

## Fast Kinetic Measurements with Nanometer-Sized Pipets. Transfer of Potassium Ion from Water into Dichloroethane Facilitated by Dibenzo-18-crown-6

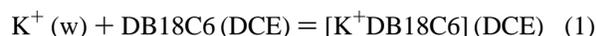
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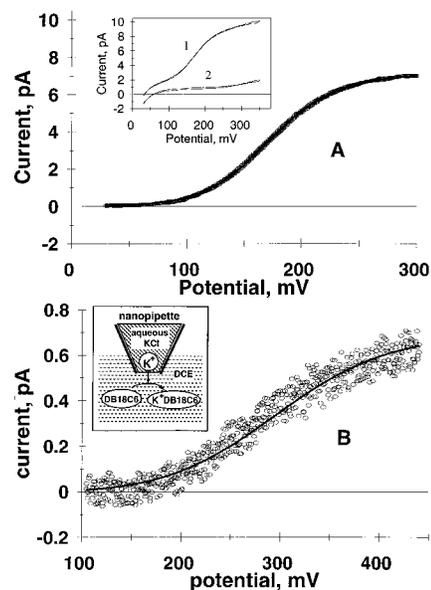
We report here steady-state voltammetric measurements of ion transfer (IT) kinetics using nm-size pipets. The rate of very fast facilitated transfer of potassium ion across the interface between two immiscible electrolyte solutions (ITIES) was measured. The upper limit for the determinable heterogeneous rate constant is extended to about 10 cm/s.

IT across the ITIES is one of the fundamental physicochemical processes.<sup>1</sup> It is also relevant to many important biological and technological systems from chemical sensors to drug delivery systems in pharmacology to biological membranes.<sup>2</sup> The experimental problems typical for electrochemical measurements at a metal/electrolyte interface are even more severe in the case of ITIES. For instance, it is hard to completely eliminate the  $iR$ -drop effect in highly resistive nonaqueous solvents and separate faradaic current from double-layer charging. The kinetics of IT are often very fast and hard to measure. For example, during the last two decades several groups tried to measure the rate constant of  $K^+$  transfer from water into 1,2-dichloroethane (DCE) facilitated by dibenzo-18-crown-6 (DB18C6) which is used in a potassium sensor<sup>2c,3</sup>



This may be the fastest facilitated IT process studied to date.<sup>1c</sup> All previous measurements at large (i.e., mm-sized) ITIES were affected by resistive and capacitive effects. Recently, Girault et al. employed impedance spectroscopy and steady-state voltammetry at micron-sized ITIES and concluded that the  $k^o$  value is inaccessible by electrochemical measurements.<sup>3a,b</sup> Similarly, only the lower limit for the standard rate constant ( $k^o > 0.5$  cm/s) was obtained from pulse voltammetry at the micro-ITIES.<sup>3c</sup>

The current produced by facilitated transfer of  $K^+$  from aqueous solution inside a nanopipet<sup>4</sup> into the outer DCE solution (see inset in Figure 1B) was measured with a BAS 100B potentiostat. Comparably sized pipets (i.e.,  $\geq 20$ -nm radius) have recently been employed in amperometric experiments.<sup>6</sup> Under experimental conditions of ref 6, the measured current was primarily controlled by ion motion inside the pipet. In contrast, with the concentration of KCl inside a pipet much higher than the concentration of DB18C6 in DCE, the current



**Figure 1.** Background-subtracted steady-state voltammograms of transfer of  $K^+$  from water to DCE at (A) 54-nm radius and (B) 5-nm radius nanopipet electrodes facilitated by DB18C6. DCE contained 0.25 mM DB18C6 and 10 mM TBATPBCl;  $c_{KCl}$  was 100 mM (A) and 10 mM (B). Solid lines show the best theoretical fit. Sweep rate was 20 mV/s. The effective radius values were calculated from eq 2. (A) The inset shows the original voltammogram before subtraction (curve 1) and the background current (curve 2). (B) The inset shows the scheme of the water/DCE interface formed at the pipet tip.

is limited by diffusion of DB18C6 to the pipet orifice and/or kinetics of reaction 1. The mechanism of this reaction was shown to be a transfer by interfacial complexation, for which the potential dependence of the heterogeneous rate constant is expected to obey Butler–Volmer equation.<sup>1c,3,7</sup>

Figure 1A contains a typical steady-state voltammogram of facilitated IT of  $K^+$  obtained at a 54-nm-radius pipet.<sup>8</sup> One should notice the high quality of the voltammogram, which is completely retraceable and possesses a well-defined, flat plateau and base line. This was achieved by using background subtraction (see inset in Figure 1A). The background voltammogram to be subtracted was obtained with the same pipet electrode in a DCE solution of the same composition but with no DB18C6 present. The background-subtracted curves were in an excellent agreement with the conventional voltammetric theory (solid line in Figure 1A). The sub-pA current to much smaller pipets (e.g., 5-nm radius; Figure 1B) was somewhat noisier. As expected, the diffusion limiting current was directly proportional to concentration of DB18C6 in DCE ( $c_{DB18C6}$ ) and pipet radius ( $r$ ; was found by optical microscopy for  $\mu$ m-sized pipets) and independent of  $c_{KCl}$  in water as long as  $c_{KCl} \gg c_{DB18C6}$ .

(5) Model P-2000 Micropipet Puller - Instruction Manual, Sutter Instrument Co., Novato, CA, 1993.

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(8) A two-electrode setup was employed with a 0.25 mm Ag wire coated with AgTPBCl serving as an organic reference electrode; (TBA = tetrabutylammonium; TPBCl = tetrakis[4-chlorophenyl]borate),  $x$  is 10, 25, or 100. The ITIES formed at the pipet tip was polarizable, and the voltage applied between the micropipet and the reference electrode provided a driving force for the IT process.

Ag/AgCl/0.01 M TBACl/0.01 M TBATPBCl +  
outer DCE solution  
0.25 mM DB18C6// $x$  mM KCl/AgCl/Ag  
nanopipet

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(4) The 3–500-nm radius nanopipets were made from quartz capillaries using a Sutter Model P-2000 laser-based puller. The orifice radius and the length of the narrow shaft were controlled by choosing appropriate values of pulling parameters.<sup>5</sup> A pulling program was developed to produce short (patch-type) pipets in order to minimize the resistive potential drop inside the narrow shaft. The pipets were filled with an aqueous solution from the back using a small syringe. A 0.25 mm Ag silver wire coated with AgCl was inserted into each pipet from the back.

**Table 1.** Measured Resistances ( $R$ ) and Diffusion Limiting Currents ( $i_d$ ) and Estimated Values of the Maximum  $iR$ -Drop for Various Nanopipets<sup>a</sup>

$r$ (nm)	$R$ (M $\Omega$ )	$i_d$ (pA)	$iR$ (mV)
180	7.0	23.9	0.2
109	8.7	14.5	0.1
87	9.4	11.5	0.1
4	83.3	0.5	0.04

<sup>a</sup>  $c_{\text{KCl}} = 0.1$  M;  $c_{\text{DB18C6}} = 0.25$  mM.**Table 2.** Kinetic Parameters for Facilitated Transfer of Potassium with DB18C6 from Steady-State Voltammograms at Nanopipets<sup>a</sup>

$r$ (nm)	$c_{\text{KCl}}$ (mM)	$k^\circ$ (cm/s)	$\alpha$	$\Delta E_{1/4}$ (mV)	$\Delta E_{3/4}$ (mV)
248	100	1.3	0.40	30.2	31.9
180	100	1.4	0.42	30.5	33.0
54	100	1.6	0.58	30.8	32.5
221	25	0.8	0.38	33.0	39.9
6	25	1.6	0.42		
109	10	0.9	0.50	32.7	35.3
79	10	0.8	0.34	33.4	38.4
73	10	0.8	0.37	34.3	38.1
5	10	1.7	0.44		

<sup>a</sup>  $c_{\text{DB18C6}} = 0.25$  mM;  $D_{\text{DB18C6}}/D_{\text{K}^+ + \text{DB18C6}} = 1.6$ .**Table 3.** Effect of KCl and DB18C6 Concentrations on the Rate of Facilitated Transfer of  $\text{K}^+$  into DCE

$r$ (nm)	$c_{\text{KCl}}$ (M)	$c_{\text{DB18C6}}$ (mM)	$k^\circ$ (cm/s)	$\alpha$	$\Delta E_{1/4}$ (mV)	$\Delta E_{3/4}$ (mV)
131	0.01	0.125	0.9	0.31	32.8	35.4
123	0.01	0.125	1.2	0.37	31.0	35.0
127	0.01	0.25	0.6	0.35	33.5	38.8
118	0.01	0.50	0.8	0.31	36.2	42.7
180	0.1	0.25	1.4	0.42	30.5	33.0
168	0.1	0.50	0.9	0.36	32.7	38.8

The knowledge of the electrode size and shape is essential for extraction of kinetic parameters from voltammetric data.<sup>9</sup> The evaluation of size and shape of small pipets is easier and more reliable than characterization of nm-sized solid electrodes. The effective radius of a pipet found from steady-state voltammetry is fairly close to its geometrical radius.<sup>3a,7a,10</sup> Organic solvents (e.g., DCE and nitrobenzene) do not penetrate thin glass capillaries, so there is no possibility of a recessed interface similar to the "lagooned" electrode geometry.<sup>9a,b</sup> As the liquid/liquid boundary may not contain vertexes or other sharp features, the pipet/solution interface may only be shaped as a flat disk of the size of the pipet orifice or a spherical cap. In agreement with previous results,<sup>3a</sup> the diffusion limiting current was found to follow eq 2

$$i_d = 3.35\pi n F r D c \quad (2)$$

where  $F$  is the Faraday constant,  $D = 5.2 \times 10^{-6}$  cm<sup>2</sup>/s is the diffusion coefficient of DB18C6 in DCE (this is the average of two previously reported values<sup>3a,11</sup>),  $r$  is the pipet radius, and  $n = 1$  is the charge of the transferred ion. The  $3.35\pi$  factor in eq 2 accounts for the convex shape of the meniscus formed at the pipet/DCE interface<sup>3</sup> and also reflects the increase in steady-state current of about 45% due to the small thickness of the pipet wall.<sup>12</sup>

The ohmic solution resistance ( $R$ ) was measured with a lock-in amplifier for a broad range of pipet radius (4 nm to 20  $\mu$ m radius); the results for nanopipets are shown in Table 1). The measured resistances were used to evaluate the  $iR$ -drop for each

voltammogram and also provided an independent estimate for pipet radius.<sup>3a,b,6</sup> For micrometer-sized pipets, the dependence of  $R$  on the pipet radius was in a good agreement with the previous results.<sup>3a,b</sup> For small nanopipets the measured resistance was somewhat less than expected probably because of the shorter length of the narrow shaft. As expected, the resistance was inversely proportional to  $c_{\text{KCl}}$ . At higher concentrations of KCl (i.e., 25 and 100 mM), the maximum  $iR$ -drop corresponding to the limiting current was significantly less than 1 mV for all nanopipets. At lower  $c_{\text{KCl}}$  (i.e., 10 mM), the largest measured  $iR$ -drop was about 1.5 mV.

The application of steady-state voltammetry at ultramicroelectrodes to measurements of rapid heterogeneous ET kinetics was discussed previously.<sup>13</sup> The developed methodologies are applicable to IT assuming that the potential dependence of the rate constant follows Butler–Volmer equation<sup>1c,3</sup> (this assumption seems to be justified by excellent agreement between the theory and experimental voltammograms). Two phenomena discussed above, i.e., the diffusion from the back of the pipet and the meniscus shaped as a spherical cap, should decrease the edge effect and produce an almost uniform current distribution.<sup>12,14</sup> Assuming uniform accessibility of the electrode surface one can find the standard rate constant ( $k^\circ$ ) and transfer coefficient ( $\alpha$ ) by fitting the experimental data to the theory for a steady-state voltammogram at a uniformly accessible electrode [eq 9 in ref 13b]. The solid line in Figure 1A represents an example of such fit. Alternatively, the kinetic parameters of the electrode reaction can be evaluated by the three-point method, i.e., the half-wave potential,  $E_{1/2}$ , and two quartile potentials,  $E_{1/4}$  and  $E_{3/4}$ .<sup>13b</sup> A single table containing the above parameters for all possible pairs of  $\Delta E_{1/4} = E_{1/4} - E_{1/2}$  and  $\Delta E_{3/4} = E_{1/2} - E_{3/4}$  (see Table 1 in ref 13b) is suitable for any kind of uniformly accessible electrode. This method also provides two useful diagnostic criteria: (i) reliable values of kinetics parameters can only be obtained if  $\Delta E_{1/4} \geq 30.5$  mV and  $\Delta E_{3/4} \geq 31$  mV (otherwise the voltammogram is essentially Nernstian); and (ii) the inequality  $|\Delta E_{3/4}| \geq |\Delta E_{1/4}|$  holds true for any undistorted quasi-reversible voltammogram. Essentially the same values of kinetic parameters were obtained by both methods from a number of voltammograms at different nanopipets (Table 2). No kinetic parameters could be extracted from essentially Nernstian voltammograms obtained at larger pipets (i.e.,  $r > 300$  nm). This gives the lower limit for  $k^\circ$  of  $\sim 1$  cm/s. A number of voltammograms obtained at 5–250-nm pipets yielded similar values of the standard rate constant ( $k^\circ = 1.3 \pm 0.6$  cm/s) and  $\alpha = 0.4 \pm 0.1$ . Importantly, there is no apparent correlation between the measured rate constant and the pipet size. The determined kinetic parameters are also independent of  $c_{\text{DB18C6}}$  (Table 3). A minor decrease in measured  $k^\circ$  at lower  $c_{\text{KCl}}$  (i.e., 0.01 M) is due to the  $iR$ -drop inside the pipet.

In summary, we have demonstrated the possibility of quantitative voltammetric measurements with nanopipet electrodes. This methodology allows one to study rapid kinetics of both facilitated and unassisted IT processes which are ubiquitous in biological systems. The possibility of high-resolution electrochemical imaging of ion-transfer properties of biological and artificial membranes with a nanopipet used as a tip of the scanning electrochemical microscope (SECM) is currently being explored in our laboratory.

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