu_{(d)}} \xrightarrow{k_{1d}} \mathrm{Cu_{(m)}} \xrightarrow{k_{2a}} \mathrm{Cu_{(a)}} \qquad (1)$$

where $\mathrm{Cu_{(d)}}$ and $\mathrm{Cu_{(a)}}$ are hydrated copper ions in the aqueous donor and aqueous acceptor phases, respectively, while $\mathrm{Cu_{(m)}}$ is the copper−carrier complex in the liquid membrane (organic phase). k_{1d} is the apparent first-order membrane entrance rate constant, while k_{2a} represents the corresponding apparent first-order membrane exit rate constant.

The basic idea in the present treatment is that the metal ions present in the different phases are considered as different chemical species obeying the laws of chemical kinetics.

According to eq 1, the rate of change of the different copper ion species may be expressed by the following differential equations:

$$\frac{\mathrm{d}C_d}{\mathrm{d}t} = -k_{1d}C_d \qquad (2)$$

$$\frac{\mathrm{d}C_m}{\mathrm{d}t} = k_{1d}C_d - k_{2a}C_m \qquad (3)$$

$$\frac{\mathrm{d}C_a}{\mathrm{d}t} = k_{2a}C_m \qquad (4)$$

where C_d, C_m, and C_a are the copper ion concentrations (in M units) in the donor, membrane, and acceptor phases, respectively.

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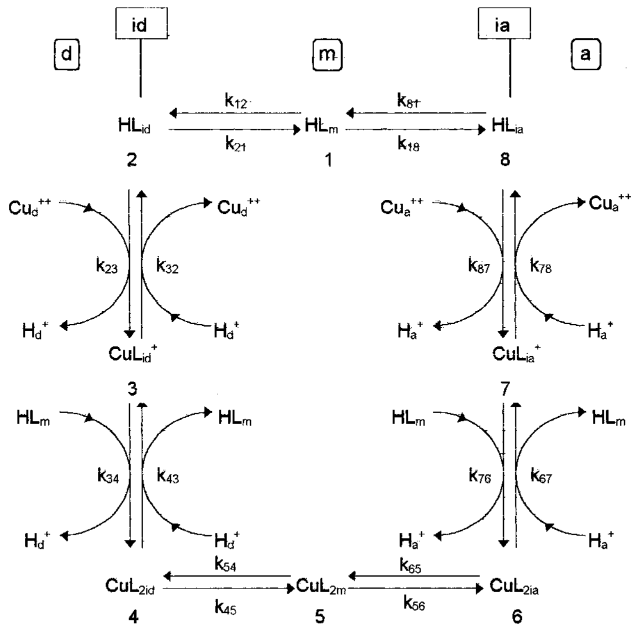
SCHEME 1



Integration of these equations leads to the classical time evolution expressions of the different copper species[30]

$$C_d = C_{d0} \exp(-k_{1d}t) \tag{5}$$

$$C_m = C_{d0} \frac{k_{1d}}{k_{2a} - k_{1d}}[\exp(-k_{1d}t) - \exp(-k_{2a}t)] \tag{6}$$

$$C_a = C_{d0}\left[1 - \frac{1}{k_{2a} - k_{1d}}[k_{2a} \exp(-k_{1d}t) - k_{1d} \exp(-k_{2a}t)]\right] \tag{7}$$

C_{do} is the initial copper concentration in the donor phase, and $C_{mo} = C_{ao} = 0$. It can be seen that the donor phase copper concentration has a monoexponential evolution while the membrane and acceptor phase species show biexponential behavior.

This formal kinetic treatment allowed the interpretation of all the various results obtained.[17−19] Also, calculations based on reversible membrane entrance and exit steps did not allow the establishment beyond experimental errors of the intervention of backward reactions. Furthermore, the complete monoexponentiality of the membrane entrance step maintained till the end of the transport (reversibility would lead to a biexponential kinetic curve) favors also strongly the irreversible kinetic scheme (eq 1). Therefore, this latter is adopted for the subsequent analysis in agreement with literature data.[15] The virtual irreversibility of the first step is quite likely due to the high extraction constant observed for copper in the presence of Acorga P-50 used as carrier.[10,11] On the other hand, the irreversibility of the membrane exit step is strongly increased by the high proton gradient imposed by the acidity of the acceptor phase.

Clearly, k_{1d} and k_{2a} are only apparent rate constants and their exact form has to be established in order to account for the kinetic responses to the variation of different physicochemical factors. Therefore, a more detailed and more realistic chemical scheme is proposed for this purpose (Scheme 1).

In establishing this scheme, it was supposed that all the metal−carrier reactions take place at the water−membrane interfaces (donor phase−membrane interface, id; acceptor phase−membrane interface, ia) between species present at the interfaces and those coming from the bulk. It was also supposed that no leakage of carrier or of its complex with copper from membrane into aqueous phases could take place.

According to Scheme 1, the monobasic carrier Acorga P-50 present in the bulk membrane (m), HL_m, diffuses to the interface id and gives the adsorbed form HL_{id}.

$$\underset{\mathbf{1}}{HL_m} \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} \underset{\mathbf{2}}{HL_{id}} \tag{8}$$

where k_{ij} designates the rate constant of transformation of species i into species j.

HL_{id} undergoes a chemical reaction with a copper ion coming from the bulk donor phase (d), Cu_d^+, and a proton H_d^+ is released simultaneously to the donor phase.

$$\underset{\mathbf{2}}{HL_{id}} + Cu_d^{++} \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} \underset{\mathbf{3}}{CuL_{id}^{+}} + H_d^{+} \tag{9}$$

The intermediate complex CuL_{id}^+ reacts in its turn with a free carrier molecule HL_m coming from the bulk membrane to form the neutral complex CuL_{2id}. In this step, a second proton H_d^+ is released into the bulk donor phase.

$$\underset{\mathbf{3}}{CuL_{id}^{+}} + HL_m \underset{k_{43}}{\overset{k_{34}}{\rightleftharpoons}} \underset{\mathbf{4}}{CuL_{2id}} + H_d^{+} \tag{10}$$

The complex CuL_{2id} then leaves the interface id by diffusion and penetrates into the bulk membrane to become CuL_{2m}.

$$\underset{\mathbf{4}}{CuL_{2id}} \underset{k_{54}}{\overset{k_{45}}{\rightleftharpoons}} \underset{\mathbf{5}}{CuL_{2m}} \tag{11}$$

This species is quickly transported to the acceptor side by fast stirring where it diffuses into the membrane-acceptor phase interface ia to give CuL_{2ia}.

$$\underset{\mathbf{5}}{CuL_{2m}} \underset{k_{65}}{\overset{k_{56}}{\rightleftharpoons}} \underset{\mathbf{6}}{CuL_{2ia}} \tag{12}$$

The neutral complex CuL_{2ia} gives rise subsequently to the following elementary steps leading eventually to the release of copper into the acceptor phase.

$$\underset{\mathbf{6}}{CuL_{2ia}} + H_a^{+} \underset{k_{76}}{\overset{k_{67}}{\rightleftharpoons}} \underset{\mathbf{7}}{CuL_{ia}^{+}} + HL_m \tag{13}$$

$$\underset{\mathbf{7}}{CuL_{ia}^{+}} + H_a^{+} \underset{k_{87}}{\overset{k_{78}}{\rightleftharpoons}} Cu_a^{++} + \underset{\mathbf{8}}{HL_{ia}} \tag{14}$$

Finally, the free carrier present at the interface ia, HL_{ia}, diffuses back into the bulk membrane.

$$\underset{\mathbf{8}}{HL_{ia}} \underset{k_{18}}{\overset{k_{81}}{\rightleftharpoons}} \underset{\mathbf{1}}{HL_m} \tag{15}$$

and the whole cycle of elementary steps may start again. Since the carrier is chemically stable and does not leak out from the membrane, its turnover is virtually infinite.

Membrane Entrance Step (k_{1d}). Supposing that steady-state approximation may apply for the interface species,[9] we can write, according to Scheme 1,

$$-\frac{d[Cu^{++}]_d}{dt} = \frac{d[CuL_2]_m}{dt} = k_{45}[CuL_2]_{id} - k_{54}[CuL_2]_m \tag{16}$$

In this equation, the concentration of CuL_{2m} can be known at any moment from material balance if the interface species are neglected, while the concentration of CuL_{2id} is given by the steady-state condition

$$[CuL_2]_{id} = \frac{k_{34}[CuL^+]_{id}[HL]_m + k_{54}[CuL_2]_m}{k_{43}[H^+]_d + k_{45}} \tag{17}$$

with obvious notations. The concentration of other interface species (CuL_{id}^+ and HL_{id}) can be obtained in a similar way.

Substituting these concentrations into eq 16, we obtain the final general form of the membrane entrance rate

$$\frac{d[Cu^{++}]_d}{dt} = \frac{A[H^+]_d^{\,2}[CuL_2]_m - B[HL]_m^{\,2}[Cu^{++}]_d}{C[H^+]_d^{\,2} + D[H^+]_d + (E + F[Cu^{++}]_d)[HL]_m} \tag{18}$$

where $A = k_{21}k_{32}k_{43}k_{54}$, $B = k_{12}k_{23}k_{34}k_{45}$, $C = k_{21}k_{32}k_{43}$, $D = k_{21}k_{32}k_{45}$, $E = k_{21}k_{34}k_{45}$, and $F = k_{23}k_{34}k_{45}$.

Membrane Exit Step (k_{2a}). For the membrane exit step characterized by the apparent rate constant k_{2a} (eq 1), we can write similarly to eq 16

$$\frac{d[Cu^{++}]_a}{dt} = -\frac{d[CuL_2]_m}{dt} = k_{56}[CuL_2]_m - k_{65}[CuL_2]_{ia} \tag{19}$$

Proceeding as for the establishment of eq 18 in the steady-state approximation of interfacial species concentration, we can obtain the required rate equation. A less tedious way can be followed by noting that the bulk membrane is chemically symmetrical, i.e., it involves at its interfaces id and ia the same type of chemical species even if at different concentrations. Therefore, each rate constant and concentration factor of eq 18 can be replaced by the corresponding quantity belonging to the acceptor side, i.e., k_{12} may be replaced by k_{18}, k_{23} by k_{87}, H_d^+ by H_a^+, CuL_{id}^+ by CuL_{ia}^+, etc., and we obtain finally the general form of the membrane exit rate

$$\frac{d[Cu^{++}]_a}{dt} = \frac{A[H^+]_a^{\,2}[CuL_2]_m - B[HL]_m^{\,2}[Cu^{++}]_a}{C[H^+]_a^{\,2} + D[H^+]_a + (E + F[Cu^{++}]_a)[HL]_m} \tag{20}$$

where $A = k_{56}k_{67}k_{78}k_{81}$, $B = k_{65}k_{76}k_{87}k_{18}$, $C = k_{67}k_{78}k_{81}$, $D = k_{65}k_{78}k_{81}$, $E = k_{65}k_{76}k_{81}$, $F = k_{65}k_{76}k_{87}$. It can be seen that eqs 18 and 20 have similar mathematical structures. However, different symbols are used to designate the same elementary steps but occurring at different interfaces (e.g., k_{12} and k_{18}, etc.). This is because each elementary step involves at least one interface species the free energy of which varies with the quality of the interface. This latter is in turn influenced by the different composition of the two bulk aqueous phases.[20] Therefore, the chemically symmetrical bulk liquid membrane (see above) has a certain physicochemical asymmetry due to the different quality of the interfaces.

Results and Discussion

Equations 18 and 20 show that both the membrane entrance and exit rates depend on various chemical factors (copper and carrier concentrations, donor and acceptor phase acidity) in a rather complex way. However, variation of these factors allows a more detailed kinetic analysis to be realized. For this purpose, a series of experiments has been carried out in different experimental conditions, and the results obtained permitted the kinetic equations to be simplified considerably.

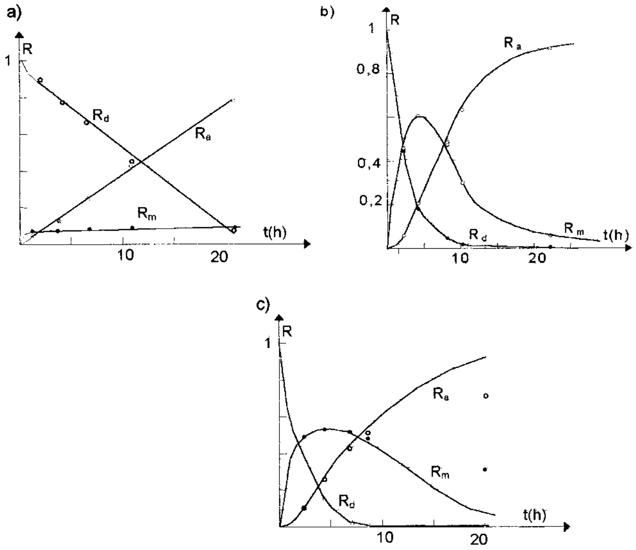


Figure 1. Kinetic curves obtained for coupled transport of copper at different ratios of initial copper, C_{do}, and carrier, C_{Ac}, concentrations. C_{do}/C_{Ac} =8 (a), 0.8 (b), 0.047 (c). *Donor phase*: C_{do}=0.01 M, I=1.3, $pH_{\alpha,\omega}$=4.6 (sodium acetate buffer). *Membrane phase*: Acorga P-50 in *n*-octane. *Acceptor phase*: 2M H_2SO_4. T=25 ± 0.1 °C (for the theoretical curves see text).

Figure 1 shows that transport experiments realized at different ratios of initial copper, C_{do}, and carrier, C_{Ac}, concentrations, C_{do}/C_{Ac}, give different types of kinetic curves, where dimensionless reduced concentrations are used for practical reasons: $R_d = C_d/C_{do}$, $R_m = C_m/C_{do}$, and $R_a = C_a/C_{do}$. The theoretical curves were also calculated with these modifications using eqs 5−7.

If C_{do}/C_{Ac} is in the range of 1.5−0.17, the kinetic curves obey eqs 5−7 till the end of the transport process (Figure 1b). This means that the membrane entrance step is characterized by first-order kinetics with respect to copper (monoexponential curve) and can be considered as virtually irreversible (see above). This might be a direct consequence of the irreversibility of the copper−carrier complex formation steps at the interface id, i.e., $k_{32} = k_{43} \approx 0$. With this irreversibility assumption, eq 18 becomes

$$-\frac{d[Cu^{++}]_d}{dt} = \frac{k_{12}k_{23}[HL]_m[Cu^{++}]_d}{k_{21} + k_{23}[Cu^{++}]_d} \tag{21}$$

This equation can account for the saturation behavior of copper fluxes as a function of copper concentration.[11] It is completely analogous to the Michaelis−Menten kinetic law.[29] It shows also that the membrane entrance rate should be independent of the donor phase acidity (see below). On the other hand, the observed first order with respect to copper suggests that

$$k_{21} \gg k_{23}[Cu^{2+}]_d \tag{22}$$

which leads to

$$\frac{d[Cu^{++}]_d}{dt} = -\frac{k_{12}}{k_{21}}k_{23}[HL]_m[Cu^{++}]_d \tag{23}$$

Obviously, the apparent rate constant for the membrane entrance step can be defined as

$$k_{1d} = \frac{k_{12}}{k_{21}} k_{23}[\mathrm{HL}]_m \qquad (24)$$

It can be seen that the rate-limiting step of membrane entrance is the chemical reaction between $\mathrm{Cu_d^{++}}$ and $\mathrm{HL_{id}}$ (k_{23}), preceded by the diffusional kinetic equilibrium of adsorption of free carrier to the interface (k_{12}/k_{21}). This is in agreement with the same rate-limiting step obtained from extraction studies.[11,21,22]

If we admit irreversibility also for the membrane exit step, i.e., $k_{76} = k_{87} \approx 0$, eq 20 becomes

$$\frac{d[\mathrm{Cu}^{++}]_a}{dt} = \frac{k_{56}k_{67}[\mathrm{H}^+]_a}{k_{65} + k_{67}[\mathrm{H}^+]_a}[\mathrm{CuL_2}]_m \qquad (25)$$

Therefore, the apparent rate constant for the membrane exit step can be defined as

$$k_{2a} = \frac{k_{56}k_{67}[\mathrm{H}^+]_a}{k_{65} + k_{67}[\mathrm{H}^+]_a} \qquad (26)$$

showing a complex dependence on the acceptor phase acidity (see below).

Further increase of carrier concentration in the membrane ($C_{do}/C_{Ac} = 0.16-0.03$) leads to kinetic curves which can be analyzed by eqs 5−7 only partially (Figure 1c). The decrease of copper concentration in the donor phase is still monoexponential (eq 5) but the curves corresponding to the membrane and acceptor phases do not obey eqs 6−7. They suggest rather that the membrane exit step becomes reversible due to heavy overloading of the membrane with respect to carrier molecules.

On the other hand, upon decreasing the carrier concentration in the membrane ($C_{do}/C_{Ac} = 15-3$) the kinetic regime is completely changed. The kinetic curves for all three phases are in fact straight lines (Figure 1a), meaning that the time evolution of the copper concentrations in the donor and acceptor phases follows a zeroth-order kinetic law. For the membrane entrance rate the opposite of eq 22 is valid in this case and eq 21 yields

$$-\frac{d[\mathrm{Cu}^{++}]_d}{dt} = k_{12}[\mathrm{HL}]_m \equiv k_0 \qquad (27)$$

where k_0 represents the zeroth-order rate constant. Equation 27 shows that the rate-limiting step is the diffusion of uncomplexed carrier molecules into the id interface. In this case, the copper concentration in the membrane is small and remains constant throughout the kinetic runs.[25] In other words, copper is following steady-state kinetics. As a consequence, the membrane exit rate is equal to the membrane entrance rate and we have

$$-\frac{d[\mathrm{Cu}^{++}]_d}{dt} = +\frac{d[\mathrm{Cu}^{++}]_a}{dt} \equiv k_0 \qquad (28)$$

as can be seen from Table 1, entries 1 and 2. Detailed analysis of this steady-state kinetics will be published later.

All the experiments represented in Figure 1 have been realized at an ionic strength of $I = 1.3$ in the donor phase. As a matter of fact, k_{1d} is quite sensitive to ionic strength of the donor phase while k_{2a} is independent of it (Figure 2). This demonstrates clearly the physicochemical asymmetry of the bulk membrane, i.e., the two interfaces, id and ia, have different quality. For this reason, all the kinetics experiments were realized at $I = 1.3$ where both k_{1d} and k_{2a} are insensitive to donor phase composition.

TABLE 1: Kinetic Parameters of Coupled Transport of Copper(II) Ions through Bulk Liquid Membranes[a]

number	C_{do}/C_{Ac}	k_{1d} (h^{-1})	k_{2a} (h^{-1})	kinetic regime
1	8	$(3.87 \pm 0.04)\ 10^{-2}$	$(3.62 \pm 0.02)\ 10^{-2}$	s
2	3.2	$(7.2 \pm 0.1)\ 10^{-2}$	$(7.5 \pm 0.1)\ 10^{-2}$	s
3	0.8	0.417 ± 0.005	0.12 ± 0.01	ns
4	0.4	0.38 ± 0.01	0.09 ± 0.01	ns
5	0.16	0.41 ± 0.02	0.101 ± 0.002	ns
6	0.086	0.44 ± 0.01		ns, om
7	0.047	0.422 ± 0.005		ns, om

[a] Donor phase: initial copper sulfate concentration, $C_{do} = 0.01$ M, $\mathrm{pH}_{\alpha,\omega} = 4.6$, $I = 1.3$; membrane phase: Acorga P-50 in *n*-octane; acceptor phase: 2 M $\mathrm{H_2SO_4}$, $T = 25 \pm 0.1$ °C. s, steady-state kinetics; $k_{1d} = k_{od}$ and $k_{2a} = k_{oa}$; ns, nonsteady-state kinetics; om, over-loaded membrane.

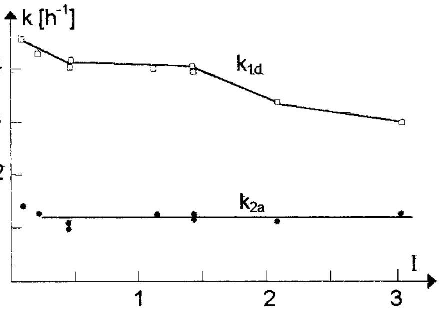


Figure 2. Influence of donor phase ionic strength (I) on the membrane entrance (k_{1d}) and exit (k_{2a}) rate constants. *Donor phase*: C_{do}=0.01 M, $\mathrm{pH}_{\alpha,\omega}$=4.6 (sodium acetate buffer*). Membrane phase:* Acorga P-50 in *n*-octane, C_{Ac}=0.012 M. *Acceptor phase*: 2M $\mathrm{H_2SO_4}$.

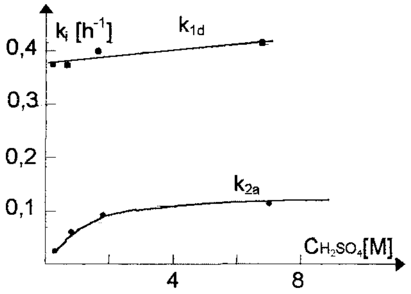


Figure 3. Dependence of membrane entrance (k_{1d}) and exit (k_{2a}) rate constants on acceptor phase acidity (same experimental conditions as for Figure 1b).

According to eq 24, k_{1d} should be independent of donor phase acid concentration $[\mathrm{H}^+]_d$. This is confirmed fairly well by experiment. The negligibly small acid dependence ((log k_{1d})/pH = 0.09) is probably due to the use of different buffers which may affect differently the id interface. Obviously, acceptor phase acidity has no influence either on k_{1d} (Figure 3).

Equation 26 shows that donor phase acidity cannot influence the membrane exit rate constant k_{2a}. On the other hand, acceptor phase acidity has a rather complex influence. Both these predictions were confirmed by experiment. k_{2a} is found to be completely insensitive to $[\mathrm{H}^+]_d$, while its dependence on acceptor phase acidity follows a parabolic saturation curve in full agreement with the mathematical structure of eq 26 (Figure 3). At low acid concentrations, we have $k_{65} \gg k_{67}\ [\mathrm{H}^+]_a$ leading to

$$k_{2a} = \frac{k_{56}}{k_{65}} k_{67}[\mathrm{H}^+]_a \qquad (29)$$

This means that the rate-limiting step of membrane exit is the splitting off of one carrier ligand from the complex CuL_{2ia} (k_{67}), preceded by an equilibrium adsorption step of this copper−carrier complex to the ia interface (k_{56}/k_{65}). On the other hand, at high acidity we have $k_{65} \ll k_{67}\,[H^+]_a$, and the new expression for k_{2a} is

$$k_{2a} = k_{56} \tag{30}$$

It can be seen that now the membrane exit rate is limited only by the diffusion of the copper−carrier complex to the ia interface. At intermediate acidity, the rate-limiting step cannot be clearly defined. In the full acidity range, eq 26 can be linearized in a double reciprocal form

$$\frac{1}{k_{2a}} = \frac{1}{k_{56}} + \frac{k_{65}}{k_{56}k_{67}}\frac{1}{[H^+]_a} \tag{31}$$

Proton activity must be taken into account since high acidity was applied in the acceptor phase. Therefore, Hammett h_o values are used in eq 31 instead of proton concentration.[26] Linearization of the experimental curve represented by Figure 3 gives

$$1/k_{2a} = (7.45 \pm 0.23) + (4.50 \pm 0.07)\,(1/[H^+]_a) \tag{32}$$

$$r = 0.9998; \quad \sigma = 0.35$$

From the intercept, we obtain $k_{56} = 0.13\ h^{-1}$ in excellent agreement with the directly measured value for 2 M H_2SO_4, 0.12 h^{-1}.

This analysis of the influence of donor and acceptor phase acidity on rate constants shows that the quality of interfaces involved may also play an important role in the transport process. This view is confirmed further by the study of carrier concentration effect. Both eqs 24 and 27 suggest that the free carrier concentration in the membrane, $[HL]_m$, should remain constant throughout the kinetic runs. This may well be the case for the zeroth order steady-state kinetics (Figure 1a), but it is certainly not true for the nonsteady-state ones for which $[HL]_m$ should vary roughly inversely with $[CuL_2]_m$ (Figure 1b). Accordingly, k_{1d} should not be constant and this would contradict all experimental observations. Furthermore, eqs 24 and 27 predict a first order dependence of rate constants on carrier concentration in full contradiction with experiment. As a matter of fact, both k_{1d} and k_{2a} are completely independent of carrier concentration (zeroth order dependence) in the concentration range studied (Table 1). This observation is expected for k_{2a} according to eq 26, but it cannot be accounted for by eq 24. It is quite likely that the independence of k_{1d} of carrier concentration is brought about by the saturation of the id interface with respect to carrier molecules. Therefore, the interface structure also must be included explicitly in the kinetic analysis. For this purpose, let P_{id}^{o} be the total concentration of id interface sites available for occupation by the carrier molecules. If the corresponding equilibrium value is P_{id}, the adsorption equilibrium of the carrier to the interface may be written as

$$HL_m + P_{id} \underset{k_{21}}{\overset{k_{12}'}{\rightleftharpoons}} HL_{id} \tag{33}$$

characterized by the adsorption equilibrium constant K_{ad}

$$K_{ad} = \frac{k_{12}'}{k_{21}} = \frac{[HL]_{id}}{[HL]_m P_{id}} = \frac{[HL]_{id}}{[HL]_m(P_{id}^{0} - [HL]_{id})} \tag{34}$$

Recalling that $k_{12}/k_{21} = [HL]_{id}/[HL]_m$ (from eq 8), eq 24 becomes

$$k_{1d} = k_{23}[HL]_{id} \tag{35}$$

With $[HL]_{id}$ calculated from eq 34 this expression leads to

$$k_{1d} = k_{23}P_{id}^{0}\,\frac{K_{ad}[HL]_m}{1 + K_{ad}[HL]_m} \tag{36}$$

It should be noted that this equation is in full agreement with the well-known results of surface adsorption kinetics[9,10] and can be applied at any degree of interface saturation. If $1 \ll K_{ad}[HL]_m$, a very simple expression can be obtained for k_{1d},

$$k_{1d} = k_{23}P_{id}^{o} \tag{37}$$

which shows complete independence of carrier concentration, in full agreement with experiment. On the other hand, if $1 \gg K_{ad}[HL]_m$, eq 36 gives eq 24 with $k_{12} = k_{12}'P_{id}^{o}$. It is interesting to note that if the interface saturation is considered from the very beginning in the derivation of eq 18, the general character of this latter is lost since eq 37 is obtained directly without the possibility of including the case of zeroth-order kinetics.[27]

It appears that in all nonsteady-state experiments presented here the id interface is saturated with respect to the carrier. This observation is strongly supported by previous findings;[9,20] surface saturation occurs at $[HL]_m > 0.01$ M.

The situation is completely different for zeroth-order steady-state kinetics (Table 1). Here, relatively low carrier concentrations were used (high C_{do}/C_{Ac}) which were not sufficient to saturate the interface. Accordingly, the rate constant k_0 seems to show a roughly first order dependence on carrier concentration, in agreement with eq 27 (Table 1). The confirmation of this observation would require more detailed kinetic analysis (see above).

The above results show clearly that the study of carrier concentration effects is complicated by interface phenomena. Further complications may arise when using too high a carrier concentration; membrane viscosity may change considerably and also the membrane exit step may become reversible (Figure 1c). On the contrary, if the carrier concentration is too low, the reaction order is changed with respect to copper ions. Therefore, one must be careful when comparing results obtained in different experimental conditions.

It can be seen from the kinetic curves (Figure 1a,b) that at the end of the kinetic runs the copper ions underwent a virtually complete translocation from the donor to the acceptor phase. This transport against the concentration gradient was possible since the copper ion transport is coupled with the transport of protons in the opposite direction, having a much greater concentration gradient. At the end of the kinetic run, the membrane entrance and exit rates are equal to zero. Therefore, eqs 18 and 20 allow the expression for the overall equilibrium constant to be obtained,

$$K = \frac{k_{12}k_{23}k_{34}k_{45}k_{56}k_{67}k_{78}k_{81}}{k_{21}k_{32}k_{43}k_{54}k_{65}k_{76}k_{87}k_{18}} = \frac{[Cu^{++}]_a[H^+]_d^{\,2}}{[Cu^{++}]_d[H^+]_a^{\,2}} \tag{38}$$

from which one can establish the coupling relationship between the copper and proton fluxes,

$$\frac{[Cu^{++}]_a}{[Cu^{++}]_d} = K\,\frac{[H^+]_a^{\,2}}{[H^+]_d^{\,2}} \tag{39}$$

This equation means that in order to realize efficient copper removal (i.e., $[Cu^{2+}]_a \gg [Cu^{2+}]_d$), a significantly higher proton gradient must be applied across the membrane in the opposite direction (i.e., $[H^+]_a \gg [H^+]_d$). Let us note that if the membrane is physicochemically symmetrical (a general assumption used frequently in the literature), the rate constants of the corresponding elementary steps involved on both sides of the membrane are equal; $k_{12} = k_{18}$, $k_{23} = k_{87}$, $k_{34} = k_{76}$, etc. In this case, $K = 1$ and the corresponding coupling relationship becomes identical with that obtained previously by using Fick's first law for the analysis of the transport process.[23]

Conclusions

The present work shows that an approach based on chemical kinetics can be applied successfully to the quantitative analysis of transport kinetics if interface phenomena are appropriately taken into account. The obtained rate equations in nonsteady-state situation are quite general and remain valid for a large variety of kinetic regimes. The parabolic dependence of membrane entrance rate on copper concentration in the donor phase appears explicitly (eq 21), leading to first-order kinetics with respect to copper at low copper concentration and to zeroth-order kinetics at high copper concentrations. This latter case corresponds also to a steady-state kinetic regime. This saturation behavior is completely analogous to the Michaelis−Menten kinetic law valid for enzyme catalyzed reactions. However, the equation presented here is not limited to initial rates but it is valid in the whole kinetic run within the irreversibility hypothesis. It appears that initial rates cannot be used to characterize the whole transport process.[28] The different sensitivity to aqueous phase acidity of the membrane entrance and exit rate constants could be also explained using the same equations and by taking into account the physicochemical quality of the aqueous-phase/membrane interfaces.

Apart from carrier saturation by copper at the id interface (zeroth-order kinetics), the occurrence of another type of saturation, namely, the interface saturation by the carrier molecules (first-order kinetics), could be used to explain that carrier concentration has no kinetic effect in the investigated concentration range. The proposed kinetic equations can also explain quite naturally the change of molecular mechanism and that of rate-limiting steps with experimental conditions. It should be noted finally that the main conclusions of this study devoted to copper transport through bulk liquid membranes are in complete agreement with those obtained from copper extraction and re-extraction studies using different techniques.[11]

Experimental Section

Materials. Copper(II) sulfate pentahydrate (Aldrich >99.99%), sodium sulfate (Aldrich >99%), Acorga P-50 (Acorga Ltd., 94% 5-nonylsalicylaldoxime in kerosene), *n*-octane (Janssen >99%), sulfuric acid (Aldrich >99%), sodium formate, and acetate buffers were used without further purification. The aqueous solutions were made up using demineralized water.

Kinetic Procedure. All the transport experiments were realized by using the apparatus, sampling, and analytical methods, numerical analysis, and computation procedure described previously.[19] The experimental conditions used for the different kinetic runs were as follows.

Donor Phase. Aqueous solutions of $CuSO_4$, $C_{do} = 0.01$ M, were buffered at different pH values (initial $pH_\alpha \approx$ final pH_ω $= pH_{\alpha,\omega}$), and their ionic strength was controlled by Na_2SO_4. The actual conditions were the following: ($pH_{\alpha,\omega} = 4.6$) sodium acetate/acetic acid buffer, $C_{salt}/C_{acid} = 0.1$ M/0.1 M, $C_{sodiumsulfate} = 0.4$ M, $I = 1.3$; ($pH_{\alpha,\omega} = 3.5$) sodium formate/formic acid buffer, $C_{salt}/C_{acid} = 0.13$ M/0.13 M, $C_{sodiumsulfate} = 0.4$ M, $I = 1.3$; ($pH_{\alpha,\omega} = 2.5$) sodium formate/formic acid buffer, $C_{salt}/C_{acid} = 0.05$ M/0.45 M; $C_{sodiumsulfate} = 0.4$ M, $I = 1.1$. All the chosen ionic strength values are situated in the interval $I = 0.5-1.5$ in which the kinetics is not sensitive to phase composition (see Figure 2).

Membrane Phase. Acorga P-50 (94% in kerosene) was dissolved in *n*-octane. The carrier concentrations used fall in the range of $C_{Ac} = 10^{-3}-0.2$ M (see Table 1). Control tests have shown that the presence of 6% kerosene has no effect at all on the kinetics.

Acceptor Phase. The acceptor phase was made up of an aqueous solution of sulfuric acid $C_{acid} = 0.1-2$ M.

All three phases were stirred magnetically.[19] Samples were taken from both aqueous phases at regular time intervals and analyzed by EDTA titration using murexide as indicator (error <2%).

Concentration variations caused by the volume changes due to sampling were corrected using the following equations:

$$R_{ai}{}^{cor} = R_{ai} + \Delta R_{ai}$$

$$R_{di}{}^{cor} = R_{di} + \Delta R_{di}$$

$$\Delta R_{ai} = \frac{v_p[\sum_{j=1}^{j=i-1} C_{aj} - (i-1)C_{ai}]}{C_{d0}V_{d0}};$$

$$\Delta R_{di} = \frac{v_p\{\sum_{j=1}^{j=i-1} C_{dj}\exp[-k_1(t_i - t_j)] - (i-1)C_{di}\}}{C_{d0}V_{d0}}$$

where: R_{fi} and C_{fi} are the reduced and actual concentrations of copper ions in phase f (donor, d, or acceptor,a) at time i (or j),respectively; v_p is the volume of the samples (cm^3) taken during the kinetic runs; V_{do} represents the initial volume (cm^3) of the donor phase.

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