CHEMISTRY AND BIOLOGY ARE TWO DISTINCTIVE CULTURES AND THE RIFT BETWEEN THEM IS SERIOUS, GENERALLY UNAPPRECIATED, AND COUNTERPRODUCTIVE.

from: A. Kornberg, The Two Cultures: Chemistry and Biology, *Biochemistry*, 26, 6889 (1987).

ORGANIC CHEMISTRY has been enriched by more than a century of impressive achievements. Organic chemists... belong to a proud and venerable science. The problem was that organic chemists place arbitrary boundary on their science. Although, in the pursuit of natural products they might still eagerly seek the challenge of an Amazonian butterfly pigment, they would not accept nucleic acid, proteins, and enzymes as proper natural products.

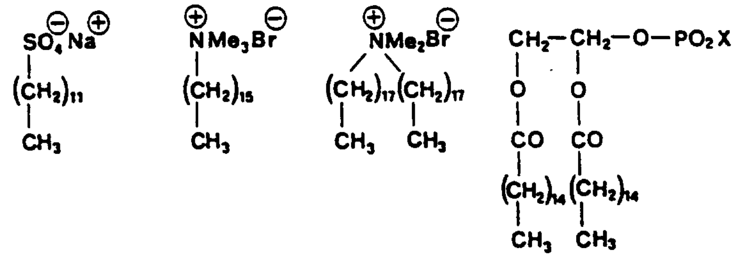
from: A. Kornberg, The Two Cultures: Chemistry and Biology, *Biochemistry*, 26, 6889 (1987)

Molecular Components of an E.coli cell (%)

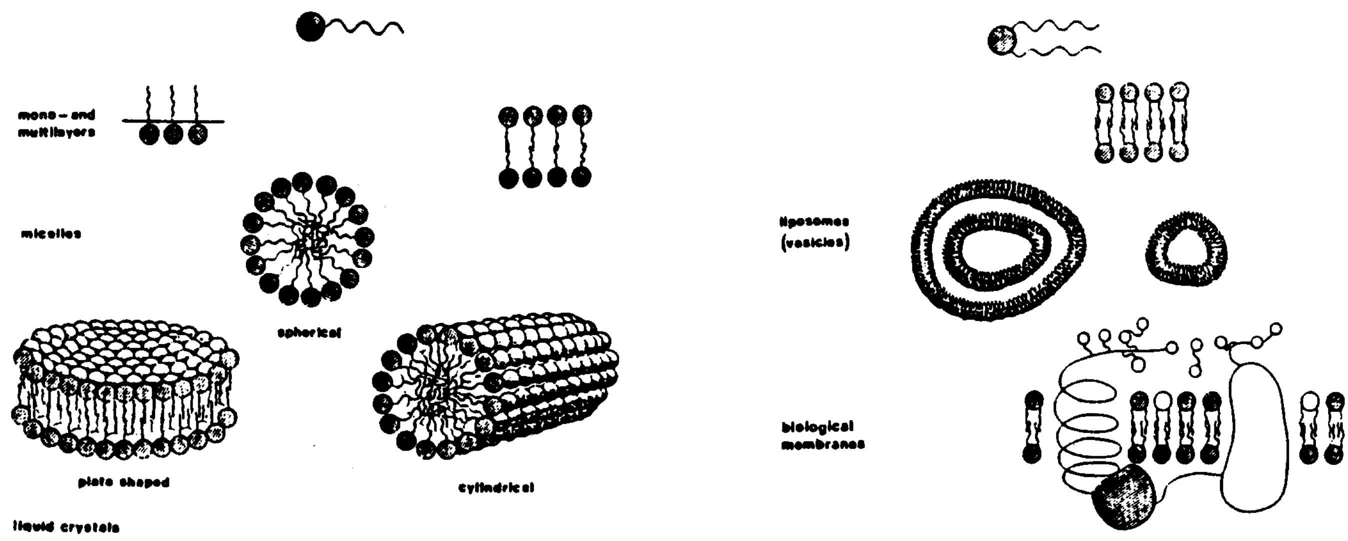
water	70
organic material*	29
inorganic material	1

*proteins (15), nucleic acids (7) polisaccharides (3), lipids (2)

from: A.L.Lehninger, "Principles of Biochemistry" Worth Pub. (1982)



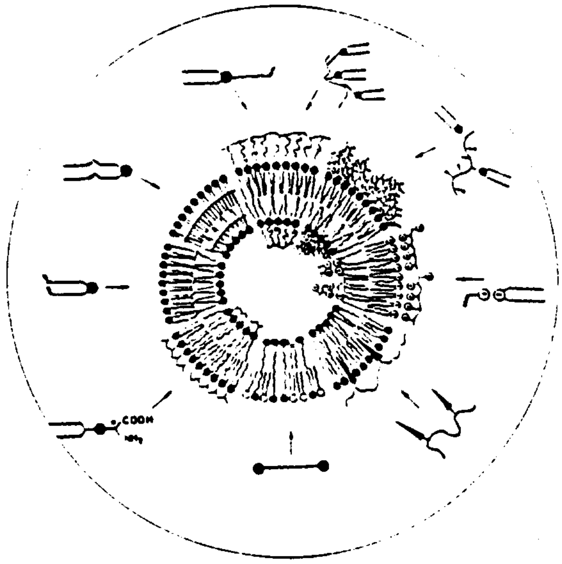
SDS CTABr DODAC



ANGEWANDTE CHEMIE

International Edition in English

Volume 27 · Number 1
January 1988
Pages 113-158

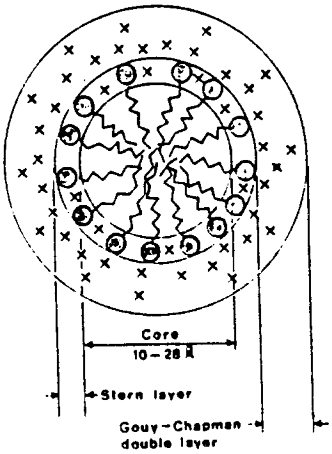


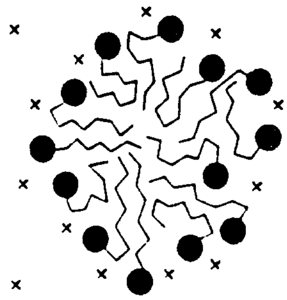
Helmut Ringsdorf, Bernhard Schlarb, and Joachim Venzmer

Molecular Architecture and Function of Polymeric Oriented Systems: Models for the Study of Organization, Surface Recognition, and Dynamics of Biomembranes

FUNCTIONALIZED AMPHIPHILIC SYSTEMS

1. Reactivity
2. Selectivity
3. Transport





Reactivity of Organic Systems in Aqueous Micelles.

G.S. Hartley, *Quart. Rev.*, 2, 152 (1948).

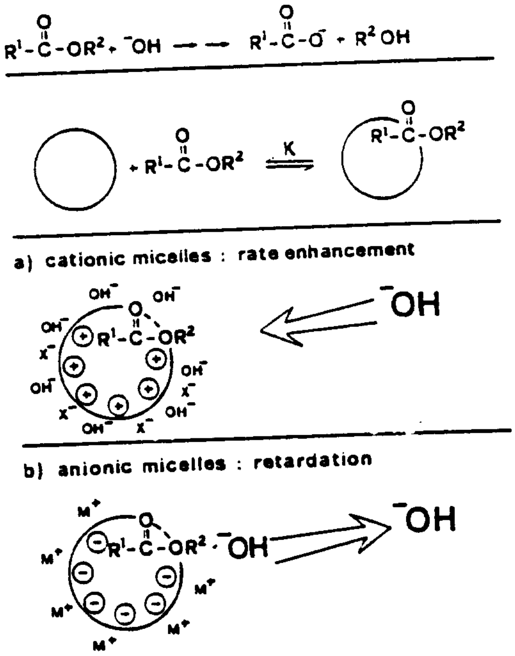
E.F. Duynstee and E. Grunwald, *J. Amer. Chem. Soc.*, 81, 4540 (1959).

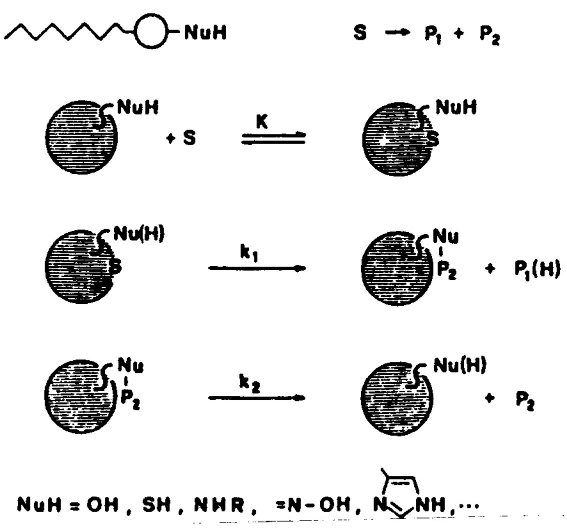
J.H. Fendler, "Membrane Mimetic Chemistry", Wiley Interscience, New York (1982).

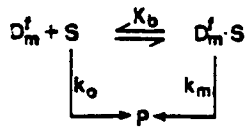
L.S. Romsted, in "Surfactants in Solution", K.L. Mittal and B. Lindman, Eds., vol. 2, Plenum Press, New York, 1015 (1984).

C.A. Bunton and G. Savelli, *Adv. Phys. Org. Chem.*, 22, 213 (1986).

and references therein.

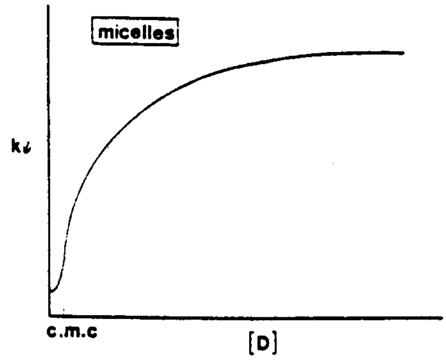






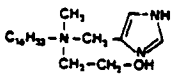
$$k_\psi = \frac{k_o + (k_m/\bar{V})\,K_b\,[D_m^f]}{1 + K_b\,[D_m^f]} = \frac{k_o + k_c\,[D_m^f]}{1 + K_b\,[D_m^f]}$$

R. Fornasier et. al. J.C.S. Faraday I, 76, 1301 (1980)



	k_c PNPA	k_c PNPH	10^{-4} x $k_{turnover}$ [b] (PNPH)
1. $[C_{16}]$ – $\overset{\oplus}{N}(Me)_2$–$(CH_2)_2$–OH	0.15	1.8	–
2. $[C_{16}]$ – CO–N(Me)–OH	300	2600	–
3. $[C_{16}]$ – $\overset{\oplus}{N}(Me)_2$–C(Ph)=N–OH	305	2500	–
4. $[C_{16}]$ – $\overset{\oplus}{N}(Me)_2$–CO–C(Ph)=N–OH	2420	~ 22000	–
5. $[C_{16}]$ – $\overset{\oplus}{N}(Me)_2$–$(CH_2)_2$–SH	650	4500	–
6. $[C_{16}]$ – $\overset{\oplus}{N}(Me)_2$–$(CH_2)_2$–$NH_2$	0.9	18	–
7. $[C_{16}]$ – CO–NH–CH(COOH)–CH_2–IM	6.5	52	55
8. $[C_{16}]$ – $\overset{\oplus}{N}(Me)_2$–$CH_2$–IM	8	290	35
9. $[C_{16}]$ – $\overset{\oplus}{N}(Me)_2$–$(CH_2)_2$–NH–CO–IM	28	1200	50
10. $[C_{16}]$ – $\overset{\oplus}{N}(Me)$–CH_2–IM (CH_2–CH_2–OH)	7.1	210	38
11. α – chymotrypsin	2000	–	140 [c]

[a] $[C_n] = n$-C_nH_{2n+1} ; IM = imidazolyl (N, NH). [b] Where not shown, $k_t < 3\ s^{-1}$. [c] With PNPA

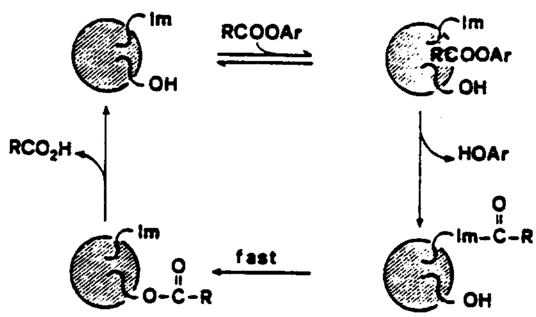


substrate : PNPH

pH 8.0

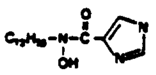
25°C, $k_{turnover}$ = 38 s^{-1}

α – chymotrypsin, 25°C, $k_{turnover}$ = 140 s^{-1}



R.A. Moss et al., J.A.C.S., 100, 5920 (1977)

U. Tonellato, J.C.S. Perkin II, 821 (1977)



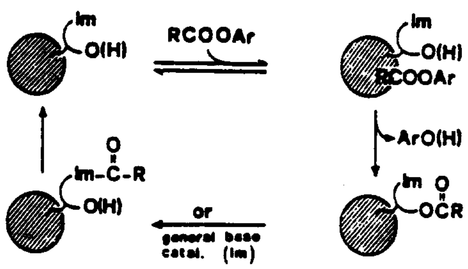
+ CTABr

substrate : PNPA

pH 8.8

30°C, $K_{turnover}$ = 380 s^{-1}

α – chymotrypsin, 25°C, $K_{turnover}$ = 150 s^{-1}



T. Kunitake et al., J.A.C.S., 98, 7799 (1976)

Main Factors Responsible for the Reactivity in Functionalized Micelles

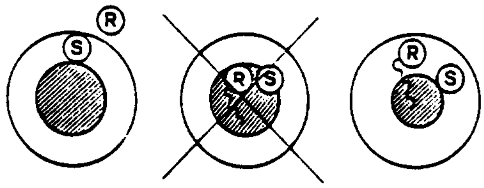
1. Concentration Effect (K_b)
2. Electrostatic Effects, ionic micelles, (pK_a)
3. Medium Effect : found not relevant

(C.A. Bunton et al., 1979 ; Fornasier & U.T., 1980)

Micellar reagent	Model	Substrate	k^2_m/k^2_w	ref
$C_{16}H_{33}\overset{+}{N}Me_2CH_2Im$	$Me_3\overset{+}{N}CH_2Im$	PNPH	1.9	a
		$(PhO)_2POOpNP$	0.5	b
$C_{16}H_{33}\overset{+}{N}Me_2CH_2CH_2OH$	$Me_3\overset{+}{N}CH_2CH_2OH$	PNPH	0.15	a
		PhCOOpNP	2	c
		$(PhO)_2POOpNP$	0.25	c

Im = pNP =

a R.Fornasier, U.Tonellato, J.C.S. Faraday T.I, 76, 1301 (1980) ; b J.C. Brown et.al., J.Org.Chem., 45, 4169 (1980) ; c G.Biresaw et.al., J.A.C.S., 106, 7178 (1984)

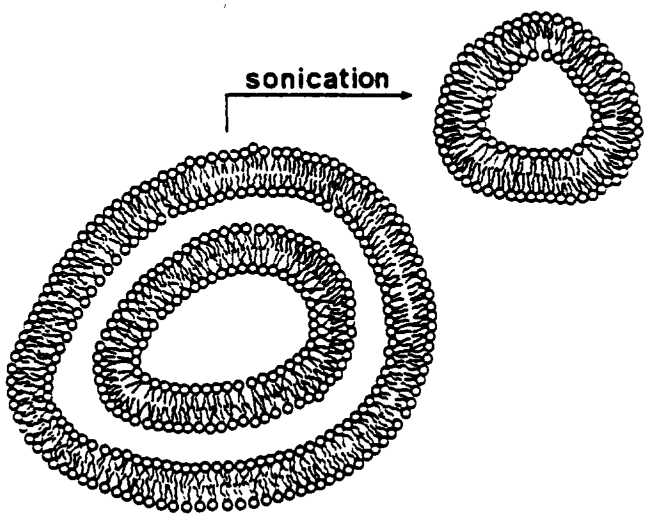


Enantioselectivity

Surfactant	Substrate	k_{fast}/k_{slow}	
$C_{12}H_{25}$-CH-CO-NH-CH-CH_2Im, with $(CH_2)_4$-$\overset{+}{N}Me_3$ and CO_2Me	Me-CO-NH-CH-CO_2pNP, with Ph-CH_2	3	a
$C_{16}H_{33}$-$\overset{+}{N}Me_2$-CHMe-CH-OH, with Ph	Ph-CH-CO_2pNP, with OMe	3.2	b

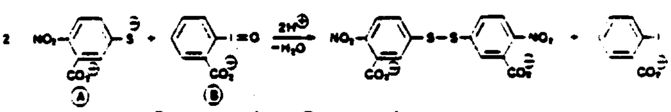
a J.M.Brown et al, J.C.S.Chem. Comm, 969 (1974)

b R.Fornasier et al, J.C.S. Perkin II, 1313 (1984)

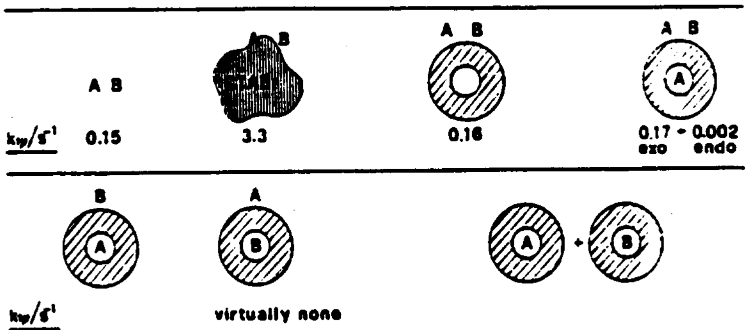


Vesicles (sonication) of DODAC $[CH_3(CH_2)_{17}]_2\overset{\oplus}{N}Me_2Cl^{\ominus}$

Reaction 2



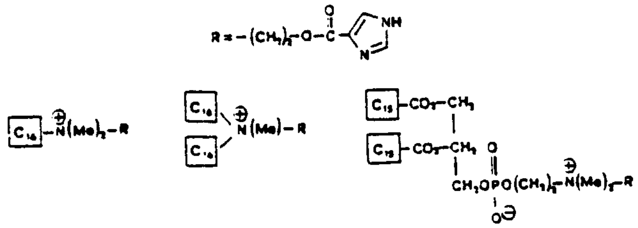
in 0.01M Tris, pH 8.0, 25°, (A) = 2.5×10^{-5}M, (B) = 5×10^{-5}M



R. A. Moss et al. J. Am. Chem. Soc., 110, 2914 (1988)

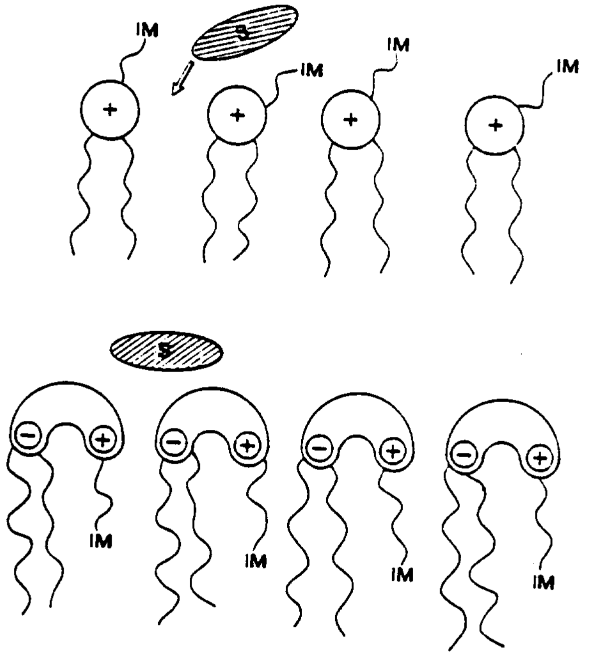
substrate : PNPH

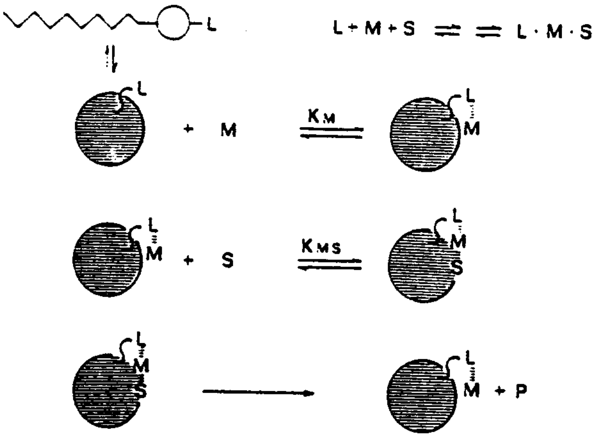
conditions : pH 8.0, 4 % EtOH, 25° [surfactant] = 2.4 x 10^{-4} M



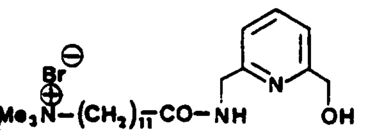
	micelles	vesicles	vesicles	covesicles +DCDABr(1:3)
k_ψ/s^{-1}	1.2	7.2	0.00012	0.032

R.A.Moss, P.Scrimin, S.Bhattacharya, S.Swarup, J.A.C.S., 109, 6209(1987); also: Israel J.Chem., 25, 11(1985)

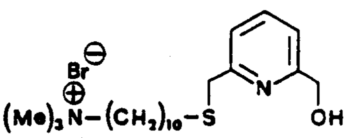




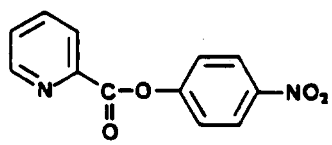
L = ligand M = metal ion

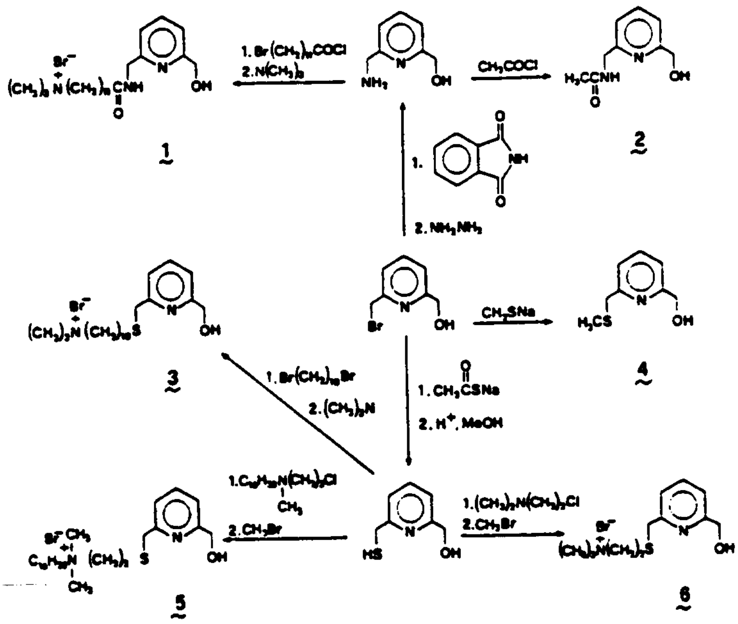


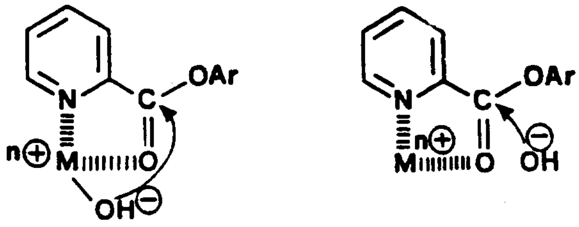
DN



DS

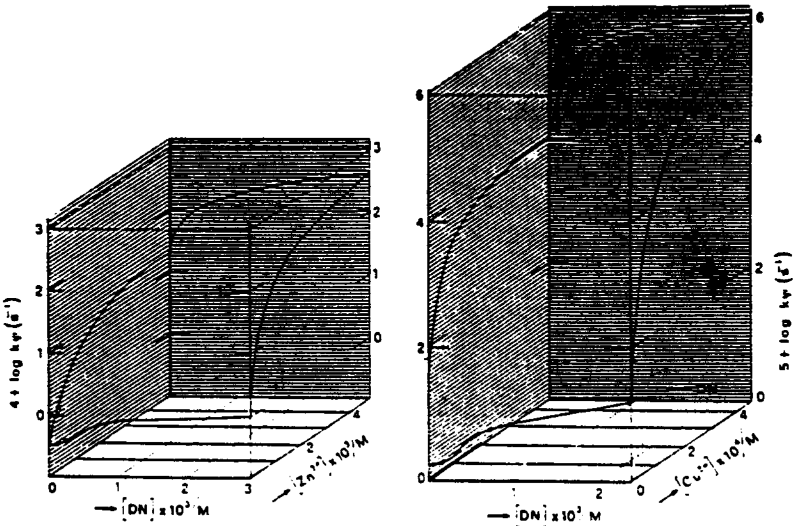


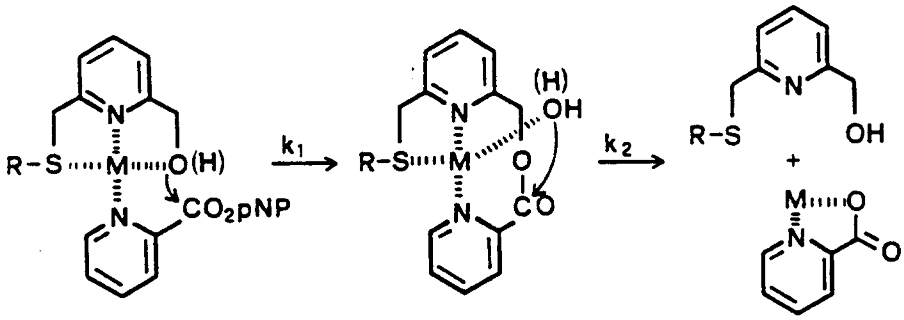


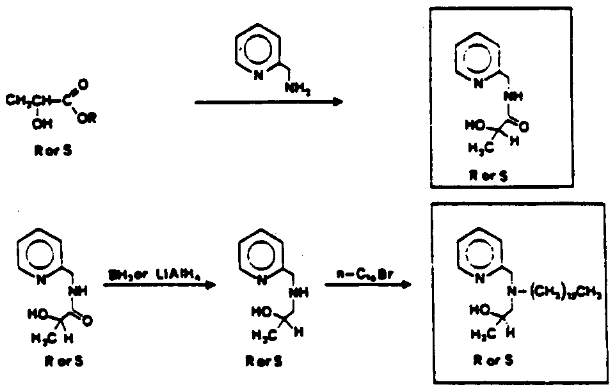


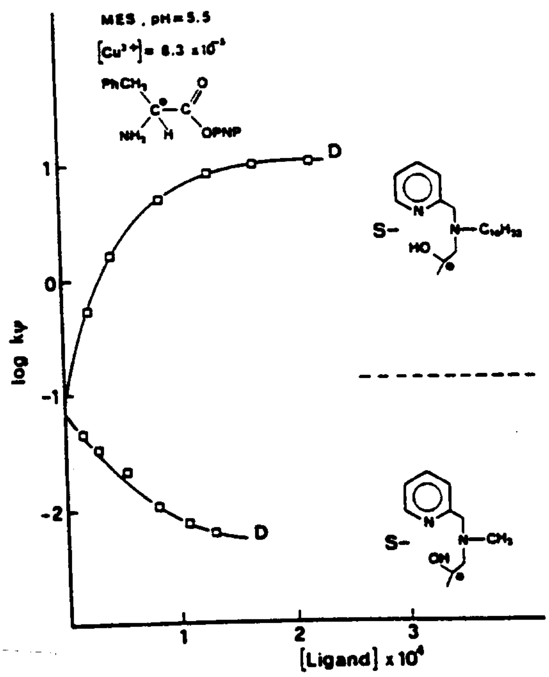
D.S. Sigman, C.T. Jorgensen, J.A.C.S., 94, 1724 (1972)

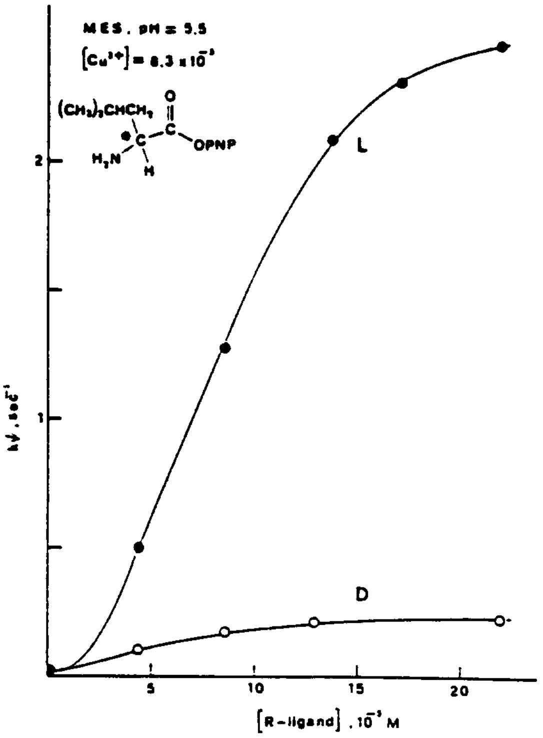
T.H. Fife, T.J. Przystas, J.A.C.S., 107, 1041 (1985)



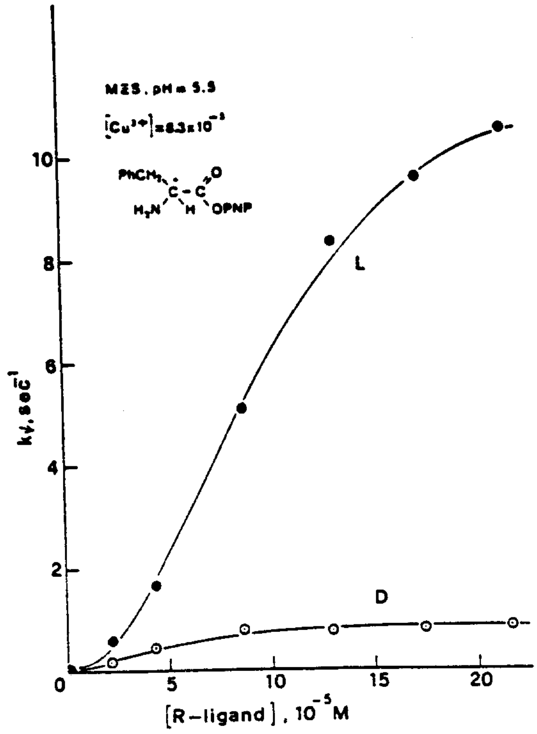




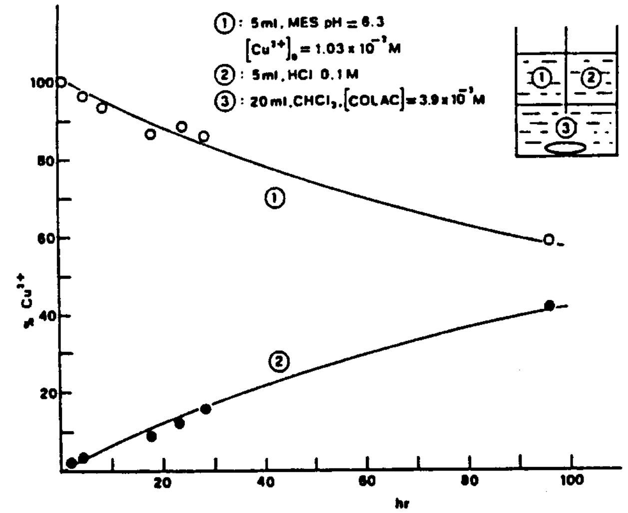




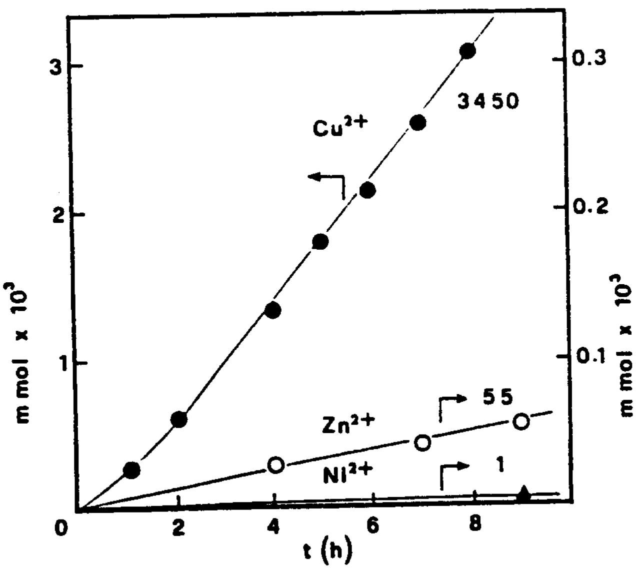
MES, pH = 5.5
[Cu²⁺] = 8.3 x 10⁻⁵
(CH₃)₂CHCH₂
OPNP
H₂N
L
D
kψ, sec⁻¹
[R-ligand], 10⁻⁵ M



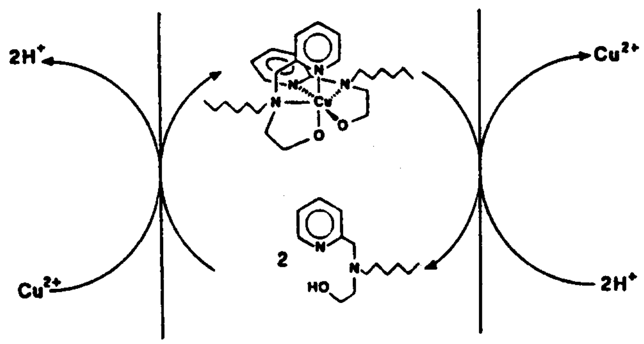
MES, pH = 5.5
[Cu²⁺] = 8.3 x 10⁻⁵
PhCH₂
H₂N
OPNP
L
D
kψ, sec⁻¹
[R-ligand], 10⁻⁵ M



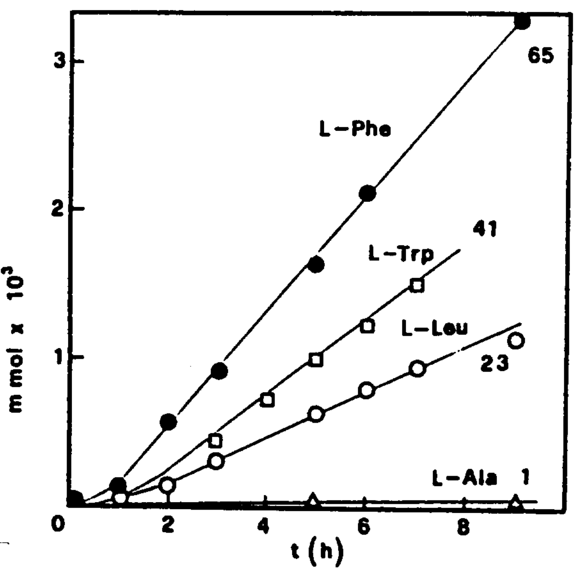
①: 5ml, MES pH = 6.3
[Cu²⁺]₀ = 1.03 x 10⁻³ M
②: 5ml, HCl 0.1 M
③: 20ml, CHCl₃, [COLAC] = 3.9 x 10⁻³ M
% Cu²⁺
hr



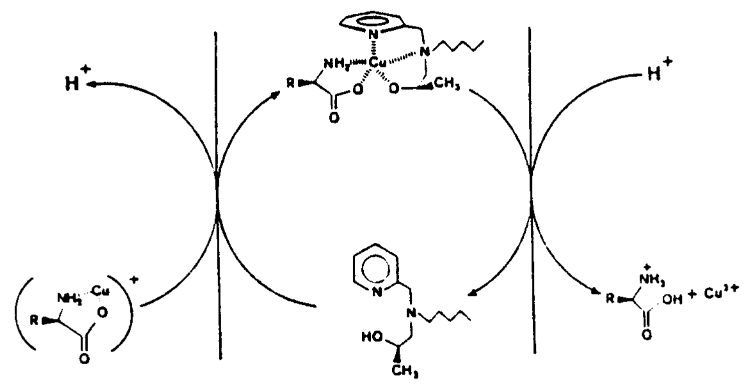
Cu²⁺
3450
Zn²⁺
55
Ni²⁺
1
m mol x 10³
t (h)



2H⁺
Cu²⁺
Cu²⁺
2H⁺
2
HO



L-Phe
65
L-Trp
41
L-Leu
23
L-Ala
1
m mol x 10³
t (h)



Transport rates of different α-amino acids (AA) by carrier (R)-1.

AA	Metal	Rel. rate	Enantio-selectivity
L-Phe	Cu(II)	65	
D-Phe	Cu(II)	51	1.29
L-Trp	Cu(II)	41	
D-Trp	Cu(II)	43	0.96
L-Leu	Cu(II)	23	
D-Leu	Cu(II)	20	1.15
L-Ala	Cu(II)	1	
L-Phe	Zn(II)	0.07	
L-Phe	Ni(II)	0.03	
L-Phe	none	no transport	

ROBERTO FORNASIER *PAOLO TECILLA*
PAOLO SCRIMIN *NICOLA ZANTA*

ENZO CASTIGLIONE

C.N.R.,
MINISTRY OF PUBLIC EDUCATION OF ITALY