Temperature effect in the ion transfer kinetics at the micro-interface between two immiscible electrolyte solutions

Antonín Trojánek, Vladimír Mareček[1], Zdeněk Samec[1,*]

J. Heyrovský Institute of Physical Chemistry of CAS, v.v.i, Dolejškova 3, 182 23 Prague 8, Czech Republic

ARTICLE INFO

ABSTRACT

Electrochemical impedance spectroscopy (EIS) was used to investigate the kinetics of the tetraethylammonium (TEA$^+$) ion transfer across the water/1,2-dichloroethane (DCE) interface supported at the tip of a thick-wall microcapillary at various temperatures. EIS measurements were carried out at the equilibrium Galvani potential difference, which was controlled by the partition of TEA$^+$ present in both the aqueous and DCE phase. The apparent standard rate constant k_0 of the TEA$^+$ ion transfer and the diffusion coefficient Dw of TEA$^+$ in the aqueous phase were determined at five temperature values in the range 15–35 °C. The values $k_0 = 0.47 \pm 0.12$ at 20 °C and $k_0 = 0.52 \pm 0.17$ cm s^{-1} at 25 °C agree well with those obtained by EIS and noise analysis under the same or similar experimental conditions in our previous studies. Comparable effects of temperature on k_0 and D^w, as indicated by nearly equal slopes of the plots of log k_0 and log D^w vs. the reciprocal absolute temperature, 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 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 favorable deformation of which is likely to control the interfacial ion transfer. The effect of temperature on the capacitance of the electric double layer at the water/DCE interface was found to be negligible, in an agreement with the prediction based on the simple Verwey-Niessen model of the back-to-back space charge (diffuse) layers.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Experimental kinetics of the simple ion transfer across the interface between two immiscible electrolytes (ITIES) has been a controversial issue [1]. This controversy is demonstrated by the poor agreement between the values of the kinetic parameters reported for the selected ion transfer reaction, namely the apparent standard rate constant k_0 and the apparent charge transfer coefficient α. These parameters are defined by the phenomenological rate equation:

$$v = i/zF = k_0\{c^w\exp[z\alpha F(\Delta_o^w\phi - \Delta_o^w\phi^{0'})/RT]$$
$$-c^o\exp[-z(1-\alpha)F(\Delta_o^w\phi - \Delta_o^w\phi^{0'})/RT]\} \quad (1)$$

where v is the ion transfer rate, i is the electric current density, z is the ion charge number, c^w and c^o are the ion concentrations in the aqueous (w) and the organic solvent (o) phase, respectively,

$\Delta_o^w\phi = \phi^w - \phi^o$ is the Galvani potential difference between the two phases, and $\Delta_o^w\phi^{0'}$ is the formal ion transfer potential difference. Table 1 summarizes the kinetic parameters reported for the tetraethylammonium (TEA$^+$) ion transfer across the water/nitrobenzene (NB) [2–8], or water/1,2-dichloroethane (DCE) [9–14] interface. First kinetic measurements of the TEA$^+$ ion transfer across a macroscopic ITIES by using chronopotentiometry (CP) and convolution potential sweep voltammetry (CPSV) provided relatively low values of $k_0 = 0.0023$ cm s^{-1} [2] and $k_0 = 0.04$ cm s^{-1} [3]. On the other hand, the values of k_0 obtained by electrochemical impedance spectroscopy (EIS) [4,6,8,12,13] or noise analysis (NA) [14] at an equilibrium potential difference, or by phase-selective AC polarography (ACP) [7], fall in the range 0.1–1.0 cm s^{-1} for both the water/NB [2–8] and water/DCE interface [9–11,12–14] irrespective of the size the interface. However, these results disagree with the kinetic data obtained by the steady-state voltammetry (SSV) of the TEA$^+$ ion transfer across the water/DCE interface supported on the tip of a nanopipette yielding the values $k_0 = 2.4$ cm s^{-1} [9], 5.2 cm s^{-1} [10] or 120 cm s^{-1} [11]. The discrepancy was suspected to be due to a lower accuracy of the kinetic measurements at a macroscopic ITIES associated mainly with the

Table 1
Apparent standard rate constant k_0 and the apparent charge transfer coefficient α for the TEA+ ion transfer across the polarized water/organic solvent interface of the various size characterized by the radius r, and measured by chronopotentiometry (CP), convolution potential sweep voltammetry (CPSV), electrochemical impedance spectroscopy (EIS), phase-selective AC polarography (ACP), steady-state voltammetry (SSV), and noise analysis (NA).

r / mm	k_0 (cm s^{-1})	α	organic solvent	temperature (°C)	Method	Ref.
11	0.0023	0.35	NB	25	CP	[2]
2.6	0.04	0.47	NB	25	CPSV	[3]
2.5	0.09	0.64	NB	20	EIS	[4]
2.0	0.15	0.55	NB	25	ACP	[5]
2.5	0.11	0.5	NB	22	EIS	[6]
1.9	0.5-1.0	–	NB	25	ACP	[7]
3.2	0.07-0.13	–	DCE	25	EIS	[12]
0.010[a]	0.21	–	NB	22	EIS	[8]
0.028	0.2	–	DCE	22	EIS	[13]
0.009	0.37		DCE	22	NA	[14]
r/nm						
89.0[a]	2.4	0.71	DCE	23	SSV	[9]
15[a]	5.2	0.40	DCE	23	SSV	[10]
1.8[a]	120	0.70	DCE	22	SSV	[11]

[a] selected from several reported values.

low ratio of the mass transport coefficient to k_0 and the large ohmic potential drop [15] or, alternatively, due to an underestimation of electrokinetic effects in the nanopipette SSV leading to an accumulation of ions in the capillary tip region [13,16,17]. It is noteworthy, that the analysis of steady-state voltammograms in Ref. [11] was revised with a conclusion that the values of k_0 are likely to be about one order of magnitude lower [10].

An insight into the dynamics of ion transfer across ITIES could be gained by investigating the temperature effect on the rate of the interfacial ion transfer. Such effect was reported for the transfer of acetylcholine cation (Ach+) across the water/DCE interface [18], and for the transfer of six quaternary ammonium and phosphonium cations including TEA+ across the water/nitrobenzene interface [6]. In both studies an important conclusion was made that the apparent activation energies for the interfacial ion transfer and the bulk ion transport are comparable, while the former process appears to be considerably slower [6,18]. However, rather low values of $k_0 = 0.032$ cm s^{-1} for Ach+ [18] and $k_0 = 0.095$–0.12 cm s^{-1} (20 °C) for other cations [6] may cast doubts on this conclusion. Hence, an examination of the temperature effect using a different experimental approach could be useful.

The purpose of the present study was to investigate the kinetics the TEA+ ion transfer across the water/DCE interface supported at the tip of a microcapillary at various temperatures (15–35 °C). Here, we made use of the novel methodology for manufacturing the reusable thick-wall microcapillaries with the orifice diameter of 1–100 μm for two-electrode polarization measurements at the ITIES [16,17]. The increased thickness of the capillary wall allowed reducing the capacitance of the parasitic coupling between the two electrodes to ca. 10 pF [16,17]. We shall show that new kinetic data support the conclusion [6,18] referred to above, and further that the observed behavior could be ascribed to the coupled ion-interface dynamics of the ion transfer across ITIES [19,20]. As a part of this study, we also examined the effect of temperature on the capacitance of the water/DCE interface, which has not been studied yet.

2. Experimental

LiCl, MgSO$_4$, tetraethylammonium chloride (TEACl), tetrabutylammonium chloride (TBACl), sodium tetraphenylborate (NaTPB), and tetrabutylammonium tetraphenylborate (TBATPB) were

purchased as analytical grade chemicals from Sigma–Aldrich and used as received. TEATPB was prepared from TEACl and NaTPB by metathesis and purified by recrystallization from acetone. Organic electrolyte solutions were prepared from 1,2-dichloroethane (puriss, p.a.), which was purchased from Fluka and used as received. Aqueous electrolyte solutions were prepared from highly purified water (Millipore).

Thick-wall microcapillaries with the orifice diameters in the range 45–70 μm were made by pulling and breaking the borosilicate glass tubing (o.d./i.d. = 2.8/1.6 mm) without grinding the orifice plane; cf. Fig. 1 for the tip shape. The diameter of the capillary orifice was determined by optical microscope (Olympus, BX 51). To silanize the outer surface of the tip, the flow of nitrogen was passed through the capillary from the back while the tip was dipped in a solution of chlorotrimethylsilane (Fluka), as described in the literature [21]. The dried-up capillary was filled with the aqueous electrolyte solution (w), and dipped into the organic electrolyte solution (o) in a 1 × 1 cm optical glass cuvette; cf. Fig. 1 (panels A and B). Filling of the capillary was accomplished by pulling the aqueous solution into the capillary from the front side by means of a syringe. The cuvette was fixed in a thermostatic holder.

Fig. 1 shows two configurations of the two-electrode cell. In the first one, the aqueous phase (w') of the organic reference/counter electrode RE1/CE1 filled the space above the organic phase (o) (panel A). The cell can be described by the scheme:
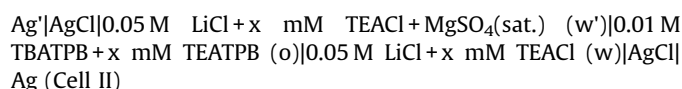
Ag'|AgCl|0.01 M TBACl (w')|0.01 M TBATPB + x mM TEATPB (o)| 0.05 M LiCl (w)|AgCl|Ag (Cell I)
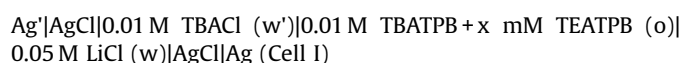
where x = 0, 0.5 or 1.0. The potential E of the Cell I can be related to the Galvani potential difference $\Delta_o^w\phi$ by:

$$E = \Delta_o^w\phi - \Delta_o^w\phi_{TBA^+}^{0'} - (RT/F)\ln(c_{Cl^-}^w/c_{Cl^-}^{w'}) \tag{2}$$

where $\Delta_o^w\phi_{TBA^+}^{0'}$ is the formal ion transfer potential difference for TBA+, and $c_{Cl^-}^w$ or $c_{Cl^-}^{w'}$ are the chloride concentrations in the phases (w) or (w'), respectively.

In the second configuration, the aqueous phase (w') of the organic reference/counter electrode RE1/CE1 was saturated with MgSO$_4$, so that its density was higher than that of the organic phase (o), and the phase filled the bottom space of the cell (panel B). The cell can be represented by the scheme:

Ag'|AgCl|0.05 M LiCl + x mM TEACl + MgSO$_4$(sat.) (w')|0.01 M TBATPB + x mM TEATPB (o)|0.05 M LiCl + x mM TEACl (w)|AgCl| Ag (Cell II)

where x = 0.2, 0.5 or 1.0. The equilibrium potential E of the Cell II was practically equal to zero (±5 mV). The cell I or II was placed in a Faraday cage.
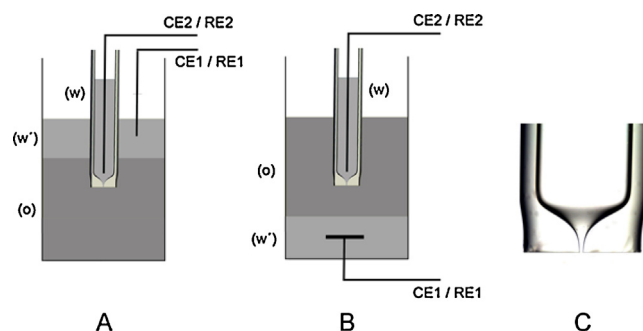
Fig. 1. Two configurations of the two-electrode cell (A,B), and detailed picture of the microcapillary tip with the orifice diameter of 46 μm (C).