Investigation of Ion Transfer Across the Micro-Water/Nitrobenzene Interface Facilitated by a Fullerene Derivative

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A functionalized fullerene derivative containing a monoaza-18-crown-6 moiety was investigated by facilitated ion (such as Li$^+$, Na$^+$, K$^+$, NH$_4^+$, Mg^{2+}, and Ca^{2+}) transfer across the micro-water/nitrobenzene interface supported at the tip of a micropipet. The current responses were detected by cyclic voltammetry and Osteryoung square wave voltammetry, which demonstrated that the facilitated ion transfer does occur by an interfacial complexation−dissociation process. The diffusion coefficient of this compound in nitrobenzene was approximately (5.90 ± 0.04) × 10^{-7} cm^2 s^{-1}, which is 1 order of magnitude less than other common ionophores due to the large size of the molecule. The selectivity of this molecule toward the metal ions followed the sequence Na$^+$ > Li$^+$ > K$^+$ > NH$_4^+$ > Ca^{2+} ∼ Mg^{2+}. In addition, this compound was also easy to form film at the water/nitrobenzene interface to inhibit the simple ion transfer of tetramethylammonium ion. However, the adsorption of this ionophore has less influence on the facilitated metal ion transfer.

Since the discovery and the large availability of macroscopic quantities, fullerene and its derivatives have triggered an extensive research interest covering a wide range of fundamental and applied aspects.[1] Multiple synthetic modifications of this molecule have been conducted. A fullerene derivative, L (Figure 1), has the characteristic of containing a monoaza-18-crown-6 (A18C6) ether moiety, which can endow the pristine fullerene with the functionality of complexing with a certain cation and perhaps allowing it to transfer across a water/organic interface.[2] Since L can form a stable Langmuir−Blodgett (LB) film at the air/water interface,[3] it may be also easy to form such film to influence an ion transfer across an interface. Therefore, it is worth studying its behavior further at a liquid/liquid interface.

In addition, since Pederson[4] first synthesized 33 cyclic polyethers and Koryta[5] primarily reported the ion transfer across a
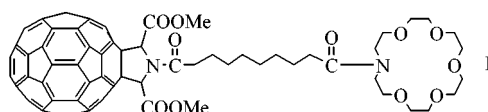

Figure 1. Planar structure of compound L.

liquid/liquid (L/L) interface could be facilitated by an ionophore, extensive efforts have been carried out on macrocycles that are highly insoluble in water. So far, one typical question in crown ether chemistry is how the selectivity in crown ether complexation emerges. The size fit theory is a widely accepted concept; namely, the size of a cation must match the cavity size of a crown ether in a flat conformation.[6] The compound L contains a close-caged fullerene moiety and an alkyl group with an A18C6, covalently attached to the buckyball. It is well known that the ball-like C$_{60}$ is extremely rigid and hydrophobic due to its unique structure, while A18C6 can distribute between the two adjacent phases under different pH in the aqueous phase to facilitate K$^+$ transfer across the water/1,2-dichloroethane (W/DCE) interface.[2] The nitrogen atom present in A18C6 is characteristic of high chemical reactivity. Modifying A18C6 by attaching a pyrrolidinofullerene derivative group to the nitrogen atom may endow it with much larger K_D than the original compound. The diffusion of L in the organic phase is doomed to be very slow due to its big molecular dimension. Furthermore, the effective cavity size turns out to be smaller because of the distortion of the crown ether cavity and there exists steric repulsion for cations, both of which are due to attaching a large substituent to the nitrogen atom. Therefore, the crown ether moiety of compound L could show some new complex behavior different with the pristine A18C6. In addition, this new type of ionophore may shine a light for design of new chemical sensors.

Electrochemistry at a L/L interface, or an interface between two immiscible electrolyte solutions (ITIES), can be applied to study the complexation between metal ions and ionophores at an interface. This process plays a significant role in the biochemical fields, such as transmembrane signaling[7] and enzymatic reactions.[8]

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It is also very important in many technological systems from extraction processes to chemical sensors.[9–15] To clarify such interfacial complexation mechanisms, ion transfer across **a** L/L interface facilitated by various types of ionophores has been extensively investigated for different cations.[9,16–19] Actually, in the case of a very lipophilic ionophore, the transfer of a cation from an aqueous to an organic phase occurs readily by a process called transfer by interfacial complexation (TIC) and the reverse transfer by interfacial dissociation (TID). This nomenclature was first coined by Shao et al. using a micro-L/L interface supported at the tip of a micropipet.[20] The methodology employed to establish a micro-L/L interface was pioneered by Taylor and Girault in 1986.[21]

In this work, a micro-water/nitrobenzene (W/NB) interface supported at the tip of a micropipet was applied to investigate the behavior of the compound L at the interface. It was focused on utilizing the complexation reactions that occurred at the W/NB interface between some cations and compound L to obtain facilitated ion transport with its crown ether host. The interactions between cations (such as Li^+, Na^+, K^+, NH_4^+, Mg^{2+}, and Ca^{2+}) and this ionophore were detected by cyclic voltammetry (CV) and Osteryoung square wave voltammetry (OSWV). In addition, it was also studied by comparison of the simple ion transfer of tetramethylammonium ion (TMA^+) in the absence and presence of L in the organic phase to find out whether it can form film at the W/NB interface to inhibit the ion transfer.
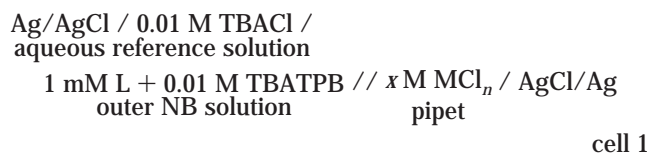
EXPERIMENTAL SECTION

Chemicals. All chemicals used were of analytical grade or better. The aqueous and organic phases were prepared by deionized water (Milli-Q, Millipore) and NB (Beijing Chemicals Co., Beijing, China), respectively. NB was washed several times by deionized water before use. Lithium chloride, sodium chloride, potassium chloride, ammonium chloride, and magnesium chloride (were purchased from Beijing Chemicals Co. Compound L was synthesized by the method described previously.[3] Tetrabutylammonium chloride (TBACl) and tetramethylammonium chloride (TMACl) was supplied by Fluka. Tetrabutylammonium tetraphenylborate (TBATPB) was used as the supporting electrolyte in the NB phase and prepared by methods reported elsewhere.[22] Specific cautions were taken for dealing with NB and other hazardous chemicals.

Fabrication of Micropipets. Micropipets were made from borosilicate glass capillaries (o.d./i.d., 1.0/0.58 mm) obtained from

Sutter Instrument using a laser-based pipet puller model P-2000 (Sutter Instrument Co.). The proper choice of the pulling parameters was critical to make a pipet with a short shank (patch-clamp type) and flat orifice. Both the orifice radius and the thickness of the pipet wall were inspected by an optical microscope. The micropipets were filled with the aqueous solution from the back using a small syringe (10 μL).

Electrochemical Cell and Electrode. The electrochemical cell used for voltammetric measurements was a two-electrode system described in detail by Beattie et al.[23] The experimental system for the investigation of cations transfer facilitated by L can be represented by the following cell (unless specified):

Ag/AgCl / 0.01 M TBACl /
aqueous reference solution

1 mM L + 0.01 M TBATPB // x M MCl$_n$ / AgCl/Ag
　　outer NB solution　　　　　　pipet

cell 1

where n is the charge number of the metal cation that was investigated and x corresponds to the value given in the text.

Electrochemical Measurements. In this work, E is referred as the Galvani potential difference $\Delta_o^w\phi$ ($\Delta_o^w\phi$, in which ϕ^w and ϕ^o are the inner Galvani potentials of aqueous and organic phases, respectively) with respect to the standard potential difference for TBA^+, $\Delta_o^w\phi_{TBA^+}^o$ (the organic and reference organic phases have the same concentration of TBA^+):

$$E = \Delta_o^w\phi - \Delta_o^w\phi_{TBA^+}^o$$

where $\Delta_o^w\phi_{TBA^+}^o = -248$ mV; it is the standard Galvani potential for TBA^+ transfer across a W/NB interface,[24] and it can be deduced from the extraction data.[25] A positive current refers to the transfer of a positive ion from the aqueous to the organic phase or a negative ion from the organic to the aqueous phase. All cyclic voltammetric experiments were performed using a BAS100B electrochemical workstation (Bioanalytical Systems). An Olympus BX-60 optical microscopy ($\times100-\times500$) (Olympus Co.) was used to determine the radii of all pulled pipets before measurements. All the experiments were carried out at room temperature (25 $\pm$ 2 °C).

RESULTS AND DISCUSSION

Facilitated Li^+ Transfer. Figure 2 showed a typical CV produced by facilitated Li^+ transfer across the micro-L/L interface supported at the tip of a micropipet with cell 1 for $x = 0.1$. The steady-state current obtained was consistent with the asymmetric diffusion regime formed at the interface due to the specific shape of the micropipet and the mechanism of the facilitated ion transfer. During the forward scan, Li^+ transferred from aqueous solution inside a micropipet to the outer NB solution facilitated by L, which was controlled by spherical diffusion of L to the interface and named a TIC mechanism. And the reverse was dominated by the same diffusion manner of the complexed ion LiL^+, a TID process.

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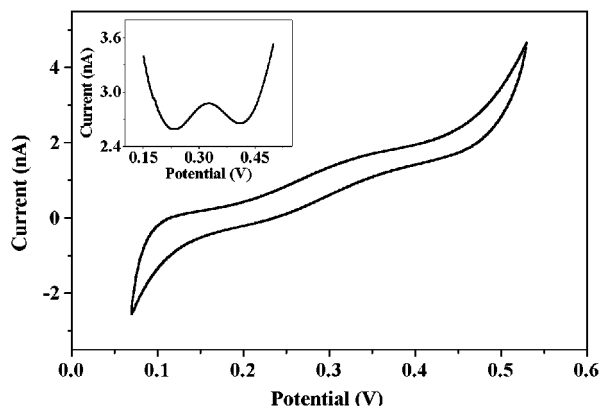(25) Rais, J. *Collect. Czech. Chem. Commun.* **1973**, *38*, 965−975.

Figure 2. Cyclic voltammogram of facilitated Li$^+$ transfer across a micro-W/NB interface supported at a 10-μm-radius micropipet. System: cell 1 with $x = 0.1$. Sweep rate was 10 mV/s. The inset showed the corresponding OSWV with sweep width 25 mV, frequency 15 Hz, and potential step 1 mV.

However, the voltammogram demonstrated pronounced capacitive current when L was present in the NB phase. As the scan rates increased, the capacitive current distorted the faradic current and resulted in an even more poorly resolved voltammogram and, thus, made the analysis essentially difficult. Consequently, Osteryoung square wave voltammetry was employed due to its inherently greater sensitivity. The inset of Figure 2 shows a typical OSWV with a quite symmetrical peaked-shape wave, which is indicative of a diffusion-controlled reversible charge-transfer reaction.

Beattie et al. demonstrated that a micro-W/DCE interface at the tip of a micropipet exhibits the following behavior:[23]

$$I_{ss} = 3.35\pi nFDac \qquad (1)$$

In general, with no external pressure applied, the water/organic interface supported at the tip of a micropipet is flat and the voltammetric response should follow the well-known theory for a microdisk electrode. However, a large deviation from theory was observed in this case. Shao and Mirkin[26] have proved that its difference with a disk-shaped microelectrode was ascribed to the partial wetting of the outer walls close to the orifice by the inner aqueous solution which escapes from the pipet since the glass wall was hydrophilic. While in this work, NB was selected as the organic solvent because L can dissolve in it better than in DCE. However, NB has a different nature with DCE, such as viscosity, dielectric constant, hydrophobicity, and so on, which destines that the behavior of a micropipet at a W/NB interface may be different. Therefore, at first it is necessary to investigate the performance of a micropipet at a W/NB interface. A well-characterized experimental system, i.e., potassium ion transfer facilitated by dibenzo-18-crown-6 (DB18C6), was studied with micropipets of different radii. The experimental system can be represented by the following cell:
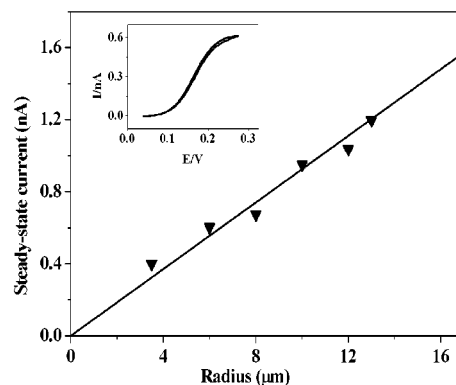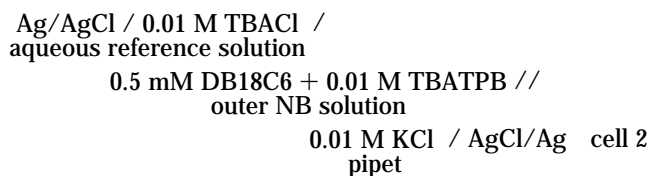
Ag/AgCl / 0.01 M TBACl /
aqueous reference solution
　　　0.5 mM DB18C6 + 0.01 M TBATPB //
　　　　　outer NB solution
　　　　　　　0.01 M KCl / AgCl/Ag　cell 2
　　　　　　　　pipet

Figure 3. Plot of steady-state current versus different pipet radius. System, cell 2. The inset showed the background-subtracted voltammogram of a 6-μm-radius micropipet.

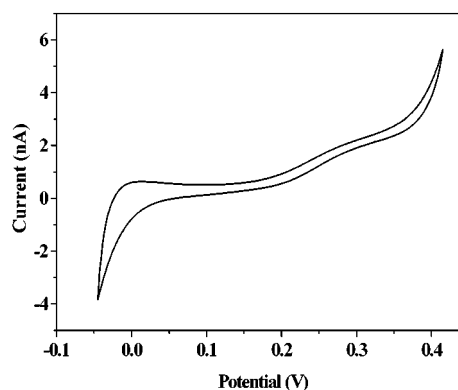**Figure 4.** Cyclic voltammogram of facilitated Na$^+$ transfer across the micro-W/NB interface supported at a 14-μm-radius micropipet. System, cell 1 with $x = 0.1$. The scan rate was 10 mV/s.

The limiting steady-state currents, I_{ss}, can be expressed by the following equation:

$$I_{ss} = \text{const } FaDc \qquad (2)$$

where F is the Faraday constant, D is the diffusion coefficient of DB18C6, c is the bulk concentration of DB18C6, a is the inner radius of the tip, and const is a value that depends on the shape of the micro-L/L interface and the geometry of the tip. The steady-state current versus pipet radius was plotted in Figure 3, from which slope const $= 3.12\pi$ was obtained using $D = 2.3 \times 10^{-6}$ cm^2 s^{-1}.[27] By estimating the steady-state currents of the facilitated ion transfer, it is possible to calculate the diffusion coefficient of L in NB phase to be 6.66×10^{-7} cm^2 s^{-1} approximately, which is 1 order of magnitude less than other common ionophores, such as dibenzo-18-crown-6 (DB18C6), due to its large size.
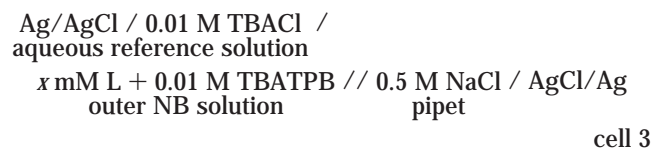
Facilitated Na$^+$ transfer. Cell 1 ($x = 0.1$) was also used to study Na$^+$ transfer facilitated by L. Figure 4 showed the cyclic voltammogram obtained with a 14-μm-radius pipet. A steady-state current of facilitated Na$^+$ transfer was observed and a much better voltammogram than that of Li$^+$ was obtained; thus, it is possible to analyze this process quantitatively. The reason for why could we obtain better CVs in this case than the rest of others may be because the nature of complexation and adsorption.

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First, the steady-state current was investigated with respect to the internal tip radius of the micropipet (cell 1, $x = 0.1$), the result of which was plotted. According to the slope and eq 2, it can be calculated that the diffusion coefficient of L in NB is $(5.90 \pm 0.04) \times 10^{-7}$ cm^2 s^{-1}, which is close to the value of 6.66×10^{-7} cm^2 s^{-1} obtained from the facilitated lithium transfer.

In addition, the steady-state current as a function of the concentration of L was studied using a series of 9-μm-radii pipets according to cell 3:

Ag/AgCl / 0.01 M TBACl /
aqueous reference solution
x mM L + 0.01 M TBATPB // 0.5 M NaCl / AgCl/Ag
    outer NB solution   pipet

cell 3

The results demonstrate that the steady-state currents are proportional to the concentration of L in the NB phase and independent of the scan rates, while the half-wave potentials do not vary with L concentration. These results clearly indicate that the facilitated transfer of Na$^+$ by L across the W/NB interface is reversible and controlled by the diffusion of the L in the organic phase and also confirm that a 1:1 complex between L and Na$^+$ was formed at the interface.

Other Cations. Other cations such as K$^+$, NH$_4^+$, Mg^{2+}, and Ca^{2+} were also investigated using the same method. Compound L displayed some effects on the system when it emerged in the organic phase, such as increasing the capacitive current and iR drop. While in the voltammetric polarization window, rather poor steady-state voltammograms of facilitated K$^+$ transfer were observed when the concentrations of K$^+$ were varied from 0.01 to 0.5 M, which were further confirmed by OSWVs without appearance of obvious peaked waves. The same results were in other cation systems. This made the quantitative analysis quite difficult or impossible.

For Li$^+$ and Na$^+$, clear evidence for the facilitated ion transfer was obtained. However, for other cations, although it is impossible to do quantitative analysis from the CVs and OSWVS, we can still find out which ion could complex with L. For example, it can be observed that in the positive end of the potential window L has a small tendency to complex with K$^+$, while there were no such phenomena for Ca^{2+} and Mg^{2+}. Thus, it can be concluded that L only exhibits a larger selectivity toward Li$^+$ and Na$^+$ and the selectivity sequence was Na$^+$ > Li$^+$ > K$^+$ > NH$_4^+$ > Ca^{2+} $\sim$ Mg^{2+} in terms of the complex stability constants (though in part not really measured). Indeed, the selectivity sequence may not change compared to A18C6 (since no complete sequence was obtained in other solvents), and for a given ligand, the selectivity sequence of various metal cations must not be necessarily the same. But here we only insisted that the selectivity ability of L toward metal ions changed as shown in Table 1 since the effective size of the crown cavity turned to be smaller when a substituent was bound to the nitrogen.

The radius of K$^+$ is close to that of NH$_4^+$ but larger than Li$^+$ and Na$^+$ as shown in Table 1. The effective cavity size turns out to be smaller because of the attachment of a large substituent to the nitrogen atom. Hence, it is reasonable that the crown ether moiety is apt to select Li$^+$ and Na$^+$ but not K$^+$ and NH$_4^+$. In addition, the steric repulsion must be considered because it is

Table 1. Ion Radius (r), Standard Transfer Potential ($\Delta_o^w\phi°$) of Relevant Cations, and Association Constants between Cations and Ionophores

ion	radius[a] (nm)	$\Delta_o^w\phi°$ [a] (V)	$\log\beta_1^{M(A18C6)^+}$	$\log\beta_1^{ML^+}$
Li$^+$	0.068	0.398	3.20[b]	6.6
Na$^+$	0.095	0.358	2.69[c] (4.60[b])	7.3
K$^+$	0.133	0.252	3.98[c] (11.1[d])	
NH$_4^+$	0.137	0.284		
Ca^{2+}	0.072	0.370	3.96[c]	
Mg^{2+}	0.099	0.354		

[a] Data from ref 28. [b] Association constants in acetonitrile obtained by dc polarography.[40] [c] Association constants determined in anhydrous methanol.[41] [d] Association constants in DCE.[2]

more difficult for the cations with bigger sizes to approach the crown ether host hampered by the huge pendant of the pyrrolidinofullerene derivative group.

Although the radii of Mg^{2+} and Ca^{2+} are close to those of Li$^+$ and Na$^+$, the selectivity shown by Mg^{2+} and Ca^{2+} systems do not support the size-matching principle. It is reasoned that size selectivity toward metal ions is also influenced by other factors, including the solvation patterns of the species involved, ligand conformation before and after complexation, and the number and nature of the chelate rings formed upon complexation.[29] So far, no general agreement has been reached. Size selectivity and size-matching effects are the dominant factors for these cases, and the interaction between crown ethers and cations may be explained using them.

Evaluation of Association Constants. According to the work of Matsuda et al.,[30] when an ionophore and a cation form a 1:1 complex and the ion transfer is controlled by the diffusion of the ionophore from the bulk organic phase to the interface, if $c_M \gg c_L$, The following equation can be obtained:

$$\Delta_o^w\phi_{1/2} = \Delta_o^w\phi_{M^+}^{o'} + \frac{RT}{zF}\ln\frac{D_L}{D_{ML^+}} - \frac{RT}{zF}\ln(\beta_1^°c_{M^+}) \quad (3)$$

Then a study of concentration dependence on the half-wave potential was carried out to evaluate the association constants of the LiL$^+$ and NaL$^+$ complexes. OSWV was employed to determine the half-wave potentials, and a batch of 10- and 7-μm-radii pipets were used, respectively. Plots A and B in Figure 5 showed the results of them, the former of which has a slope of 110 ± 4 mV/decade concentration of Li$^+$ and an intercept of 0.215, and the latter a slope of 118 ± 2 mV/decade concentration of Na$^+$ and an intercept of 0.156. Given that the potential of the silver/silver chloride electrode inside micropipet varied with the concentration of chloride ion in the aqueous phase, 1:1 complexes, that is, LiL$^+$ and NaL$^+$ formed at the interface, respectively. According to eq 3, the logarithm of the association constants of the LiL$^+$ and NaL$^+$ complexes in the NB phase, $\log\beta_1^°$, were calculated to be 6.6 and 7.3, respectively. Although a molecule with larger size, the stability

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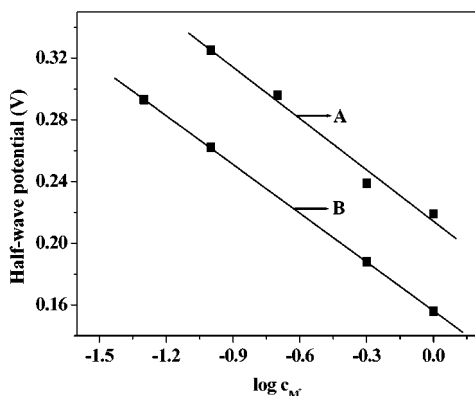
Figure 5. Plots of the half-wave potential of the complexes versus the logarithm of the metal ion concentrations. System is shown in cell 1: (A) Li^+-L system and (B) Na^+-L system.

constants of L with Li^+ and Na^+ in the NB phase can match the reported values for other ionophores, such as 7,19-dibenzyl-2,3-dimethyl-7,19-diaza-1,4,10,13,16-pentaoxacyloheneicosane-6,20-dione (7.44, 5.80),[31] dibenzo-18-crown-6 (4.8, 7.3), dibenzo-24-crown-8 (5.5, 7.7), dibenzo-30-crown-10 (7.5 only for Na^+),[32] dibenzyl-14-crown-4 (6.3, 4.0), phosphododecyl-14-crown-4 (7.5, 5.0),[33] naphtho-15-crown-5 (6.7, only for Na^+),[34] and a series of other crown ethers investigated by Harris et al.[35] Since no experimental current versus potential data could be obtained for other cations systems, the association constants cannot be deduced.

Effect on the Simple Ion Transfer of TMA^+. It has been reported that L can form a stable LB film by depositing its chloroform spreading solution on the subphase of deionized water.[2] In our experimental system, when the organic phase containing L makes contact with the aqueous phase, it is possible to form film at the interface supported at the tip of a micropipet to inhibit ion transfer in and out of the micropipet. The electrochemical cell 4 was employed to see what would happen.

Ag/AgCl / 0.01 M TBACl /
aqueous reference solution
1 mM L + 0.01 M TBATPB //
outer NB solution
0.01 M $MgCl_2$ + 0.4 mM TMACl / AgCl/Ag   cell 4
pipet

Since no facilitated Mg^{2+} transfer was observed, $MgCl_2$ can be chosen as the supporting electrolyte of the aqueous phase to investigate the effect of compound L on the transfer of TMA^+ across the W/NB interface. As can be seen from Figure 6A, besides increasing capacitive current and iR drop, L showed a quite obvious inhibition of the TMA^+ transfer. The current corresponding to the transfer of TMA^+ from the aqueous phase inside the micropipet to the outer organic phase decreased markedly after 40 min in the presence of L in the organic phase and the process changed to be irreversible, which confirmed the film formation. The time dependence of current was shown in
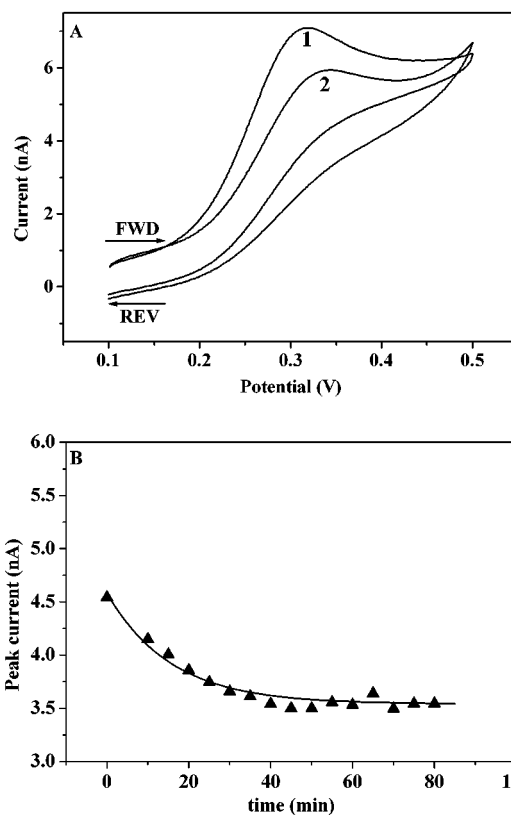

Figure 6. (A) Cyclic voltammograms of TMA^+ transfer across a W/NB interface supported at a 7-μm-radius micropipet with scan rates of 100 mV/s in the absence (1) and presence (2) of L in the organic phase. Equilibrium time 40 min, (B) Dependence of the peak current for TMA^+ transfer from the aqueous to the organic phase on the time in the presence of L in the latter phase.

Figure 6B, which illustrated that the current decreased gradually and at least 40 min was needed to reach a time-invariant value due to the formation of a saturated film or reaching an adsorption equilibrium.

C_{60} can form a floating film at the air/water interface,[34] but the deposition of LB films of the C_{60} molecule has been proved to be particularly difficult and lack reproducibility due to its rigid and hydrophobic structure. Functionalization of pristine C_{60} by polar addends offers a resolution to this problem.[35] Crown ether ionophores also cannot form stable monolayers in general, because of insufficient balance between the hydrophilic and hydrophobic parts of the molecules. Modification of crown ether with long hydrocarbon chains allows surface-active derivatives to be prepared, and the crown ether moieties are likely to orient parallel to the water surface.[36,37] The film of L formed at the interface might be similar to that of phospholipid.[38,39] The interface

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in the presence of L in the organic phase can be represented as in Figure 6. The possible alignment of L in the film is that the crown ether moiety anchors at the interface while the hydrophobic fullerene core is expected to remain floating in the organic phase and the whole molecule is perpendicular to the interface. According to this model, TMA$^+$ only transferred across the interface through the pores in the film. Given that the film was not too compact to choke the tip and block the transfer of TMA$^+$ completely, the transfer was inhibited.

However, the case may be different for the facilitated ion transfer. On one hand, the adsorptive ionophore can complex with the target ion easily because the crown ether moiety tends to head to the interface. Also, the in and out of the ion destroys the adsorption again and again. So it is difficult to form a saturated film or reach an adsorption equilibrium. On the other hand, if the influence of adsorption on the facilitated transfer really exists, the egress and the ingress of an ion may show distinct differences gradually in the cyclic voltammograms, but no such phenomena were observed. These analyses and experimental results confirm that the adsorption of the ionophore has less influence on the facilitated ion transfer of metal ions.

CONCLUSIONS

The present paper demonstrated that the complex selectivity of the monoaza-18-crown-6 ether attached to a fullerene derivative toward cations at the water/nitrobenzene interface could be rather different from the nonderivatized compound. The experimental results showed that the selectivity followed the sequence Na$^+$ > Li$^+$ > K$^+$ > NH$_4^+$ > Ca^{2+} ~ Mg^{2+}. The large size of the novel ionophore results in a smaller diffusion coefficient in the nitrobenzene 1 order of magnitude less than other common ionophores. These results might provide some insight for the design of chemical sensors.

In addition, this ionophore is also easily forms a film at the W/NB interface to inhibit simple ion transfer of TMA$^+$. However, this film formation has less influence on the facilitated ion transfer. Thus, when ionophores like L are present in an organic phase, a L/L interface closely resembles biological membranes. A study of these more complicated interfaces may lead to a greater understanding of ion recognition and membrane transport in biological systems.

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