Kinetics and molecular mechanism of ion transfer across the waterorganic solvent interface

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Kinetics and molecular mechanism of the simple ion transfer across the polarized water-organic solvent interface has been a matter of continuing debate [1]. Apparent standard rate constant k_0 of the interfacial ion transfer can be evaluated using electrochemical impedance spectroscopy (EIS) [2], noise analysis [3] at the macroscopic or microscopic interfaces, or the steady-state voltammetry at the nanoscopic interfaces [4] between water and a polar organic solvent immiscible with water, each containing an electrolyte. In the present study we investigated the kinetics of the tetraethylammonium (TEA⁺) ion transfer across the water/1,2-dichloroethane (DCE) interface. EIS measurements were carried out at the equilibrium electrical potential difference, which was controlled by the partition of TEA^+ present in both the aqueous and DCE phase. Important observations include: (a) increasing k_0 with increasing temperature, and (b) decreasing k_0 with the increasing surface excess (pressure) of a phospholipid. Comparable effects of temperature on k_0 and the ion diffusion coefficient D^{w} (Fig. 1), which corresponds to the apparent activation energy of ca. 13 kJ mol⁻¹, point to the absence of an energy barrier for the ion to overcome in the interfacial region. On the other hand, the experimental values of k_0 are significantly smaller (typically 0.5 cm s⁻¹) than the upper limit of k_0 for the diffusion-type process (ca. 100 cm s⁻¹). The deceleration of the ion motion in the interfacial region could be ascribed to the slow relaxation of the interface, the favourable deformation of which is likely to control the interfacial ion transfer [5]. In the presence of a phospholipid, the relaxation of the interface slows down, and eventually an activation barrier develops leading to a blocking of the ion transfer.



Figure 1 Plot of log *y* vs. reciprocal absolute temperature T^{-1} where $y = k_0$ (cm s⁻¹) (•) or $10^5 D^{w}$ (cm²s⁻¹) (o).

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