ADDITIONS AND CORRECTIONS

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Maria Szpakowksa,* Otto B. Nagy and Stefan Màtéfy-Tempfli: Chemical Kinetic Approach to the Mechanism of Coupled Transport of Cu(II) Ions through Bulk Liquid Membranes

To understand better the functioning of copper(II) ion transport through bulk liquid membranes, a detailed mechanistic scheme has been proposed at the molecular level.[1] The experimental results could be successfully accounted for in terms of the kinetics of two consecutive irreversible reactions.[1,2] Since reversibility or irreversibility of the kinetics steps influence transport efficiency, it seemed important to reanalyze the problem using a more general kinetic scheme based on two consecutive reversible reactions

$$Cu_d \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} Cu_m \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} Cu_a \qquad (1)$$

Cu_i with i = d, m, a, represents copper ions in the donor (d), membrane (m), and acceptor (a) phases, respectively. The corresponding kinetic equations could be readily integrated.[3] The various rate constants, k_i with $i = 1, -1, 2, -2$, were obtained by iterative nonlinear curve fitting of the integrated equations to the experimental data using an appropriate computer program that we have developed for this purpose. The results are collected in Table 1.

It can be seen that in almost all cases the membrane entrance step is reversible, i.e., $k_{-1} \neq 0$ (except for entries 2 and 4), the reverse step always being less important: $k_1 > k_{-1}$. On the other hand, the membrane exit step remains irreversible, i.e., $k_{-2} = 0$ (except for entries 3 and 7). This latter observation is a direct consequence of the high proton gradient of the transport system which is powerful enough to impose full irreversibility. Entries 2 and 11 show that higher stirring speed of the donor phase allows suppression of the reversibility of the membrane entrance step.

The new analysis confirms the previously obtained conclusions.[1,2] In general, $k_1 > k_2$, except for entries 2 and 6. Furthermore, increasing viscosity, polarity, and polarizability of the membrane material brings about a systematic decrease of each rate constant. It is interesting to note that viscosity has the least influence on k_{-1}. This reverse step is the most affected by polarity and polarizability. Therefore, it is suggested that using a membrane material of high polarity and polarizability together with an appropriately high stirring speed would allow reduction or even suppression of the reversibility of the whole transport process, thereby increasing transport efficiency.

References and Notes

(1) Szpakowska, M.; Nagy, O. B. *J. Phys. Chem. A* **1999**, *103*, 1553−1559.

(2) Szpakowska, M.; Nagy, O. B. *J. Membrane Sci.* **1991**, *64*, 129−143.

(3) Frost, A. A.; Pearson, R. G. *Kinetics and Mechanism*; John Wiley & Sons: New York, 1961.

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TABLE 1: Kinetic Parameters for Coupled Transport of Cu(II) through Various Liquid Membranes (T = [25 ± 0.1] °C)

no	membrane material[a]	$k_1 \cdot 10^2$ [b]	$k_{-1} \cdot 10^2$ [b]	$(k_{-1}/k_1) \cdot 10^2$ [d]	$k_2 \cdot 10^2$ [b]	$k_{-2} \cdot 10^2$ [b]	η[e]	$[(n^2-1)/(n^2+2)] \cdot 10^2$ [e]	$[(\epsilon-1)/(2\epsilon+1)] \cdot 10^2$ [e]
1	methylcyclohexane	8.2	3.1	37.8	6.7		0.72	24.47	20.24
2	*n*-octane	11.2			12.5		0.548	24.11	19.36
		(11.1)[c]			(12.6)[c]				
3	kerosene (Aldrich)	7.7	0.8	10.4	3.2	0.1	0.739	26.48	
4	kerosene (Fluka)	7.7			5.6		0.856	26.35	
		(7.8)[c]			(5.6)[c]				
5	isopropylbenzene	5.9	3.1	52.5	1.5		0.790	28.96	23.98
6	2-chlorobutane	5.3	3.4	64.2	6.7		0.457	23.97	40.12
7	*n*-decane	19.3	1.2	6.2	9.7	0.9	0.907	24.88	19.92
8	*n*-dodecane	15.6	0.7	4.5	6.2		1.504	25.38	20.19
9	*n*-tetradecane	17.8	0.7	3.9	5.9		2.180	25.47	20.44
10	*n*-hexadecane	16.4	0.7	4.3	3.7		3.44	26.06	20.61
11	*n*-octane	16.2	11.6	71.6	6.3				

[a] Membrane stirring speed: 250 rpm (entries 1−6) and 200 rpm (entries 7−11). [b] All rate constants in hr^{-1} units. [c] Values obtained with irreversibility approximation.[2] [d] Degree of reversibility in %. [e] ϵ, dielectric constant (20 °C); n, refractive index (20 °C); η, viscosity (cP); values from ref 2.