

MECHANISM OF THE FACILITATED ION TRANSFER ACROSS A LIQUID/LIQUID INTERFACE

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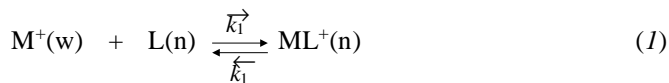
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The facilitated transfer of sodium ion across the water/nitrobenzene interface was examined by faradaic impedance measurements at the thermodynamic equilibrium potential. Kinetic data for the interfacial reaction $\text{Na}^+(\text{w}) + \text{L}(\text{n}) \rightleftharpoons \text{NaL}^+(\text{n})$ (L = dibenzo-18crown-6, w = water, n = nitrobenzene) were confronted with the theoretical predictions for three possible reaction mechanisms, and a conclusion was reached that the reaction occurs via a single electrochemical step. Its pseudo-first order rate constant depends on the interfacial potential difference and falls between 0.01 and 1 cm s^{-1} , i.e. it is comparable with the first order rate constant for a simple ion transfer.

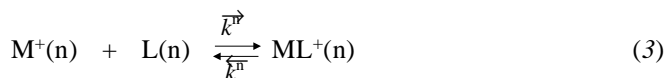
The equilibrium partition of an ion M between two immiscible solvents w and n in contact can be shifted in one or the other direction by introducing a ligand L, which forms stable complexes with the ion M. The effect depends on the magnitude of the stability constant of complexes in both phases, and on the magnitude of the partition coefficients of the ligand and of other ions present^{1,2}. Under the suitable experimental conditions, the facilitated ion transfer, e.g.



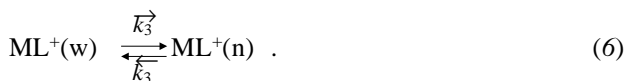
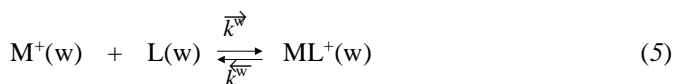
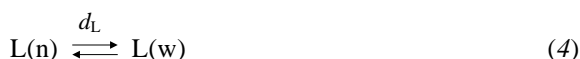
can be measured directly³.

By assuming that the Nernst equilibrium is established at the liquid/liquid interface, the theory of the cyclic voltammetry of the facilitated ion transfer was outlined³ and developed further for various complex stoichiometries⁴ and for the successive complex formation⁵. Analogously, the theory of the stationary current-potential curves was derived⁶. However, the reversible behaviour does not permit to make any conclusion about the mechanism of the overall reaction. In principle, the mechanistic considerations should rely on kinetic effects⁷. The kinetic analysis⁷ makes it possible to distin-

guish between the E mechanism represented by the simple electrochemical step (1), the EC mechanism



and a CE type of mechanism



However, such an analysis has been carried out only for the Na^+ ion transfer across the water/nitrobenzene interface facilitated by dibenzo-18-crown-6 (ref.⁷), though other quasi-reversible reactions of this sort have been reported⁸⁻¹⁰. In this respect, the diagnosis of the mechanism of the K^+ ion transfer between aqueous solutions and PVC membranes containing valinomycin¹¹ is worth comparing, because there seems to be little difference between the ion transfer across the interface between two immiscible electrolyte solutions (ITIES) and the PVC supported ITIES (ref.¹²).

The main purpose of this work was to measure the rates of the facilitated ion transfer across an ITIES by a somewhat different method consisting of the faradaic impedance measurements at a thermodynamic equilibrium potential. We note that the previously claimed application of this method⁹ actually used the impedance measurements at a quasi-equilibrium potential, which is established after the dc faradaic current drops to zero.

EXPERIMENTAL

The ITIES with an area of 0.196 cm^2 was formed in a glass electrochemical cell equipped with four electrodes (two reference electrodes and two current electrodes). The potential between reference electrodes was measured by means of a high-impedance voltmeter.

A Solartron 1250 Frequency Response Analyser, which was operated by a 40 kB microcomputer, was employed in impedance measurements.

The electrochemical cell was connected to FRA through a laboratory-made four electrode potentiostat.

Analytical grade sodium bromide, which served as the aqueous base electrolyte, was dissolved in twice-distilled water. The non-aqueous phase consisted of nitrobenzene (purriss. p.a., Fluka), tetrabutylammonium tetraphenylborate (TBATPB, purriss. p.a., Fluka) as the base electrolyte, dibenzo-18-crown-6 (db18c6, purum, Fluka) and its complex db18c6Na^+ . The complex was prepared by dissolving the equimolar amounts of db18c6 and NaTPB (purriss. p.a., Fluka) in nitrobenzene. In order to prepare the equilibrated electrochemical system the aqueous and organic solvent phases were brought into contact and were shaken; the mixture was then left to stay for 2 – 5 h.

All measurements were performed at ambient temperature, i.e. $23 \pm 2 \text{ }^\circ\text{C}$.

RESULTS AND DISCUSSION

Potentiometric Measurements

Under the equilibrium conditions the Nernst potential E should establish in the galvanic cell,

$$E = E^0 - (R T/z F) \ln K^n + (R T/z F) \ln [a_{\text{NaL}}^n / (a_{\text{Na}}^w a_{\text{L}}^n)] , \quad (7)$$

where E^0 is the standard potential of the transfer of Na^+ , K^n is the stability constant of NaL^+ in nitrobenzene, and a 's are activities of the three components involved. Potentiostatic measurements were carried out in such a way that concentrations of two components were held constant and the concentration of the third one was varied. The plots of the equilibrium potential vs concentration are shown in Figs 1a – 1c. Slope of these plots are close to $\pm 59 \text{ mV}$, in agreement with the Nernst equation (7). Hence the system exhibits the behaviour characteristic for the thermodynamical equilibrium.

Impedance Measurements

Impedance plots of the system are displayed in Fig. 2. The plot 1, which characterizes the facilitated Na^+ ion transfer, points to the dominant role of the mass transport, cf. the near-unity slope of this plot. On the other hand, impedance spectrum of base electrolytes 2 shows only small effect of faradaic processes and resembles that of series combination of solution resistance and the double-layer capacitance.

The faradaic admittance \bar{Y}_F (or the impedance \bar{Z}_F) of the Na^+ ion transfer was evaluated from the impedances \bar{Z}_i measured in the presence ($i = 1$) or the absence ($i = 0$) of the ligand and the complex, by assuming that various faradaic and non-faradaic contributions to \bar{Z}_i are additive. Hence, we adopted an equivalent electrical circuit consisting of the parallel combination of the interfacial capacitance Z_C , the faradaic impedance Z_f due to the transfer of base electrolyte ions and the faradaic impedance Z_F due to the facilitated ion transfer, with the solution resistance R_Ω in series. Then the complex admittance \bar{Y}_F is given by

$$\bar{Y}_F = \bar{Y}_1 - \bar{Y}_0 \quad (8)$$

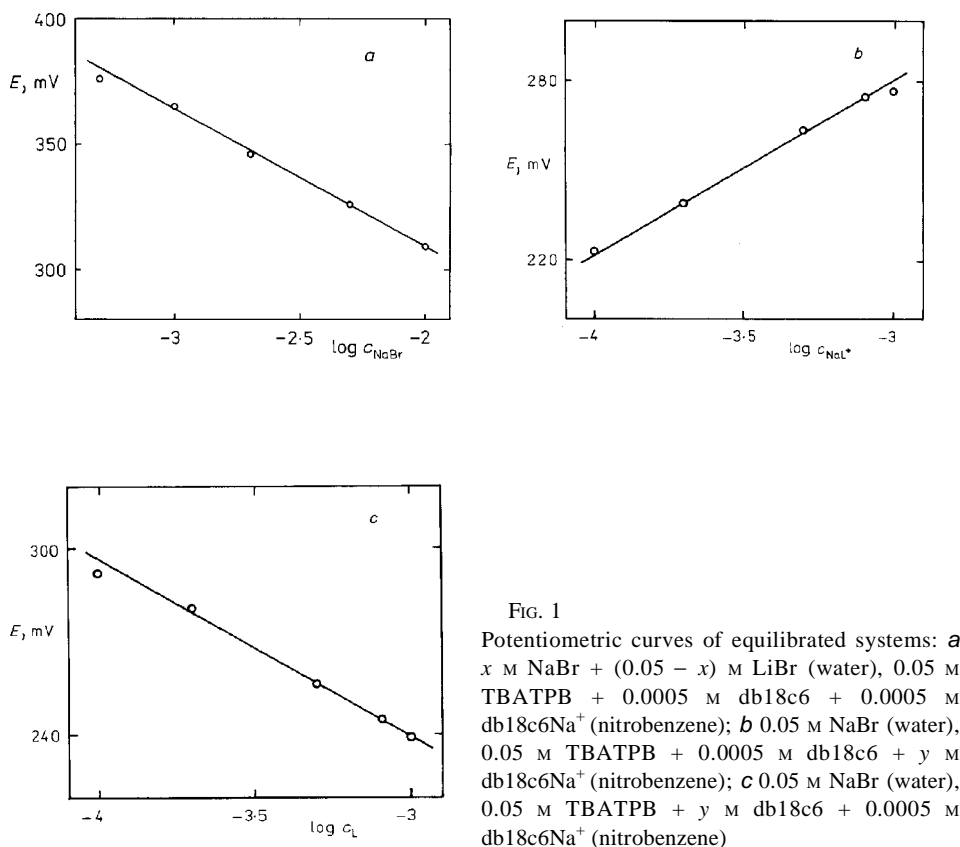


FIG. 1
Potentiometric curves of equilibrated systems: *a* x M NaBr + $(0.05 - x)$ M LiBr (water), 0.05 M TBATPB + 0.0005 M db18c6 + 0.0005 M db18c6Na⁺ (nitrobenzene); *b* 0.05 M NaBr (water), 0.05 M TBATPB + 0.0005 M db18c6 + y M db18c6Na⁺ (nitrobenzene); *c* 0.05 M NaBr (water), 0.05 M TBATPB + y M db18c6 + 0.0005 M db18c6Na⁺ (nitrobenzene)

Secondly, the effect of the ligand concentration c_L^n on the faradaic resistance R_F makes it possible to distinguish between the E and CE mechanisms on the one hand, and the EC mechanism on the other hand. Assuming that the ligand partition coefficient $d_L = c_L^n/c_L^w \gg 1$, the complex formation in the organic phase is shifted largely in favour of the complex, and the rate constants of the ligand partition and the complexation \bar{k}^w and \bar{k}^n are large enough, the following relationships have been derived⁷

$$R_F = \frac{RT}{z^2 F^2 A} \frac{(1 + \eta)}{\bar{k}_1^w(E) c_M^w c_L^n} \quad (12)$$

$$R_F = \frac{RT}{z^2 F^2 A} \left[\frac{1}{\bar{k}_2^w(E) c_M^w} + \frac{K^n}{\eta} \left(\frac{1 + \eta}{\bar{k}^n D_L^n c_L^n} \right)^{1/2} \right] \quad (13)$$

$$R_F = \frac{RT}{z^2 F^2 A} \frac{(1 + \eta) d_L}{K^w c_M^w c_L^n} \left[\frac{1}{\bar{k}_3^w(E)} + \left(\frac{K^w (K^w c_M^w + 1)}{\bar{k}^w D^w} \right)^{1/2} \right] \quad (14)$$

for the E, EC or CE mechanism, respectively. Here A is the interfacial area, c 's are the bulk concentrations, D 's are the diffusion coefficients, K 's are the stability constants, \bar{k} 's are the rate constants defined by equations (1) through (6) and η is the function of the equilibrium potential E_{eq} ,

$$\eta = \exp [F (E_{eq} - E_{1/2}^{rev})/RT] \quad (15)$$

where $E_{1/2}^{rev}$ is the reversible half-wave potential. The assumptions involved are obviously plausible in the present case. The stability constant K^n of the complex db18c6Na^+ in nitrobenzene and the ligand partition coefficient d_L are rather high; $K^n = 1 \cdot 10^7 \text{ mol}^{-1} \text{ l}$ (ref.⁷) or $7.9 \cdot 10^6 \text{ mol}^{-1} \text{ l}$ (ref.¹³), and $d_L = 2.3 \cdot 10^4$ (ref.¹⁴). The same probably applies to the rate constants \bar{k}^w or \bar{k}^n of complex formation^{15,16}, though data for db18c6Na^+ in water and nitrobenzene are not available. Thus, e.g. the complexation of Na^+ by db18c6 in methanol or dimethylformamide is characterized by $\bar{k}^n = 1.6 \cdot 10^7$ or $3.2 \cdot 10^8 \text{ mol}^{-1} \text{ l s}^{-1}$ (ref.¹⁵) and the complexation of Na^+ by 18-crown-6 in water by $\bar{k}^w = 2.2 \cdot 10^8 \text{ mol}^{-1} \text{ l s}^{-1}$ (ref.¹⁷). Equations (12) – (14) predict that R_F is inversely proportional to c_L^n for the E and CE mechanisms, while it is inversely proportional to $(c_L^n)^{1/2}$ for the EC mechanism. The latter behaviour is due to the fact that the thickness of the reaction layer μ is related to the pseudo-first order rate constant of the complexation, $\mu = (D_L^n \bar{k}^n c_L^n)^{1/2}$. Figure 4 shows the plots of R_F vs $(1/c_L^n)^{1/2}$ or $1/c_L^n$. It is apparent that the former plot has negative intercept, which contradicts to Eq. (13). Hence, the EC mechanism is not probable in the present case.

Thirdly, Eqs (12) – (14) impose a lower limit on the faradaic resistance R_F , which follows for infinite values of transfer rate constants \vec{k}_1^{\rightarrow} , \vec{k}_2^{\rightarrow} or \vec{k}_3^{\rightarrow} . These lower limits can be estimated as $R_F = 0$, $R_F = 1.4 \cdot 10^5 \Omega$, $R_F = 1.8 \cdot 10^4 \Omega$, respectively, by taking $\eta = 1$, $D^w \approx 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, $D_L^n = 2.3 \cdot 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ (ref.⁷), $K^w = 14.6 \text{ mol}^{-1} \text{ l}$ (ref.¹⁸) and the other parameters given above. Since experimental data ($R_F < 50 \Omega$) are consistent only with the former limit, we conclude that the reaction occurs via a single electrochemical step described by Eq. (1).

Formal kinetics of the E mechanism is described by the second-order rate law

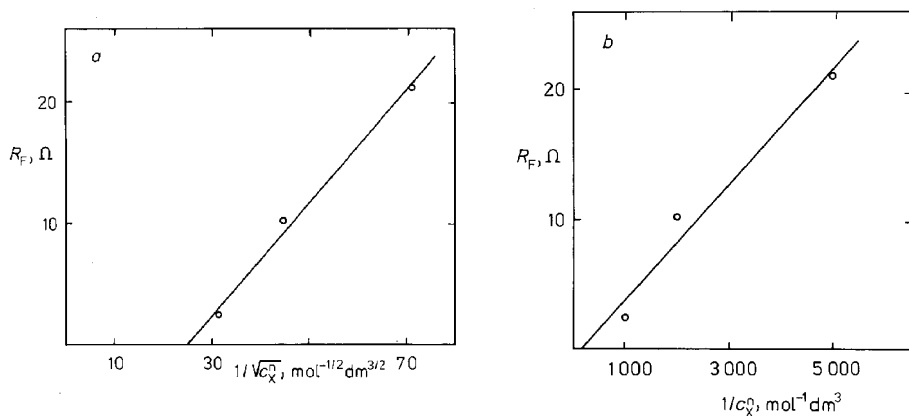


FIG. 4

Plots of faradaic resistance R_F vs **a** $(1/c_L^n)^{1/2}$, or **b** $1/c_L^n$, $E_{\text{c}q} = 269 \pm 3 \text{ mV}$

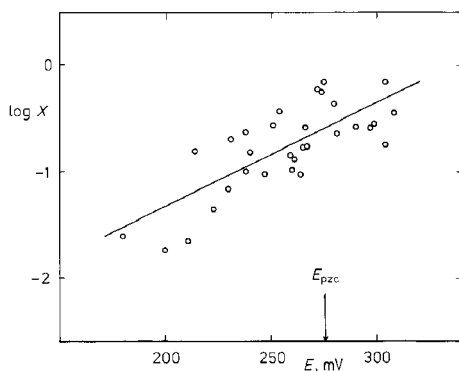


FIG. 5

Plot of pseudo-first order rate constant $\vec{k}_1^w c_M^w$ (X , in cm s^{-1}) vs equilibrium potential E

$$I = F A (\bar{k}_1^{\rightarrow} c_M^w c_L^n - \bar{k}_1^{\leftarrow} c_{ML}^n) , \quad (16)$$

where I is the electrical current. However, because the concentration of the metal ion M^+ is much higher than that of the ligand L , the ion transfer to the organic phase proceeds as the pseudo-first order reaction. Figure 5 shows the dependence of the pseudo-first order rate constant $\bar{k}_1^{\rightarrow} c_L^w$ on the equilibrium potential. The apparent kinetic parameters, i.e. the apparent rate constant $\bar{k}_1^{\rightarrow} c_M^w = 0.07 \text{ cm s}^{-1}$ and the apparent charge transfer coefficient $\alpha_{\text{app}} = 0.57$ at the standard potential $E^{\circ'} = E^{\circ} - (RT/F) \ln K^n = 0.221 \text{ V}$ of the facilitated Na^+ ion transfer, are comparable with kinetic data for the simple ion transfer¹⁹. These data offer another argument in favour of the E mechanism. The homogeneous rate constant of the complex formation in nitrobenzene \bar{k}^{\rightarrow} is probably of order of $10^8 \text{ mol}^{-1} \text{ l s}^{-1}$. At the ITIES, the same reaction, i.e. the reaction (1), proceeds in a small volume $\delta V \approx A \delta$ of the interfacial region of thickness $\delta \approx 1 \text{ nm}$. The corresponding pseudo-first order rate constant can be estimated as $\bar{k}_1^{\rightarrow} c_M^w \approx \bar{k}^{\rightarrow} \delta c_M^w \approx 0.5 \text{ cm s}^{-1}$, which is actually the value found experimentally at the potential of zero charge E_{pzc} , cf. Fig. 5.

Thus we have reached at the same conclusion about the mechanism of the facilitated ion transfer at the ITIES, as Senda et al.⁷ did. The same mechanism seems to prevail in the case of the K^+ ion transfer across the interface between an aqueous solution and the PVC membrane containing valinomycin as the ligand under the conditions that the valinomycin/ K^+ ratio in the membrane is greater than 1.1 (ref.¹¹).

REFERENCES

- Hung L. Q.: *J. Electroanal. Chem.* *115*, 159 (1980).
- Makrlík E.: *Electrochim. Acta* *28*, 573 (1983).
- Homolka D., Hung L. Q., Hofmanová A., Khalil M. W., Koryta J., Marecek V., Samec Z., Sen S. K., Vanýsek P., Weber J., Brezina M., Janda M., Stibor I.: *Anal. Chem.* *52*, 1606 (1980).
- Homolka D., Holub K., Marecek V.: *J. Electroanal. Chem.* *138*, 29 (1982).
- Kakiuchi T., Senda M.: *Bull. Chem. Soc. Jpn.*, in press.
- Makrlík E.: *J. Colloid Interface Sci.* *97*, 595 (1984).
- Kakutani T., Nishiwaki Y., Osakai T., Senda M.: *Bull. Chem. Soc. Jpn.* *59*, 781 (1986).
- Samec Z., Homolka D., Marecek V.: *J. Electroanal. Chem.* *135*, 165 (1982).
- Seno M., Iwamoto K., Chen Q.: *Electrochim. Acta*, *35*, 127 (1990).
- Campbell J. A., Stewart A. A., Girault H. H.: *J. Chem. Soc., Faraday Trans. 1* *85*, 843 (1989).
- Armstrong R. D., Lockhart J. C., Todd M.: *Electrochim. Acta* *31*, 591 (1986).
- Dvorak O., Marecek V., Samec Z.: *J. Electroanal. Chem.* *284*, 205 (1990).
- Sabela A., Weber E., Koryta J.: *J. Electroanal. Chem.*, in press.
- Iwachido T., Minami M., Sadakane A., Toei K.: *Chem. Lett.* *1977*, 1511.
- Liesegang G. W., Eyring E. M. in: *Synthetic Multidentate Macrocyclic Compounds* (R. M. Izatt and J. J. Christensen, Eds). Academic Press, New York 1978.
- Simon W., Morf W. E., Meier P. C.: *Structure and Bonding*, Vol. 16, p. 113. Springer, Berlin 1973.

17. Liesegang G. W., Farrow M. M., Vazquez A., Purdie N., Eyring E. M.: *J. Am. Chem. Soc.* 99, 3240 (1977).
18. Shchori E., Nae N., Jagur-Grodzinski J.: *J. Chem. Soc., Dalton Trans.* 22, 2381 (1975).
19. Wandlowski T., Marecek V., Holub K., Samec Z.: *J. Phys. Chem.* 93, 8204 (1989).

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