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On the Mechanism of Coupled Transport of Cu(II) Ions Through Bulk Liquid Membranes

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ABSTRACT

Transport of Cu(II) ions through liquid membranes using 5-nonylsalicylaldoxime as a carrier implies the presence of a 1 : 2 metal–carrier complex. The mechanism of formation of this latter is examined in the light of two possible alternatives. It is shown that chemical kinetics alone does not allow to settle the problem.

Key Words: Cu(II) ions; Metal–carrier complex; Liquid membranes; Membrane interface.

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INTRODUCTION

Transport of copper(II) ions through liquid membranes as well as their extraction process are known to involve several elementary steps.[1–3] The intervention of both bulk and interface species makes it difficult to establish the corresponding mechanism at the molecular level.

When 5-nonylsalicylaldoxime is used as carrier in transport or as extractant in extraction (HL), the penetration of copper(II) ions into the organic phase (membrane) requires the formation of an 1 : 2 complex between the metal ions and the complexing agent (CuL_2). Apparently, general agreement exists as to the formation of the 1 : 1 complex intermediate (CuL^+). It is believed that this latter is formed at the aqueous donor (d) and acceptor (a) phase/membrane interfaces (id: donor interface and ia: acceptor interface; see also Sch. 1) between carrier molecules present in the interface (HL_{id} and HL_{ia}) and copper(II) ions coming from the aqueous phases.[1–5] The attachment of a second molecule of HL to the 1 : 1 complex (CuL^+) is more controversial. As a matter of fact, the second complexing molecule may come either from the aqueous donor and acceptor phases where it appeared by partitioning from the organic phase,[1,4] or directly from the membrane (m) phase.[3,5]

The majority of investigators seem to favor the first alternative, despite the high hydrophobicity and very low water solubility of the carrier molecules.[1] On the other hand, a detailed kinetic analysis was published recently based on the second alternative.[3] Therefore, it seems important to examine whether the kinetic approach is able to settle this problem since the kinetic equations obtained [3] are quite general. They account successfully for the different experimental observations in the concentration ranges studied: steady- and nonsteady-state cases, switches from one to zero of the kinetic order with respect to copper, insensitivity of the membrane entrance rate to aqueous donor phase acidity, interface saturation effects, and different behavior of membrane entrance and exit rates.

In the present article, we examine whether these general conclusions remain valid when the first mechanistic alternative is used to establish the kinetic equations, i.e., when the second complexing molecule comes from the aqueous phases.

EXPERIMENTAL

All the experimental results used in the present work were obtained from experiments described previously.[3] For actual experimental details (apparatus, composition of the three phases involved, and kinetic procedure) see Szpakowska and B.Nagy.[3]

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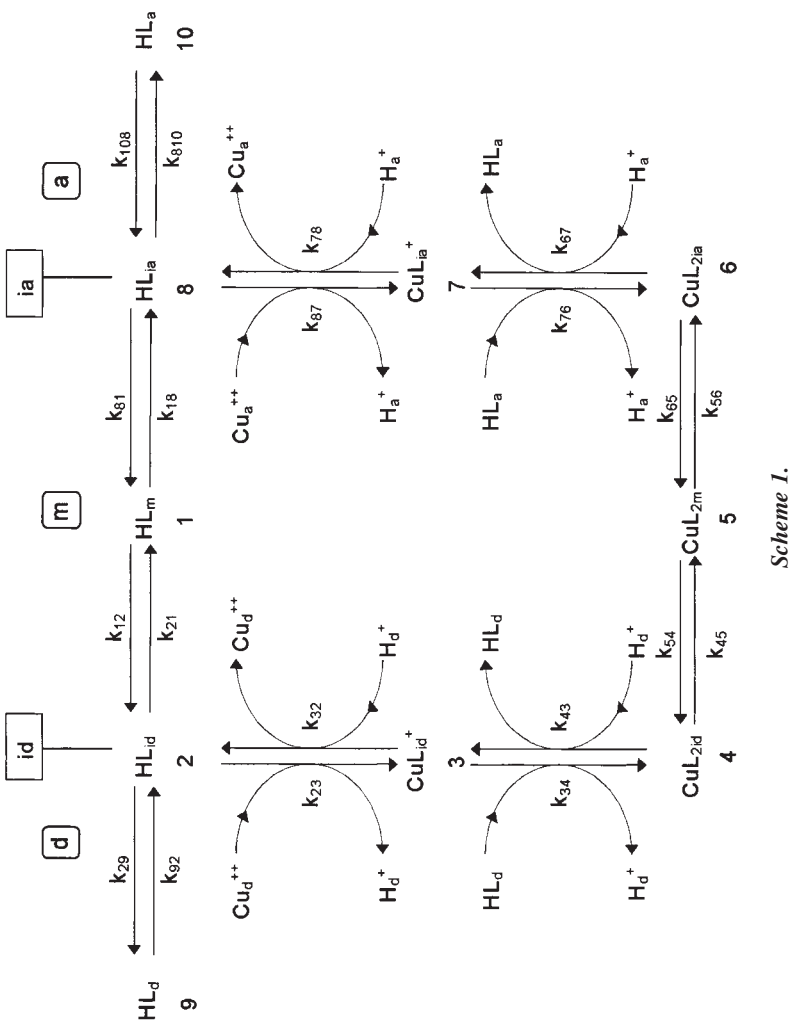

Scheme 1.

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RESULTS AND DISCUSSION

As it was shown previously, the facilitated transport of Cu(II) ions through bulk liquid membranes may be represented formally as a consecutive, irreversible first-order reaction:

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

$Cu_{(d)}$ and $Cu_{(a)}$ represent copper ions in the aqueous donor and aqueous acceptor phases, respectively, while $Cu_{(m)}$ is the copper–carrier complex in the liquid membrane phase. k_{1d} and k_{2a} are the apparent first-order rate constants for the membrane entrance and the membrane exit steps, respectively.

The time-evolution of the various copper ion species may be expressed by the following differential equations:

$$\frac{dC_d}{dt} = -k_{1d}C_d \quad (2)$$

$$\frac{dC_m}{dt} = k_{1d}C_d - k_{2a}C_m \quad (3)$$

$$\frac{dC_a}{dt} = k_{2a}C_m \quad (4)$$

where C_x represents copper ion concentrations (in M units) in the various phases (x = d, m, a). Straight forward integration of these equations allowed the determination of the apparent rate constants k_{1d} and k_{2a}.[3] However, their detailed form must be known for establishing the actual transport mechanism at the molecular level.

For this purpose, the following mechanistic scheme is proposed (see Sch. 1).

Scheme 1 is very similar to that previously published[3] except for two mechanistic details. First, partitioning of the carrier HL is allowed at both aqueous phase/membrane interfaces, leading to the appearance of HL in the donor (HL_d) and the acceptor (HL_a) aqueous phases. Second, these aqueous carrier species (HL_d and HL_a) are responsible for the formation of the 1 : 2 metal–carrier complexes (CuL_{2id} and CuL_{2ia}).

In elaborating this scheme, it was supposed that each metal–carrier reaction takes place at the water/membrane interfaces (donor phase/membrane interface, id; acceptor phase/membrane interface, ia) between species present already at the interfaces and those coming from the bulk.

It can be seen that the whole transport process is broken up into a series of coupled elementary steps. The various rate constants k_{ij} designate the

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transformations of species i into species j, while k_{ji} represents the corresponding reaction in the reverse direction.

Scheme 1 shows that the monobasic carrier Acorga P-50 is partitioned between the bulk membrane (HL_m) and the membrane/aqueous phase interfaces (HL_{id} and HL_{ia}) on one hand and between these interfaces and the bulk aqueous phases (HL_d and HL_a) on the other:

$$\underset{1}{HL_m} \underset{k_{21}}{\overset{k_{12}}{\rightleftarrows}} \underset{2}{HL_{id}} \tag{5}$$

$$\underset{1}{HL_m} \underset{k_{81}}{\overset{k_{18}}{\rightleftarrows}} \underset{8}{HL_{ia}} \tag{6}$$

$$\underset{2}{HL_{id}} \underset{k_{92}}{\overset{k_{29}}{\rightleftarrows}} \underset{9}{HL_d} \tag{7}$$

$$\underset{8}{HL_{ia}} \underset{k_{108}}{\overset{k_{810}}{\rightleftarrows}} \underset{10}{HL_a} \tag{8}$$

Copper(II) ions are extracted from the aqueous donor phase (Cu_d^{2+}) to the id interface by the carrier molecules HL_{id} according to the equilibrium:

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

The intermediate complex CuL_{id}^{+} reacts with a second carrier molecule, which is originating this time from the bulk aqueous donor phase:

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

This step represents the main mechanistic difference with the previously published transport scheme. It should be recalled that there, the second carrier molecule came from the membrane phase. The present work tries to establish whether a formal kinetic analysis allows one to distinguish the two mechanistic possibilities.

Further mechanistic steps imply the desorption of the neutral complex CuL_{2id} into the membrane phase (CuL_{2m}) and adsorption to the aqueous acceptor phase/membrane interface (CuL_{2ia}), as shown clearly by Sch. 1. The complex CuL_{2ia} undergoes a stepwise decomposition at the ia interface according to a mechanism that is just the reverse of the formation of CuL_{2id}.

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Finally, the Cu(II) ions are released into the aqueous acceptor phase (Cu_a^{2+}). The free carrier molecules HL_m return to the aqueous donor phase/membrane interface to begin a new transport cycle.

The entering of Cu(II) ions into the membrane obeys the following rate equation:

$$-\frac{d[Cu^{2+}]_d}{dt} = \frac{d[CuL_2]_m}{dt} = k_{45}[CuL_2]_{id} - k_{54}[CuL_2]_m \tag{11}$$

Supposing that quasi-steady state approximation applies for interface species we can write:

$$[CuL_2]_{id} = \frac{k_{34}[CuL^+]_{id}[HL]_d + k_{54}[CuL_2]_m}{k_{43}[H^+]_d + k_{45}} \tag{12}$$

Proceeding the same way for the other interface species (CuL_{id}^+ and HL_{id}) and substituting the obtained steady-state values into the kinetic equation [Eq. (11)], we obtain the following rate equation for the membrane entrance step:

$$V_{dm} = -\frac{d[Cu^{2+}]_d}{dt} = \frac{(A[HL]_m[HL]_d + B[HL]_d{}^2)[Cu^{2+}]_d - (C+D)[H^+]_d{}^2\ [CuL_2]_m}{(E+F)[H^+]_d{}^2 + (G+J)[H^+]_d + (K+M+N[Cu^{2+}]_d)[HL]_d} \tag{13}$$

where:

$$A = k_{12}k_{23}k_{34}k_{45}; \quad B = k_{23}k_{34}k_{45}k_{92}; \quad C = k_{21}k_{32}k_{43}k_{54};$$
$$D = k_{32}k_{43}k_{54}k_{29}; \quad E = k_{21}k_{32}k_{43}; \quad F = k_{32}k_{43}k_{29};$$
$$G = k_{21}k_{32}k_{45}; \quad J = k_{32}k_{45}k_{29}; \quad K = k_{21}k_{34}k_{45};$$
$$M = k_{34}k_{45}k_{29}; \quad \text{and} \quad N = k_{23}k_{34}k_{45}$$

Completely identical analysis gives the corresponding expression for the membrane exit step.[3] In particular, the exit of Cu(II) ions from the membrane into the aqueous acceptor phase may be expressed by the rate equation:

$$\frac{d[Cu^{2+}]_a}{dt} = -\frac{d[CuL_2]_m}{dt} = k_{56}[CuL_2]_m - k_{65}[CuL_2]_{ia} \tag{14}$$

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Again, applying the quasi-steady state approximation to the interface species, the following kinetic equation is obtained for the membrane exit step:

$$V_{ma} = \frac{d[Cu^{2+}]_a}{dt} = \frac{(A+B)[H^+]_a{}^2[CuL_2]_m - (C[HL]_a[HL]_m + D[HL]_a{}^2)[Cu^{2+}]_a}{(E+F)[H^+]_a{}^2 + (G+J)[H^+]_a + (K+M+N[Cu^{2+}]_a)[HL]_a} \quad (15)$$

where:

$A = k_{81}k_{78}k_{67}k_{56}$; $B = k_{78}k_{67}k_{56}k_{810}$; $C = k_{18}k_{87}k_{76}k_{65}$;
$D = k_{87}k_{76}k_{65}k_{108}$; $E = k_{81}k_{78}k_{67}$; $F = k_{78}k_{67}k_{810}$;
$G = k_{81}k_{78}k_{65}$; $J = k_{78}k_{65}k_{810}$; $K = k_{81}k_{76}k_{65}$;
$M = k_{76}k_{65}k_{810}$; and $N = k_{87}k_{76}k_{65}$

It can be seen that the relatively small mechanistic modification introduced in the present transport scheme brings about a considerable increase of the complexity of the rate equations. Actually, they contain almost twice as many constants as the previously published rate laws.[3]

Again, if the mechanistic steps leading to the formation of CuL_{2id} and to the decomposition of CuL_{2ia} may be considered as essentially irreversible, i.e., $k_{32} = k_{43} \approx 0$ and $k_{87} = k_{76} \approx 0$, respectively, Eqs. (13) and (15) take the following much simpler forms [Eqs. (16) and (17)]:

$$V_{dm} = \frac{(k_{12}k_{23}[HL]_m + k_{23}k_{92}[HL]_d)[Cu^{2+}]_d}{k_{21} + k_{29} + k_{23}[Cu^{2+}]_d} \quad (16)$$

$$V_{ma} = \frac{(k_{81}k_{67}k_{56} + k_{67}k_{56}k_{810})[H^+]_a[CuL_2]_m}{(k_{81}k_{67} + k_{67}k_{810})[H^+]_a + (k_{81}k_{65} + k_{65}k_{810})} \quad (17)$$

Accordingly, the first-order membrane entrance rate constant is given by Eq. (18):

$$k_{1d} = \frac{k_{12}k_{23}[HL]_m + k_{23}k_{92}[HL]_d}{k_{21} + k_{29}} = \left(\frac{k_{12}k_{23}}{k_{21} + k_{29}} + \frac{k_{23}k_{92}}{k_{21} + k_{29}} \cdot \frac{[HL]_d}{[HL]_m}\right)[HL]_m \quad (18)$$

Considering that $[HL]_{id}/[HL]_m = k_{12}/k_{21}$ and $[HL]_{id}/[HL]_d = k_{92}/k_{29}$ we obtain, after some algebra,

$$k_{1d} = \frac{k_{12}}{k_{21}}k_{23}[HL]_m \quad (19)$$

This expression is identical to Eq. (24) of Ref.[3]. In other words, it can account completely for the influence of carrier concentration on the

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membrane entrance rate when the interface properties are properly taken into account.[3]

On the other hand, the zeroth order membrane entrance rate constant is Eq. (20)

$$k_0 = k_{12}[\mathrm{HL}]_\mathrm{m} + k_{92}[\mathrm{HL}]_\mathrm{d} = \left(k_{12} + k_{92}\frac{[\mathrm{HL}]_\mathrm{d}}{[\mathrm{HL}]_\mathrm{m}}\right)[\mathrm{HL}]_\mathrm{m} \tag{20}$$

Using the same transformation as for Eq. (18) above, we obtain

$$k_0 = k_{12}\left(1 + \frac{k_{29}}{k_{21}}\right)[\mathrm{HL}]_\mathrm{m} \tag{21}$$

This equation is different from Eq. (27) of Ref.[3] ($k_0 = k_{12}[\mathrm{HL}]_\mathrm{m}$). However, these equations cannot be distinguished chemically since the difference is based only on the interpretation of the constant obtained.

The membrane exit rate constant is

$$k_{2a} = \frac{(k_{81}k_{67}k_{56} + k_{67}k_{56}k_{810})[\mathrm{H}^+]_\mathrm{a}}{(k_{81}k_{67} + k_{67}k_{810})[\mathrm{H}^+]_\mathrm{a} + (k_{81}k_{65} + k_{65}k_{810})} \tag{22}$$

that becomes after simplification

$$k_{2a} = \frac{k_{56}k_{67}[\mathrm{H}^+]_\mathrm{a}}{k_{65} + k_{67}[\mathrm{H}^+]_\mathrm{a}} \tag{23}$$

This equation is identical with the corresponding Eq. (26) of Ref.[3]. It shows a complex dependence of membrane exit rate on the acceptor phase acidity and a total absence of the influence of the donor phase acidity. These predictions were fully borne out by experiment.[3]

CONCLUSIONS

It can be seen that, except for the indistinguishable case of k_0 [Eq. (21)], the same kinetic laws are obtained for the previously published and the presently considered mechanistic alternatives. In other words, the new kinetic equations can also account for the experimental results published previously.[3] Therefore, whether the second carrier molecule comes from the membrane or from the aqueous donor and acceptor phases cannot be established by using only a chemical kinetic approach.

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