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RATE-DETERMINING STEP IN THE DIFFUSION OF SOLUTES ACROSS A LIQUID/LIQUID INTERFACE

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1. Introduction

In order to gain a better understanding of the factors that govern the penetration of solutes through cell membranes, frequently studies are carried out on model systems comprising liquid/liquid interfaces [1–7]. In those systems, the rate of change of the concentration of the solute is measured in one phase or at the interface. The following approach is well accepted to interpret the results on a molecular scale [8]: a molecule that passes across a liquid/liquid interface encounters a total resistance R_t . This resistance consists of the two liquid phase resistances (R_{L_1} , R_{L_2}) and the resistance of crossing the interface (R_i):

$$R_t = R_{L_1} + R_i + R_{L_2} \quad (1)$$

In a static system, R_i is negligible as compared to the two other terms [8,9]. The diffusional liquid phase resistances decrease when stirring is applied, and only then R_i may start to play a role in the transport process. Actually, this introduction of a stirring process is the only way to detect R_i . However, in analyses of these dynamic processes, great care should be taken to separate the complex hydrodynamical from the physico-chemical effects properly.

In biophysical reports on this topic, the stirring speed is usually low [2–5] (30 rev/min is often used). Under these conditions, the transfer from one phase to the other is then considered to be the rate-limiting process, without further proof. This is tantamount to neglecting $R_{L_1} + R_{L_2}$ in (1). This assumption is in sharp contrast to the approach chosen in studies of extraction processes [8,12]. The stirring speed in these

processes is much higher (200–1000 rev/min). In spite of this, R_i is neglected as compared to $R_{L_1} + R_{L_2}$ under these conditions.

In order to arrive at more pertinent conclusions, a new study of a stirred system has been undertaken, in which the transport of electrolyte from one phase to another is measured. From the results it can be inferred that the rate of transport is mainly determined by the hydrodynamic conditions at the interface, i.e. by $R_{L_1} + R_{L_2}$. The resistance to transfer of the solute from one phase to another plays only a minor role.

2. Experimental

At 25.0°C, the transport rate of KCl from water to 1-butanol (mutually saturated) has been measured with an experimental arrangement essentially equal to that of Ting et al. [4]. A detailed description of the dimensions of the cell and of the measuring technique is given in [7]. The KCl-concentration in the butanol phase has been measured conductometrically.

Assuming ideal mixing in the bulk phases, a general rate equation can be derived for the solute transport from one phase (water) to the other (butanol) [7]:

$$-V_b \ln(1 - C_b/C_b^e) = \frac{A(1 + aP_{bw})}{P_{bw}/k_w + P_{bw}/k_{wb} + 1/k_b} t = Ht \quad (2)$$

where V_b means the volume of the butanol phase, C_b the KCl concentration in this phase at time t , C_b^e the same at equilibrium ($t = \infty$), A the cross-sectional area of the interface, a the ratio between the volumes of the butanol and water phase, P_{bw} the distribution constant for KCl between the butanol and the water

phase, k_w and k_b the individual mass transfer coefficients in the water and butanol phase, and k_{wb} the interfacial mass transfer coefficient from water to butanol. Provided that stirring rate, temperature and distribution coefficient do not change during the experiment, all constants can be combined in the symbol H , that equals the slope of the $-V_b \ln(1 - C_b/C_b^e)$ versus t plot. The mass transfer coefficients can be correlated with the resistances introduced in (1) according to:

$$R_{L1} = P_{bw}/k_w \quad (3A)$$

$$R_O = P_{bw}/k_{wb} \quad (3B)$$

$$R_{L2} = k_b^{-1} \quad (3C)$$

k_w and k_b are dependent on the hydrodynamic conditions in the interfacial region. The interfacial mass transfer coefficient k_{wb} provides inference on the biophysically interesting interfacial transfer rate.

The hydrodynamics at the interface can be correlated with the hydrodynamics of the bulk phases, provided that no Marangoni or gravitational instabilities exist during the transport processes [14,15]. This correlation has been introduced by Levich [10] and Davies [12,13]. Levich developed the diffusion boundary layer theory in which attenuation of turbulent pulsations close to the interface is assumed. Molecular and convective diffusion play an important role. The main concentration drop takes place in the diffusion boundary layer (δ), which is of a mathematical rather than of a physical nature. As no interfacial instabilities exist in the concentration range covered in this study (0.05–0.15 M KCl at $t = 0$ in the water phase), the individual mass transfer coefficients can formally be written as:

$$k_w = X_w^1 D_w / \delta_w \quad (4A)$$

$$k_b = X_b^1 D_b / \delta_b \quad (4B)$$

where D_w and D_b are the solute diffusion coefficients in the water and butanol phase and X_w^1 and X_b^1 are proportionality constants. In analogy to conclusions arrived at for solid/liquid and liquid/gas interfaces [8,10,11,16], we assume both δ 's to be proportional

to $N^{-\alpha}$, where N is the rate of stirring and α is a constant. This gives:

$$k_w = X_w D_w N^\alpha \quad (5A)$$

$$k_b = X_b D_b N^\alpha \quad (5B)$$

with X_w and X_b as new proportionality constants. Substitution of (5A,B) in (2) leads to:

$$-V_b \ln(1 - C_b/C_b^e) = \frac{B t}{P_{bw}/k_{wb} + C N^{-\alpha}} = H t \quad (6)$$

$$\text{with } B = A(1 + a P_{bw}) \quad (7)$$

$$C = P_{bw}(X_w D_w)^{-1} + (X_b D_b)^{-1} \quad (8)$$

B and C are constants, because P_{bw} is constant in the concentration range studied. The variable stirring rate is kept low enough to cause no waves at the interface, so that A does not vary. From (6) we obtain the relation:

$$H^{-1} = \frac{P_{bw}}{B k_{wb}} + \frac{C}{B} N^{-\alpha} \quad (9)$$

with N as the only variable. This makes it possible to separate the hydronic part ($\frac{C}{B} N^{-\alpha}$) from the physico-chemical part ($P_{bw}/B k_{wb}$) of the overall transfer coefficient.

3. Results and discussion

H was determined several times for different values of the stirring rate N . The standard deviation of H was always better than 4%. The results are shown in table 1. From these, α was determined with an iterative procedure. Firstly, $\log(H)^{-1}$ was plotted against $\log N$, from which a value α_1 was obtained. In the next step, $\log[H^{-1} - P_{bw}/(B k_{wb})]$ was plotted against $\log N$, leading to α_2 . This procedure was repeated until $\alpha_{n+1} = \alpha_n$.

Finally, it was found that $\alpha = 0.65$, while $P_{bw}/k_{wb} = 64 \text{ s. cm}^{-1}$. The value of α is in reasonable agreement with the values 0.67 obtained for the solid/liquid and 0.71 for the liquid/gas interface [9,16]. As $P_{bw} =$

Table 1

N (rev/min)	H (cm ³ /h)
15	123
20	141
25	165
30	188
35	200
40	225
45	240
50	255
60	280

0.0171, for k_{wb} the value of $28 \times 10^{-5} \text{ cm} \cdot \text{sec}^{-1}$ is obtained. On the basis of the Eyring theory of absolute reaction rates, from k_{wb} the free energy of transfer of KCl from the water phase to the butanol phase is calculated to be $51 \text{ kJ} \cdot \text{mol}^{-1}$.

With this procedure it is possible to separate the hydro-dynamical from physico-chemical contributions to the resistance of crossing an interface. It implies that for $N = 30 \text{ rev/min}$ (a stirring speed representative for many data in biophysical literature), the interfacial resistance ($P_{bw}/k_{wb} = 64 \text{ s} \cdot \text{cm}^{-1}$) can almost be neglected as compared to the diffusional resistances ($1/k_b + P_{bw}/k_w = 1070 \text{ s} \cdot \text{cm}^{-1}$). When studying the influence of proteins or polymers adsorbed at the interface, a similar approach is required in the analysis. Any observed effect [5–7] must primarily be ascribed to the influence of the adsorbate on the hydrodynamics near the interface.

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