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Emergence of the electrochemical instability in transfer of decylammonium ion across the 1,2-dichloroethane|water interface formed at the tip of a micropipette

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Abstract

The effect of the size of a liquid|liquid interface on the electrochemical instability (EI) has been studied voltammetrically for the transfer of decylammonium ions (DeNH_3^+) across the 1,2-dichloroethane|water interface formed at the tip of a micropipette. An abnormally increased irregular current (AIIC) reproducibly appears on the voltammogram without the positive feedback for the iR compensation. This fact confirms that the AIIC is not an artifact associated with the positive feedback usually employed for the iR compensation at a liquid|liquid interface of conventional size. The emergence of the AIIC at the micro liquid|liquid interface supported at the tip of the micropipette is suppressed by either a decrease in the concentration of DeNH_3^+ or a decrease in the diameter of the interface. The concentration of DeNH_3^+ required to induce the AIIC at the micro liquid|liquid interface is significantly higher than that at an interface of conventional size. The effect of the diameter of the micropipette on the AIIC is in line with the case of the aspect-ratio effect on the formation of cellular convection of the Marangoni instability.

1. Introduction

The electrochemical instability (EI) of a liquid|liquid interface [1] is a thermodynamic instability that occurs when

$$\left[\frac{\partial^2 \gamma}{\partial (\Delta_{\text{O}}^{\text{W}} \phi)^2} \right]_{T,P,\mu_i} > 0 \quad (1)$$

where γ is the interfacial tension and $\Delta_{\text{O}}^{\text{W}} \phi$ is the phase-boundary potential. This condition may be fulfilled through the interplay of the potential-dependent adsorption and partition of

surface-active ions between the two phases [2]. The EI explains the characteristic features of the instability experimentally found at the liquid|liquid interface when surface-active ions move across the interface [3–7]. Three main features of the EI are the existence of the instability window of the phase-boundary potential, the location of the instability window close to the half-wave potential, and a positive finite value of γ when the interface becomes unstable.

When a liquid–liquid two-phase system falls in the state of the EI due to the transfer of surface-active ions across the liquid|liquid interface, the Marangoni convection is induced owing to the heterogeneity of the interfacial tension. Because the convection enhances the mass-transfer of surfactant ions to the interface, the abnormally increased irregular current (AIIC) emerges in the ion-transfer voltammogram [3–5, 7, 8].

The area of the liquid|liquid interface where the EI has so far been found is relatively large, about 0.1 [3–6, 8] or 50 cm² [7]. Since the EI is a thermodynamic concept as expressed in equation (1), it is supposed to be independent of the dimension and the shape of the interface, as has been found previously [3–5, 7, 8]. However, when the area of the liquid|liquid interface is very small, the appearance of the EI can be different. It is known that the interface is stabilized with a decrease in the interfacial area in the case of the thermally induced Marangoni convection [9–11].

The ion transfer across the micro liquid|liquid interface has been studied [12–14] at the tip of a micropipette, where the aspect ratio (ratio of diameter of the pipette to the depth) is very small. In the Marangoni convection in a cylinder caused by the temperature gradient [9, 10], the convective motion is suppressed due to the presence of the wall of the cylinder when the aspect ratio is small. Then, it is natural to expect that the Marangoni convection due to the EI can also be suppressed at the interface formed at the tip of the micropipette.

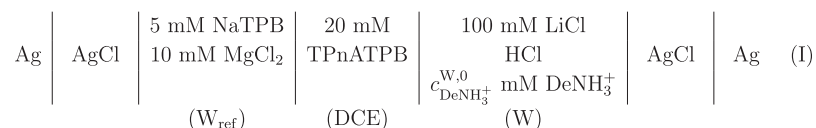
Aside from the hydrodynamic constraint due to the aspect ratio, a decrease in the interfacial area may bring about other consequences. If the turbulence of the interface occurs in a way similar to the nucleation and growth mechanism, that is, the initial formation of unstable microdomains at the interface followed by the growth of these domains, the onset of the EI should be proportional to the interfacial area, provided that the frequency of the nucleation per unit area and unit time is constant. Then, with decreasing area of the interface, a stochastic nature of the EI would surface. The effect of the edge of the interface on the EI may also become appreciable at a nanometre-sized pipette because of the electrical double layer on the surface of a glass pipette.

The present paper reports a study of the EI at the micro liquid|liquid interface supported at the tip of a micropipette [12–14]. An advantage of using a micro liquid|liquid interface is that the positive feedback for the iR compensation is not required. At a liquid|liquid interface of conventional size, we cannot rule out the possibility that the positive feedback which is mandatory in recording voltammograms causes the EI. In this work, we demonstrate that the EI appears without the iR compensation. We also describe some new features of the EI at the micro liquid|liquid interface supported at the tip of a micropipette.

2. Experimental details

Tetrapentylammonium tetrphenylborate (TPnATPB) used as the supporting electrolyte in the 1,2-dichloroethane (DCE) phase was prepared from tetrapentylammonium iodide (Tokyo Kasei Kogyo, 98%) and sodium tetrphenylborate (NaTPB, Dojindo Lab., 99.5%), as described elsewhere [15]. Lithium chloride monohydrate (Wako Chemical Industries, 99.9%), magnesium chloride (Merck, pro analysis), and sorbitan monooleate (Span80, Wako Chemical Industries) were used without further purification. DCE (Wako Chemical Industries, 99.5%) was washed with water three times before use. A stock solution containing 10 mmol dm⁻³

decylamine (Tokyo Kasei Kogyo, 95%), 12 mmol dm⁻³ HCl, and 0.1 mol dm⁻³ LiCl was diluted with a 0.1 mol dm⁻³ LiCl aqueous solution to prepare test solutions at desired concentrations of decylammonium ions (DeNH₃⁺). The electrochemical cell employed in the present study is represented as



where M stands for mol dm⁻³, W_{ref} is the aqueous phase for the reference of the potential in DCE, W is the aqueous phase containing DeNH₃⁺, and $c_{\text{DeNH}_3^+}^{\text{W},0}$ is the initial concentration of DeNH₃⁺ in the W phase. The potential of the right-hand terminal with respect to the left is hereafter denoted as E . The current, I , corresponding to the flow of the positive charge from W to DCE is taken to be positive.

Micropipettes were made from borosilicate glass capillaries (G-1, Narishige, od/id = 1.0 mm/0.6 mm) using a pipette puller (PC-10, Narishige). An optical microscope (BX-60, 200×-1000×, Olympus) was used to observe the tip of a pipette to determine the inner diameter of the tip, d , prior to an electrochemical measurement. A micropipette filled with the W phase was immersed in the DCE phase to form a micro liquid|liquid interface. The interface supported at the tip of a micropipette was confirmed using a digital camera (C7190-20, Hamamatsu Photonics) equipped with a long-working-distance objective (100×, LMPlanFL, Olympus).

Electrochemical measurements were made using either a microelectrode potentiostat (HECS-972C, Fusou Electro Chemical System) without Ohmic drop compensation or a four-electrode potentiostat (HA1010mM1A, Hokuto Denko Co) with a positive feedback for the iR drop compensation in the cases when d was 580 μm and 5 mm. Cyclic voltammograms were recorded with a homemade computer-controlled system.

3. Results and discussion

In previous studies, the abnormally increased irregular currents (AIIC) in voltammograms, that is, the irregular currents whose magnitude far exceeds the diffusion-limited current, were taken as evidence of the EI [3–5]. In the present study, we found that the emergence of the AIIC in voltammograms for the transfer of DeNH₃⁺ across the micro liquid|liquid interface supported at the tip of a micropipette was dependent on the concentration of DeNH₃⁺ ($c_{\text{DeNH}_3^+}^{\text{W},0}$), d , and the scan rate of the applied voltage (v). In the following, we first describe typical voltammograms that exhibit the AIIC. We then describe the effects of the concentration of DeNH₃⁺, the area of the interface formed at the tip of the micropipette, and v on the emergence of the AIIC.

3.1. AIIC at the micro liquid|liquid interface

Curve 1 in figure 1 shows a voltammogram for the transfer of DeNH₃⁺ across the micro liquid|liquid interface supported at the tip of the micropipette when $d = 25 \mu\text{m}$, $v = 100 \text{ mV s}^{-1}$, and $c_{\text{DeNH}_3^+}^{\text{W},0} = 10 \text{ mmol dm}^{-3}$. The solid line and the broken line represent the traces in the forward and reverse scans, respectively. In the forward scan, the potential where the AIIC began (E_1) was -340 mV and the potential where the AIIC ended (E_2) was -230 mV . Thus, the instability window that was seen in the transfer of DeNH₃⁺ at the conventional liquid|liquid interface [5] also appeared at the micro liquid|liquid interface without the positive feedback for iR compensation. The AIIC was also seen in the reverse scan. The potential

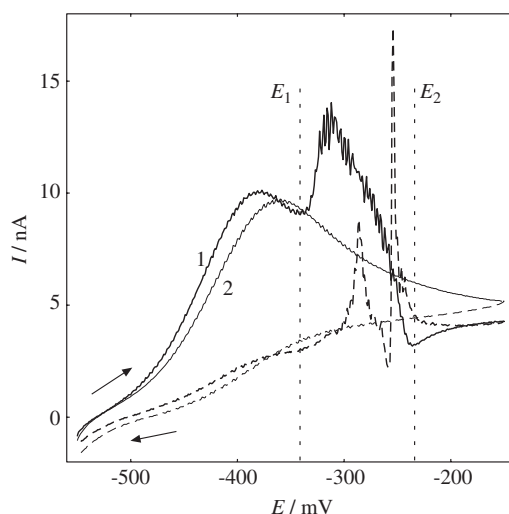


Figure 1. Cyclic voltammograms for the transfer of DeNH_3^+ across the DCE|W interface supported at the tip of a micropipette, when the W phase filling the pipette contained 10 mmol dm^{-3} DeNH_3^+ , d was $25 \mu\text{m}$, and v was 100 mV s^{-1} (curve 1). Curve 2 is a voltammogram recorded when the DCE phase contained 6 mmol dm^{-3} Span80. Solid and broken lines show the forward and backward scans, respectively. E_1 and E_2 represent potentials of the beginning and the end of the AIIC respectively.

where the AIIC resurged was close to E_2 and subsided at about -300 mV . The current was large and positive in the AIIC region in both forward and reverse scans. The width of the AIIC region in the reverse scan was narrower than that in the forward scan.

Curve 2 in figure 1 shows the voltammogram recorded when the DCE phase contained 6 mmol dm^{-3} Span80, which is a nonionic surfactant and is known to suppress the AIIC [3–5, 7, 8]. The shape of this voltammogram reflects the diffusion-controlled transfer of DeNH_3^+ in the micropipette [16], which is characterized by the appearance of a peak caused by the linear diffusion in the forward scan and a sigmoidal voltammogram in the reverse scan. The AIIC is thus suppressed in the voltammograms in the presence of Span80.

The determination of the half-wave potential of DeNH_3^+ transfer based on the voltammogram using the micropipette is not straightforward because of the asymmetric diffusion of DeNH_3^+ on both sides of the interface, that is, the approximately linear diffusion inside the pipette and the radial diffusion in the DCE phase [13, 17, 18]. We therefore fitted numerically simulated voltammograms, taking account of the shape of the micropipette [16], to experimental voltammograms for determining the formal potential of the transfer of DeNH_3^+ ($E^{0'}$). The obtained value, $E^{0'} = -380 \text{ mV}$, is close to the point of inflection in the voltammogram in the reverse scan in figure 1.

All features of the AIIC found at the micro liquid|liquid interface, that is, the existence of the AIIC as an instability window, the location of the instability window being close to $E^{0'}$, and the disappearance of the AIIC by addition of Span80 in DCE, are similar to the features of the EI reported at the liquid|liquid interface of conventional size [5]. The emergence of the AIIC at the micro liquid|liquid interface supported at the tip of the micropipette thus ascertains the generality of the EI. The fact that the AIIC was confirmed without applying the positive feedback for the iR compensation demonstrates that the EI is not an artifact caused by the positive feedback.

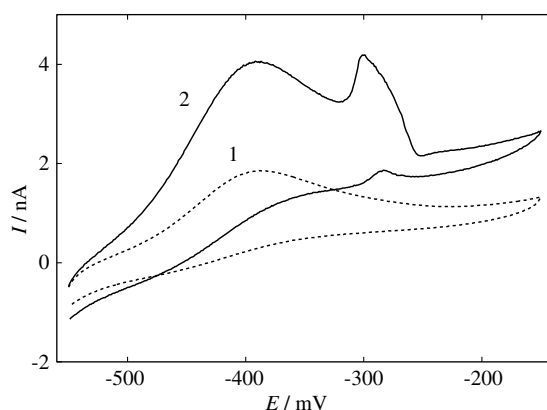


Figure 2. Effect of the bulk concentration of DeNH_3^+ in W on the shape of the voltammograms. $c_{\text{DeNH}_3^+}^{\text{W},0}$: 2 (curve 1) and 5 (curve 2) mmol dm^{-3} . d : 25 μm . v : 100 mV s^{-1} .

Curve 1 in figure 1 shows significantly larger currents than the diffusion-limited current (curve 2) between the initial potential of the voltammogram and E_1 , before the onset of the AIIC. According to the electrocapillary curve reported by Kasahara *et al* [5], DeNH_3^+ adsorbs at the interface in this potential range. The increase in the current in the absence of Span80 when $E < E_1$ is probably attributable to the desorption of DeNH_3^+ , as is the case of voltammograms in the presence of weakly adsorbed reactants on an electrode [19]. At the potentials more positive than E_2 , the current of curve 1 was considerably lower than that of curve 2. This reflects the exhaustion of DeNH_3^+ inside the pipette after the AIIC.

3.2. Effect of the concentration and the interfacial area on the AIIC

Although the AIIC was confirmed in figure 1, the value of $c_{\text{DeNH}_3^+}^{\text{W},0}$, 10 mmol dm^{-3} , is at least ten times higher than that required to cause the AIIC at the interface of a conventional size. Figure 2 shows voltammograms for two different concentrations of $c_{\text{DeNH}_3^+}^{\text{W},0}$, 2 mmol dm^{-3} (curve 1) and 5 mmol dm^{-3} (curve 2), recorded at $v = 100 \text{ mV s}^{-1}$ and $d = 25 \mu\text{m}$. Surprisingly, the AIIC was not detected at $c_{\text{DeNH}_3^+}^{\text{W},0} = 2 \text{ mmol dm}^{-3}$ as shown in the voltammogram (curve 1). By raising the concentration to 5 mmol dm^{-3} , the AIIC did appear between $E_1 = -320 \text{ mV}$ and $E_2 = -260 \text{ mV}$ (curve 2). The threshold level for the AIIC at this interface resides between 2 and 5 mmol dm^{-3} . This is in marked contrast with the case of AIIC at the DCE|W interface of conventional size, where the AIIC was detected at $c_{\text{DeNH}_3^+}^{\text{W},0} = 0.5 \text{ mmol dm}^{-3}$ [5]. The decrease in the area of the interface apparently stabilizes the interface against the AIIC; the occurrence of the AIIC depends on the size of the interface and $c_{\text{DeNH}_3^+}^{\text{W},0}$.

We systematically examined the influence on the AIIC of three factors, d , v , and $c_{\text{DeNH}_3^+}^{\text{W},0}$. The results are summarized in figure 3 at two values of v , 10 (a) and 200 mV s^{-1} (b). The AIIC always appeared when $c_{\text{DeNH}_3^+}^{\text{W},0}$ was high and d was large (\bullet). The AIIC never appeared when $c_{\text{DeNH}_3^+}^{\text{W},0}$ was low and d was small (\circ). Between these two cases, the AIIC occasionally emerged (Δ) for multiple measurements. In each set of the experimental conditions, voltammograms were recorded at least twice. There seems to be a demarcation line shown as a dashed line in each panel of figure 3 that divides the experimental conditions into two groups, that is, the conditions that make the interface AIIC prone and those that make it AIIC resistant.

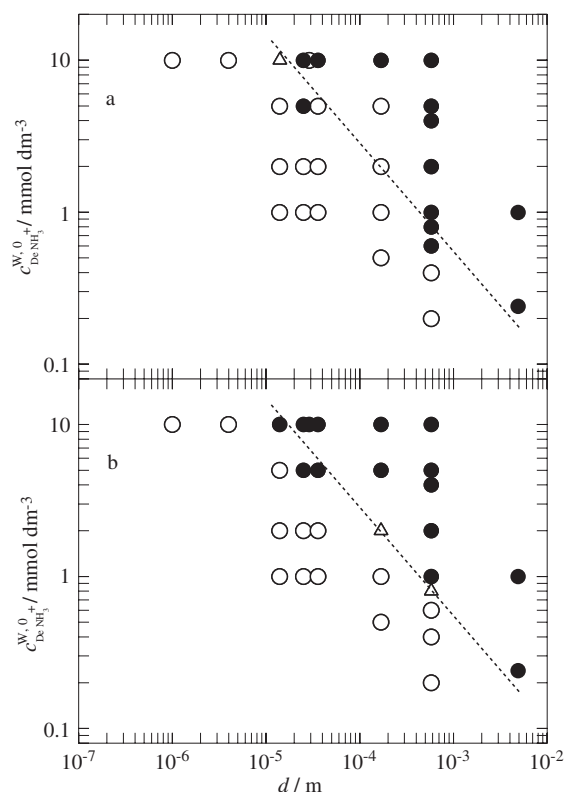


Figure 3. Effect of the inner diameter of the pipette orifice and the concentration of DeNH_3^+ on the appearance of the AIIC on voltammograms. v : 10 (a) and 200 mV s^{-1} (b). The filled circles, open triangles, and open circles show the case when the AIIC was observed, occasionally observed, and not observed, respectively. Dashed lines show the demarcation between the filled circles and the open circles.

According to the studies of the thermally induced Marangoni convection in a cylinder, the convection is suppressed when the aspect ratio is small [9, 10]. Since the aspect ratio of the pipette decreases with the decrease in d , the inner space of the pipette is probably too small to allow the formation of rolls. In other words, the suppression of the AIIC at small values of d in figure 3 is likely to be explained by the effect of the aspect ratio on the Marangoni convection.

It is known that the driving force of the surfactant induced Marangoni convection is proportional to the concentration gradient of the surfactant normal to the interface [20, 21]. In the present case of the EI-induced Marangoni convection, the slopes of the dashed lines in figure 3 at both scan rates have the same value, -0.7 . This suggests that for the AIIC to occur c^3 is approximately equivalent to d^2 , i.e., the concentration is more effective than the increase in the size of the interface.

Another possible factor that can cause the observed dependence (dashed lines in figures 3(a) and (b)) is the edge effect due to the double layer of the wall of the pipette, which may be responsible for possible nonuniform distribution of the potential at the interface, nonuniform flow of DeNH_3^+ , and streaming potential. However, this edge effect is expected to be small because the thickness of the double layer is thin in comparison with the size of the tip of the micropipette.

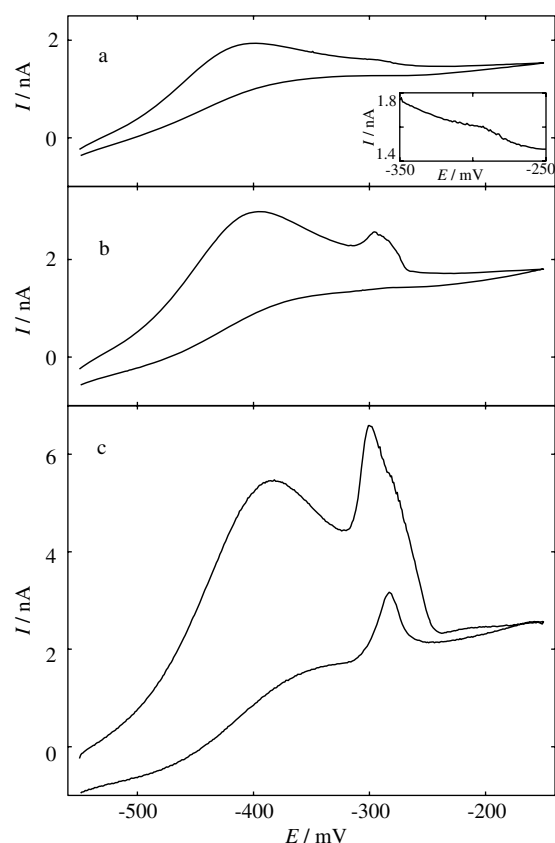


Figure 4. Effect of the scan rate on the shape of the voltammograms. v : 10 (a), 50 (b), and 200 mV s^{-1} (c). $c_{\text{DeNH}_3^+}^{\text{W},0}$: 5 mmol dm^{-3} . d : 25 μm . The inset in a shows a magnified view of the forward scan where the AIIC emerged.

If the probability of the occurrence of electrochemically unstable domains in the interface is proportional to $c_{\text{DeNH}_3^+}^{\text{W},0}$ and the area of the interface, the dashed line in figure 3 is expected to have a slope of -2 . However, the experimental slope is considerably smaller, about -0.7 , as described above. The nucleation-and-growth-type process, if any, does not seem to be a determining factor of the AIIC under the present experimental conditions.

3.3. Depletion of DeNH_3^+ in pipette due to the AIIC

One thing we should be aware of in studying the EI using a micropipette is the depletion of surfactant ions inside the pipette during recording a voltammogram, as exemplified at the positive end of curve 1 in figure 1. Since the depletion depends on the total number of surfactant ions transferred across the interface, it should also depend on v . We therefore examined the effect of v on the appearance of the AIIC in voltammograms.

3.3.1. Effect of the scan rate on the AIIC. Figure 4 shows voltammograms recorded at three different values of v , 10 (a), 50 (b), and 200 mV s^{-1} (c) when $d = 25 \mu\text{m}$ and $c_{\text{DeNH}_3^+}^{\text{W},0} = 5 \text{ mmol dm}^{-3}$. In figure 4(a), the AIIC was barely visible around $E = -300 \text{ mV}$. In figures 4(b) and 4(c), the AIIC was clear. The degree of AIIC judged from the magnitude of the AIIC thus depends on v . A decrease in the peak area of the AIIC with a decrease in v means that the charge transported across the interface due to the AIIC reduces with decreasing v .

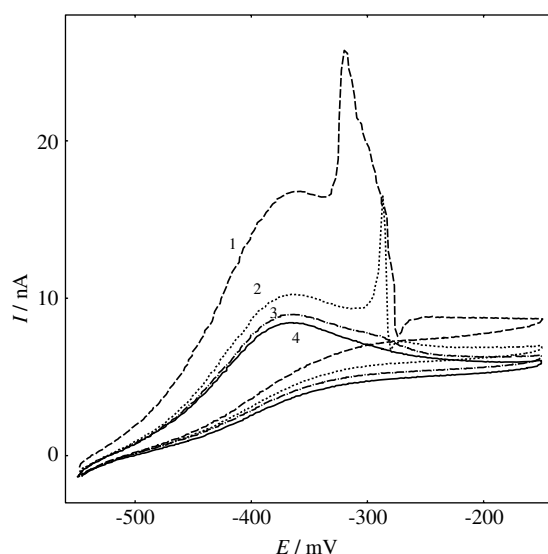


Figure 5. Effect of the cycles on the cyclic voltammograms of the transfer of the DeNH_3^+ . v : 50 mV s^{-1} . $c_{\text{DeNH}_3^+}^{\text{w},0}$: 10 mmol dm^{-3} . d : $33 \text{ }\mu\text{m}$. The numbers show the number of cycles.

This dependence indicates that the diffusion-layer thickness for the transfer of DeNH_3^+ or the concentration gradient of DeNH_3^+ inside the pipette affects the degree of AIIC. Since this type of scan rate dependence is not observed at an interface of conventional size, the depletion of DeNH_3^+ inside the pipette is likely to be responsible for the dependence of the degree of the AIIC on v .

Moreover, the shape of the voltammogram during the AIIC recorded at the micro liquid|liquid interface is different from that recorded at the liquid|liquid interface of conventional size. The shape of all voltammograms exhibiting the AIIC (figures 1, 2, and 4) is a triangle. In contrast, at an interface of conventional size, the magnitude of the AIIC is almost independent of v ; the shape of the voltammogram during the AIIC is trapezoidal [5]. The steady current during the AIIC means that the convective transport of DeNH_3^+ is independent of time. In contrast, the AIIC of a triangle shape in the present case indicates that the transport of DeNH_3^+ by the convection inside the capillary decreases with time because of the depletion of DeNH_3^+ .

3.3.2. AIIC in the multiple cyclic voltammogram. To further demonstrate the exhaustion of DeNH_3^+ in the vicinity of the tip of the pipette, we recorded voltammograms with consecutive scans of the applied voltage. Figure 5 shows the voltammograms recorded at $v = 50 \text{ mV s}^{-1}$ when $d = 33 \text{ }\mu\text{m}$ and $c_{\text{DeNH}_3^+}^{\text{w},0} = 10 \text{ mmol dm}^{-3}$. The number indicated by each curve indicates the number of cycles of the voltage scan, n . The AIIC clearly appeared in the first cycle, but was narrower and smaller in curve 2 and was even smaller in curve 3. The AIIC completely disappeared in curve 4. E_1 shifted to the positive potentials with n . Obviously, the concentration of DeNH_3^+ in the pipette decreases with n . In the fourth cycle, the concentration of DeNH_3^+ in the vicinity of the tip of the pipette is estimated to be 4 mmol dm^{-3} from the diffusion-limited peak current (curve 4). This concentration is within the stable region in figure 3.

The results in figures 4 and 5 raise a concern that at smaller values of d and $c_{\text{DeNH}_3^+}^{\text{W},0}$ the EI may not be detected as AIIC, because of the depletion of DeNH_3^+ inside the capillary.

One of the methods free from this depletion problem is the use of a liquid|liquid interface formed at a micro-hole [22] in a thin membrane separating two immiscible electrolyte solutions. Since the two semi-infinite bulk phases assure the supply of DeNH_3^+ even under the AIIC, there should be no depletion problem unlike micropipette experiments above. We plan to conduct experiments using a micro liquid|liquid interface at the micro-hole to examine the effect of interfacial area on the AIIC.

4. Conclusion

The AIIC caused by EI has been shown to take place in the transfer of DeNH_3^+ across the DCE|W interface formed at the tip of the micropipette. The AIIC without the positive feedback for the iR compensation confirmed that the EI is not an artifact caused by the positive feedback. The effect of the size of the pipette and the concentration of DeNH_3^+ on the AIIC is in accordance with other Marangoni instabilities. Care must be exercised in studying the EI at the micro liquid|liquid interface formed at the tip of the micropipette because of the problem of the depletion of ions in the vicinity of the interface.

Acknowledgments

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