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MicroITIES Detection of Nitrate by Facilitated Ion Transfer

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A microITIES array, created by laser photoablation of a 12-μm polyester film, was used to investigate electroassisted anion transfer between two immiscible electrolyte solutions. Besides measuring directly the transfer of nitrate to the organic phase, the enhancement of transfer of the cation (K⁺) by facilitated anion (counterion) transfer was measured as well. In the presence of a triamide derived from tris(2-aminoethyl)amine (tren), which is known to function as a host for nitrate, the current responses for both nitrate and potassium transfer were monitored. The linear relationships between the current responses and nitrate concentration formed the basis of an anion sensor with a dynamic range from 0.1 to 5 mM. A dual facilitated transfer mechanism is proposed to explain the enhancement phenomenon.

The analysis of anions, especially oxo anions, presents a significant challenge to chemists worldwide.[1] For example, in nuclear waste streams and other groundwater contamination, the latter often from detergents and agriculture-related processes, a variety of anions make their way into the environment.[2,32,3] Among these are nitrates, phosphates, sulfates, carbonates, and heavy metal oxo anions such as arsenates, chromates, and pertechnetates. Wherever these ions are present in abundance, it is efficacious to remove them selectively during cleanup procedures. However, it has proven difficult to devise reagents that are sufficiently selective to permit reliable anion removal and determination.

To investigate the effects of complementarity via hydrogen-bonding interactions on anion selectivity, we have been exploring a series of simple polyammonium macromonocycles and their bicyclic corollaries as hosts for anions,[4–8] focusing primarily on nitrate.[4–6] Nitrate in particular is a problem, since it is present in

high concentrations in nuclear waste streams.[9] To date, however, reports of receptors for this trigonal ion are small in number.[4,5,10–18] As a result of our studies, we now know that polyammonium macrocycles can form interesting complexes encapsulating nitrate ion.[4,5] However, because of their high solubility in aqueous media as well as the pH dependence on their selectivity, these systems do not present the optimal solution for applications in either liquid–liquid separations or as sensors. To address these analytical issues, we applied design parameters,[5] similar to what we used in the polyammonium receptors using the tripodal tris(2-aminoethyl)amine (tren) as backbone, to obtain a series of lipophilic hosts, with a goal of obtaining receptors insensitive to pH and insoluble in aqueous media. We predicted that these new receptors would be capable of binding anions, however, via appropriately placed amide as opposed to ammonium functionalities. Others have investigated tren-based amide systems, even including some amides as anion receptors, but not as selective agents for nitrate.[19–22] Our recent studies, in collaboration with Moyer and co-workers, indicate significantly enhanced concomitant extraction of both nitrate and cesium ion,[18] using a relatively new concept of *dual* cation/anion recognition.[23]

Dual host strategies are clearly emerging as a new and exciting area of supramolecular chemistry, with promise in a variety of

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applications-oriented endeavors.[23] Rather than designing a receptor selective for a given anion or cation, a dual receptor system can be fabricated with a host or hosts that recognize both the desired anion and its partner cation or vice versa. This technique is especially of interest in situations where dual contaminants exist in tandem, for example, in nuclear wastewater situations where both $^{137}Cs^+$ and nitrate coexist in large concentrations.[9] The simplest of systems involves two separate receptor molecules, and in our aforementioned study,[18] these hosts consisted of a series of tripodal amides derived from tren as receptors for nitrate, and tetrabenzo-24-crown-8 crown ether, as a selective agent for Cs^+ ion. Results indicated significant enhancement of Cs^+ coextraction from solutions of $CsNO_3$ by addition of the tripodal nitrate receptors. While the dual host concept has thus been applied to bulk liquid−liquid extraction applications,[17,18,21] it has not previously been used as a tool to enhance ion sensitivity in sensor systems for ion analysis.

The measurement of the potential developed across an interface between two phases for many years has formed the basis for ion-selective electrodes, widely used in physiological and other measurements. As such, a number of antibiotics and also crown ethers have shown highly desirable selectivity for both monovalent and divalent cations. Considerably less progress has been made with anions due to the paucity of suitable anion receptors, although ionophores for halides, NO_2^-, S^{2-}, and phosphate have been reported.[24,25][24,25] The kinetics of simple transfer of a few anions (PF_5^-, ClO_4^-, BF_4^-, SCN^-) has been reported.[26] Hundhammer[27] designed an amperometric detector in a flow injection system to determine anions. Shioya[28] reported a hydrogen-binding ionophore for facilitated sulfate transfer by polarography, which may be one of the first examples of facilitated anion transfer.

ITIES (*i*nterface between *t*wo *i*mmiscible *e*lectrolyte *s*olutions), an electrochemically based technique applied to liquid−liquid transfer and the analysis of ions, is a methodology that has been known for more than 20 years.[29] In the ITIES measurement, additional experimental control is gained over strict potentiometric measurements, as both the rate and the characteristic applied interfacial potential can be used as the basis for the analytical method. The first example of ITIES was reported by Koryta and involved the transfer of potassium ions from water to nitrobenzene facilitated by the natural antibiotic valinomycin and the synthetic ionophore dibenzo-18-crown-6.[29] Early studies then focused on theoretical considerations involving natural ionophores and alkali metals as a means of modeling in vivo transport processes.[30−37]

Other metal ions, such as Pb^{2+}, Zn^{2+}, Cd^{2+}, and Cu^{2+},[38] as well as nonmetallic ammonium ions (NR_4^+, R = H, and mixed R,R′ with 1−3 alkyl groups)[39−46] and organic cations (methyl orange, choline),[47−50] have been studied by simple phase transfer or facilitated ion phase transfer. The receptors used for those ions cover a wide range from a variety of natural ionophores such as valinomycin,[30,31] nigericin,[32] and synthetic macrocycles.[29]

The investigation of non-Faradaic charge transfer reactions at ITIES has proven to be a powerful way of studying kinetic and thermodynamic aspects of ion−receptor complexation and extraction. Compared to the conventional ion-selective electrode method, the ITIES technique measures the rate at which ions are transported across the interface instead of the potential developed by the ion activity change. The energy needed to transfer an ion from one phase to another is dependent on the difference between dehydration and resolvation energies and is related to the difference of electrochemical potential applied to two adjacent phases when the ion transfer occurs. The difference between the standard Gibbs energies of hydration and solvation is effectively the work that is required transferring an ionic species, *i,* from the bulk aqueous phase (w) to the bulk organic phase (o). This standard Gibbs energy of transfer $\Delta G_{tr,i}^{0,w\rightarrow o}$ for the specified ion of interest is related to the standard potential of transfer $\Delta_o^w \phi_i^0$ as given in eq 1,

$$\Delta_o^w \phi_i^0 = -\Delta G_{tr,i}^{0,w\rightarrow o}/Z_i F \tag{1}$$

where Z_i is the charge carried by the transferring ion. To discriminate one ion from another, the two ions must have different Gibbs transfer energies and therefore transfer at a different potential. In the case of a microelectrode array, the actual ion transfer potential, which can be derived from the voltammogram, is the half-wave potential $\Delta_o^w \phi_i^{1/2}$. This potential differs substantially from the standard transfer potential because the ion has different activity and diffusion characteristics in the organic

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phase as compared to the aqueous phase (eq 2),

$$\Delta_o^w \phi_i^{1/2} = \Delta_o^w \phi_i^0 + RT/z_i F \ln(\gamma_i^o D_i^w / \gamma_i^w D_i^o) \qquad (2)$$

where D_i^w and D_i^o are the diffusion coefficients of the ion in the aqueous and organic electrolyte phases, respectively. The current passing through the interface is determined by the ion flux, which is, in the case of a microdisk interface, given by the steady-state relationship

$$I^{w \to o} = 4 m z_i F D_i^w C^w r \qquad (3)$$

where C^w is the bulk aqueous concentration of the ion and r is the radius of the individual microinterfaces constituting an array of m elements.

In this study, we apply the dual host strategy to the ITIES experiment. The most promising tripodal amide from the aforementioned study,[18] N-{2-[bis[2-(4-tert-butylbenzoyl)aminoethyl]-amino]ethyl}4-tert-butylbenzamide (**1**) was selected for nitrate binding, and a commercially available crown ether, dibenzo-18-crown-6 (**2**) was chosen as a cohost for potassium ion. The focus was on utilizing the complexation reaction between nitrate and its amide receptor to obtain assisted potassium transport with its crown ether host.
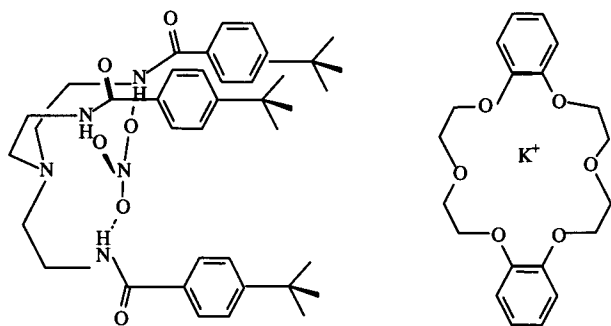
N-{2-[*bis*-(2-(4-*tert*-butylbenzoyl) aminoethyl)-amino]-ethyl}4-*tert*-butylbenzamide, **1**, (idealized drawing with NO₃⁻ bound inside)

Dibenzo-18-crown-6, **2**, (K⁺ known to bind inside cavity)

Through this dual recognition system, the interaction between nitrate and the receptor is indirectly detected by observing the current response of the facilitated potassium transfer, the latter being well-defined and easy to measure. Our experimental results indicate that this indirect method is useful for investigating complex information between nitrate and its receptor. This information, in conjunction with nitrate transfer and homogeneous phase binding studies, could be used to identify selective receptors with favorable structural characteristics for further industrial and environmental applications.

EXPERIMENTAL SECTION
Materials. Dibenzo-18-crown-6 (DBC) (Fluka), LiCl (Sigma), tetrabutylammonium nitrate (TBANO₃) (Fluka), and potassium chloride (Fluka) were AR grade or better and were used as purchased. Nanopure water (18 MΩ) was prepared with a

Barnstead Nanopure II filtering system. The solvent 1,2-dichloroethane (DCE) (Fluka) was used as purchased.

Synthesis. Bis(triphenylphosphoranylidene)ammonium tetrakis(4-chlorophenyl)borate (BTPPATPBCl) was prepared by metathesis of bis(triphenylphosphoranylidene)ammonium chloride (Fluka) and potassium tetrakis(4-chlorophenyl)borate (Fluka). The precipitates formed by mixing the two ethanol solutions together were recrystallized twice from a methanol–acetone mixture in order to obtain pure product free of inorganic salts. *The purity of this supporting electrolyte is essential to obtaining low background currents.* BTPPATPBCl is very lipophilic and therefore gives a wide potential window. Because of the limited solubility of BTPPACl in water, additional LiCl is needed to prepare the aqueous part of the Ag/AgCl | BTPPACl (+LiCl) | BTPPATPBCl reference electrode in order to maintain similar ionic strengths for minimum junction potential.

N-{2-[Bis[2-(4-tert-butylbenzoyl)aminoethyl]amino]ethyl}4-tert-butylbenzamide (**1**; TTB) was synthesized by condensation of 2,2′,2″-triaminotriethylamine (tren) (Aldrich) and p-tert-butylphenylcarboxylic acid (Fluka) in the presence of triphenyl phosphite (Sigma) as a coupling agent with yields in the 80–90% range.[18]

Methodology. The applied potential is the sum of several contacting potential differences. The standard Gibbs transfer energy is related to the potential difference directly across the interface. To calibrate the transfer potential, it is necessary to define a potential scale. The "TATB" assumption is most commonly used.[51] It states that the cation and anion of tetraphenylarsonium tetraphenylborate (TPAsTPB) have equal standard Gibbs transfer energies for any pair of solvents, assuming that the solvation energies for both the cation and the anion are equal.[29,52] On this basis, a scale for standard Gibbs energies of ion transfer and therefore for the standard transfer potential or the formal transfer potential can be obtained. For instance, the formal transfer potential of tetramethylammonium (TMA⁺) at a water/DCE interface can be estimated as 0.160 V on this scale.[53,54] Therefore, the ion transfer potential of TMA⁺ is defined as 0.160 V, and this scale is the basis for the current–voltage curve x-axes (cell II, vide infra).

To make the test solutions conducting, supporting electrolyte is needed in both the aqueous and organic phases. The supporting electrolyte used in the organic phase (DCE) is the highly lipophilic BTPPATPBCl, while the highly hydrophilic electrolyte Li₂SO₄ is used in the water phase. Within a certain potential window, the transfer of Li₂SO₄ from the aqueous to the organic phase and the transfer of BTPPATPBCl from DCE to water are negligible, due to their intrinsic hydrophilic and lipophilic properties. Within this range, the oil/water interface behaves as an ideally polarized electrode. Any cation that is less hydrophilic than Li⁺ or less lipophilic than BTPPA⁺ will transfer within the potential window and the same for any anion less lipophilic than TPBCl⁻ or less hydrophilic than sulfate. The function of selective receptors in the organic phase will be to lower the Gibbs transfer energy, thus shifting the transfer process to an applied potential toward the middle of the potential window. These types of transfer reactions

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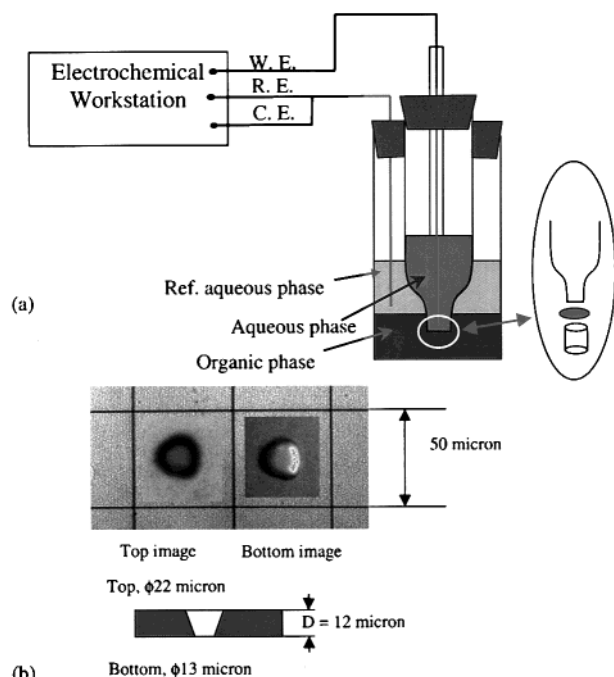
Figure 1. Schematic setup for the ITIES measurements: (a) instrumentation; (b) microhole film (6 × 11 array, only one hole shown).

are called facilitated transfer. The transfer of cations, typified by facilitated potassium transfer using dibenzo-18-crown-6, is a good example. However, the situation for anions is much more complicated. As most anions have relatively high transfer energies, direct anion transfer from the aqueous to the organic phase almost always occurs at or near the negative end of the potential window. This is in the same region where simultaneous transfer of cations such as BTPPA$^+$ from the organic to the aqueous phase contributes to the total net current. Therefore, it is difficult to distinguish anions and to separate the contribution to the current from cation transfer in the opposite direction, in the absence of some type of facilitated transfer.

Apparatus. Cyclic voltammetry and differential pulse voltammetry experiments were performed with an EG&G PAR 273 potentiostat (EG&G PAR, Princeton, NJ) interfaced to a Gateway 4DX2 computer using model 273 software (EG&G PAR) and a Cypress Systems model CYSY-1 computer-controlled electroanalysis system. A two-electrode cell with a Ag/Ag$_2$SO$_4$ reference electrode in the aqueous phase and a Ag/AgCl BTPPA$^+$ ion-selective electrode in the organic phase were used. Aqueous reference electrodes were used in order to ensure improved stability.
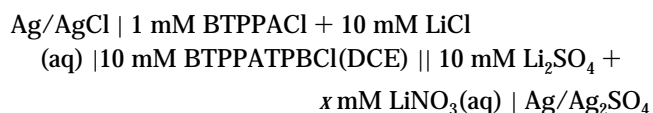
For practical reasons, it is important to establish and maintain a stable interface between the two phases. Supports such as a micropipet,[41] glass-fiber membrane,[55,56][55,56] or microhole array drilled in a poly(ethylene terephthalate) (PET) film[33,40] have been employed. The microhole array in PET film was used in our study. The interface between water and organic solvent (1,2-dichloroethane) was supported by a 12-μm-thick PET film sealed at the end of the electrode body. In the film, a microhole array of 66 holes (11 × 6) was drilled using a UV excimer laser and served as the

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ion flux channel. Due to the photoablation process, a crater is created on the side of the PET film facing the laser. The "crater" side is larger (22 μm) and more hydrophilic than the exit (distal side) (13 μm); thus, the former side is oriented toward the aqueous phase to achieve optimal wetting. The center-to-center distance of the array holes is 105 (row) and 120 μm (column).[48] The organic phase was placed in the cell, covered by a layer of aqueous reference solution, and the aqueous phase containing the anion was placed on the inner tube. At the bottom of the inner tube, the PET film was sealed with a plastic tube to serve as the interface for ion transfer. The setup of this system and the image of the film under the optical microscope are shown in Figure 1.This setup facilitates the replacement of the aqueous solution while keeping the same organic phase composition.
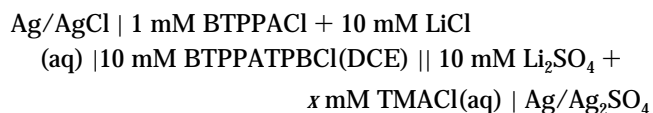
For cyclic voltammetry (CV), a voltage ramp was applied between the two electrodes through the potentiostat (two-electrode system) and the current passing through the microhole interface was then measured and recorded. For differential pulse voltammetry (DPV), a 50 mV/40 ms pulse was applied at each 2-mV step. All experiments were carried out at room temperature and within a Faraday cage.

The electrochemical cells used for this experiment are shown below. Double lines indicate the interfaces between two phases:
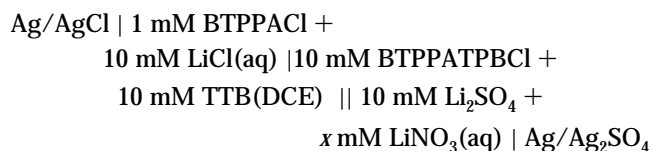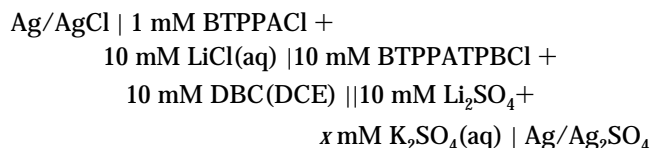
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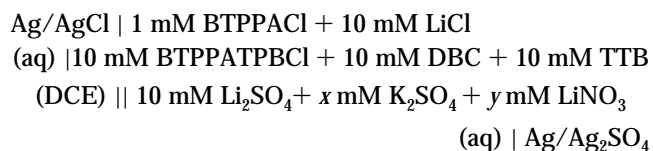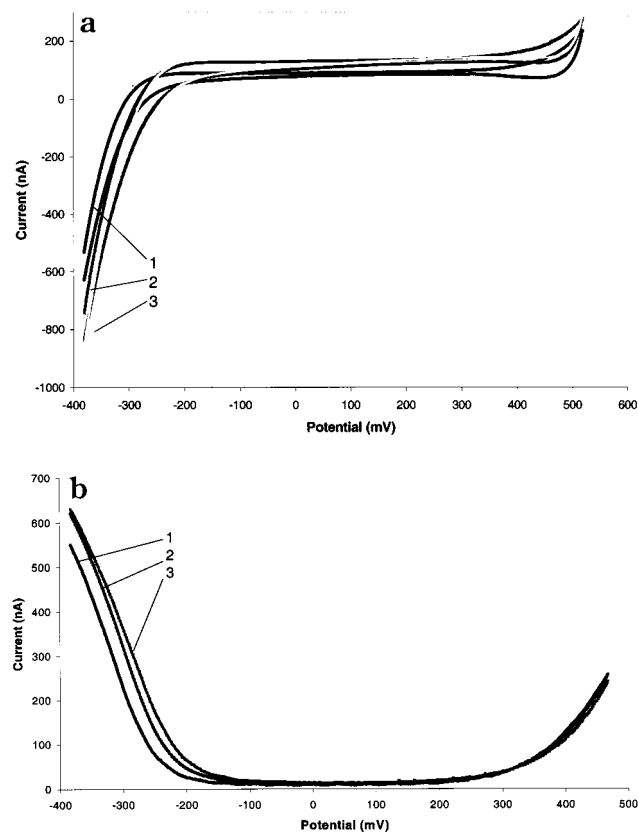
cell I

</div>

Ag/AgCl | 1 mM BTPPACl + 10 mM LiCl
(aq) |10 mM BTPPATPBCl(DCE) || 10 mM Li$_2$SO$_4$ +
x mM LiNO$_3$(aq) | Ag/Ag$_2$SO$_4$

<div align="center">

cell II

</div>

Ag/AgCl | 1 mM BTPPACl + 10 mM LiCl
(aq) |10 mM BTPPATPBCl(DCE) || 10 mM Li$_2$SO$_4$ +
x mM TMACl(aq) | Ag/Ag$_2$SO$_4$

<div align="center">

cell III

</div>

Ag/AgCl | 1 mM BTPPACl +
10 mM LiCl(aq) |10 mM BTPPATPBCl +
10 mM TTB(DCE) || 10 mM Li$_2$SO$_4$ +
x mM LiNO$_3$(aq) | Ag/Ag$_2$SO$_4$

<div align="center">

cell IV

</div>

Ag/AgCl | 1 mM BTPPACl +
10 mM LiCl(aq) |10 mM BTPPATPBCl +
10 mM DBC(DCE) ||10 mM Li$_2$SO$_4$+
x mM K$_2$SO$_4$(aq) | Ag/Ag$_2$SO$_4$

<div align="center">

cell V

</div>

Ag/AgCl | 1 mM BTPPACl + 10 mM LiCl
(aq) |10 mM BTPPATPBCl + 10 mM DBC + 10 mM TTB
(DCE) || 10 mM Li$_2$SO$_4$+ x mM K$_2$SO$_4$ + y mM LiNO$_3$
(aq) | Ag/Ag$_2$SO$_4$

RESULTS AND DISCUSSION

The transfer of NO$_3$$^-$ from the aqueous to the organic phase can be accomplished in three ways: *direct transfer, facilitated transfer,* and *dual host transfer.* In the first case, the transfer is

Figure 2. Current−voltage curves for cell I: (a) cyclic voltammetry; (b) differential pulse voltammetry. (1) $[NO_3^-] = 0$ mM; (2) $[NO_3^-] =$ 0.91 mM; (3) $[NO_3^-] = 1.67$ mM.

Figure 3. Current−voltage curves for cell III. (a) Cyclic voltamme-try: (1) $[NO_3^-] = 0$ mM; (2) $[NO_3^-] = 0.57$ mM; (3) $[NO_3^-] = 1.23$ mM. (b) Differential pulse voltammetry: (1) $[NO_3^-] = 0$ mM; (2) $[NO_3^-] = 0.57$ mM; (3) $[NO_3^-] = 1.53$ mM; (4) $[NO_3^-] = 3.59$ mM. (c) Dependence of peak current (after background subtraction) on nitrate, concentration. $E_{appl} = -280$ mV.

difficult because the anion much prefers to remain in the aqueous phase. By placing a suitable host in the organic phase, the transfer of NO_3^- can be facilitated and a corresponding shift in the transfer potential can be observed. This transfer can also be observed indirectly through dual host transfer; that is, the transfer of K^+ is enhanced due to the more facile transfer of the counterion. The behavior of NO_3^- under these three situations is discussed below.

Characteristics of the ITIES System. Figure 2 shows the current−voltage curves for cell I, which contains neither crown ether (DBC) nor tripodal amide (TTB). Curve 1 in Figure 2a is the background current ($[NO_3^-] = 0$) and indicates a potential window of ∼600 mV. At the positive end (water vs organic phase), Li^+ is forced into the organic phase (DCE) under high applied potential, giving a high current response. An analogous situation occurs at the negative limit where $BTPPA^+$ is transferred to the aqueous phase. Curves 2 and 3 indicate the current response as the concentration of nitrate in the aqueous phase is increased to 0.91 and 1.67 mM, respectively. The current at both ends of the potential window increased compared with the background (curve 1), but the nitrate transfer is obscured by the processes at the negative discharge limit, most likely transfer of $BTPPA^+$ from the organic phase.

DPV was employed (Figure 2b) to see whether the current resulting from NO_3^- transfer could be more conveniently mea-sured. We conclude that the measurement of peak potential and current is much easier to define in DPV than the half-wave potential and is more sensitive, especially for low current mea-surements. To establish the potential scale, TMA^+ is usually added
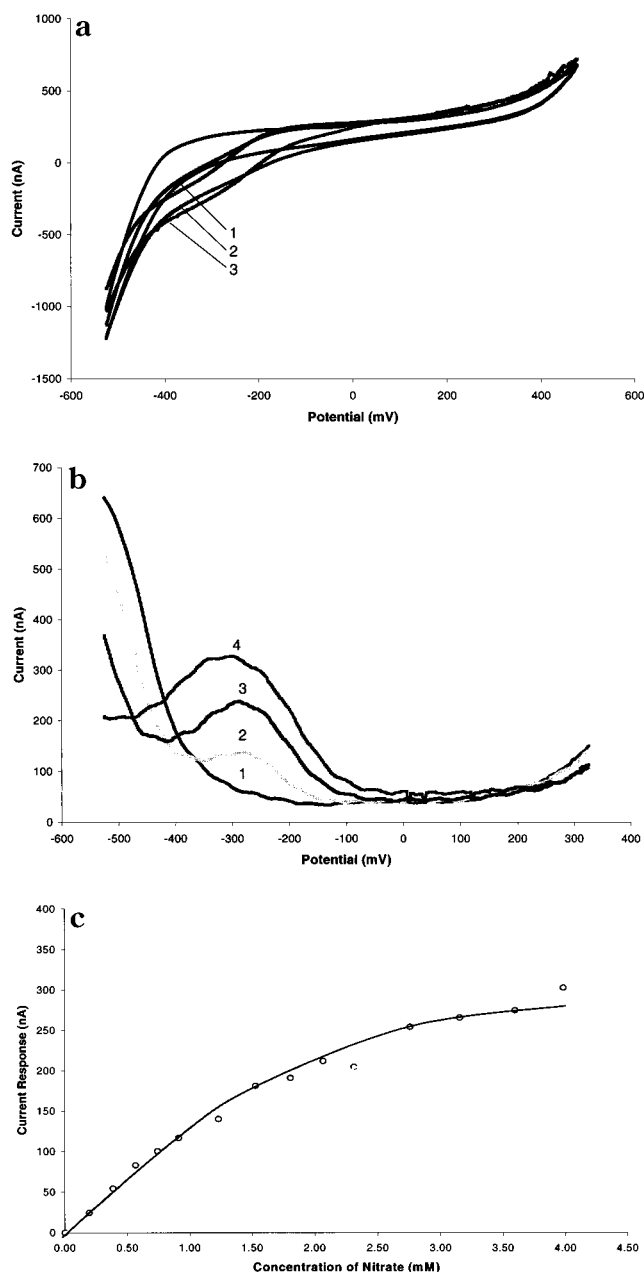
to the aqueous phase as an internal standard. Because TMA^+ is more lipophilic than Li^+, it is more easily transferred to the organic phase and the lower Gibbs transfer energy results in a less positive transfer potential. For the cyclic voltammetry the response leads to a plateau while for differential pulse voltammetry the response leads to a peak (graph not shown), consistent with the expected behavior of a microelectrode array.[39] As mentioned above, the TMA^+ is assumed to transfer at a potential of 160 mV based on the "TATB" assumption.

Direct Observation of Facilitated NO_3^- Transfer by a Triamide Receptor. Panels a and b of Figure 3 show the CV and DPV current−voltage curves for cell III, in which the triamide
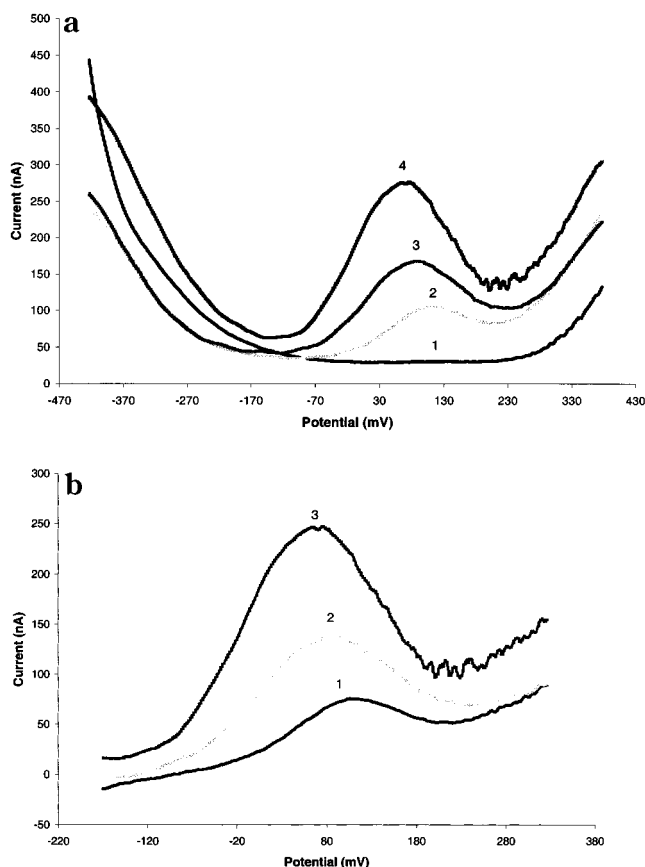
Figure 4. Current−voltage curve for cell IV. Differential pulse voltammetry after background subtraction: (1) $[K^+]$ = 0.91 mM; (2) $[K^+]$ = 2.31 mM; (3) $[K^+]$ = 3.33 mM.

Figure 5. Differential pulse voltammetry after background subtraction: (1) $[K^+]$ = 0.91 mM, $[NO_3^-]$ = 0 mM; (2) $[K^+]$ = 0.83 mM, $[NO_3^-]$ = 0.83 mM. (3) $[K^+]$ = 0.77 mM, $[NO_3^-]$ = 1.54 mM. (4) $[K^+]$ = 0.71 mM, $[NO_3^-]$ = 2.14 mM. (5) $[K^+]$ = 0.63 mM, $[NO_3^-]$ = 3.13 mM.

TTB is added to the organic phase as the nitrate receptor. In the presence of a nitrate receptor, the nitrate transfer shifts away from the negative end of the potential window. While this can be seen in Figure 3a using conventional CV, it is clearly observed in Figure 3b via DPV. The dependence of current response observed at −280 mV for DPV as a function of nitrate concentration is shown in Figure 3c. The nitrate curves are background corrected and show a linear response up to 1.5 mM, a limit of detection (LOD) of 0.2 mM, and a sensitivity of 128 nA/mM. The nonlinearity beyond 1.5 mM is due to the saturation of receptors in the organic phase. These findings clearly illustrate the efficacy of DPV over CV as a measurement tool in the ITIES experiment.

K⁺-Facilitated Transfer. Figure 4 shows the current−voltage curves for cell IV, in which potassium transfer was facilitated solely by DBC *without the assistance of nitrate and TTB*. The potassium transfer occurred at a potential of 80 mV. Figure 4b shows the DPV voltammograms, after background subtraction, when different concentrations of potassium are added to the aqueous phase. It can be observed that the crown-facilitated potassium transfer is well-defined. A small peak shift with increasing K⁺ concentration is observed due to depletion of the host at the phase boundary. Since the concentration of potassium ion in bulk aqueous solution varies from 0.9 to 3.3 mM while the crown ether concentration in the bulk organic solution is 10 mM, this concentration ratio range is not high enough to guarantee host excess at the boundary. Computer simulations in our laboratory have demonstrated that, in the absence of large host excess, the peak will shift at planar
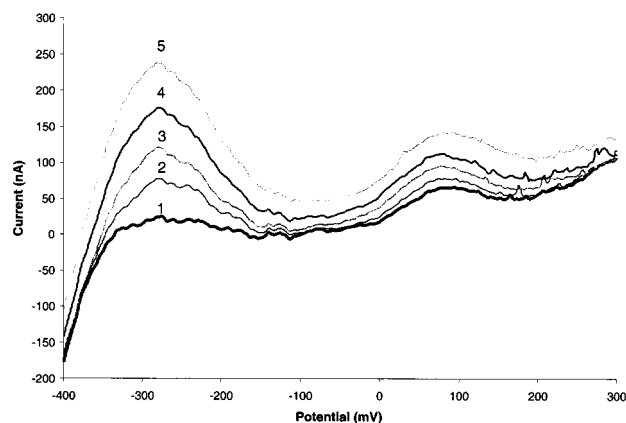
interfaces as the concentration ratio varies. The relationship between peak current response and potassium concentration, after background subtraction, is linear with a LOD of 0.2 mM and sensitivity of 68 nA/mM.

Enhancement Effect of NO_3^-−Triamide Complexation to the K⁺-Facilitated Transfer (Dual Host Transfer). Figure 5 shows the current−voltage curves for cell V containing both cation and anion receptors (DBC and TTB, respectively). After one addition of K_2SO_4 to the aqueous solution (10 mM Li_2SO_4 is used for background), $LiNO_3$ was added to the aqueous phase in discrete aliquots. As expected, the occurrence of nitratetriamide complexation enhanced the crown-facilitated potassium transfer. The current response (peak at 80 mV) for dual host potassium transfer increases with the addition of $LiNO_3$ solution, although the potassium concentration is reduced due to dilution. The picture is much clearer after background subtraction. Figure 5 shows clearly the facilitated transfer phenomenon similar to our findings in the dual host extraction studies of $CsNO_3$ carried out in collaboration with the Moyer group at Oak Ridge National Laboratory (vide supra).[18] It is postulated that nitrate complexation by the triamide lowers the overall thermodynamic barrier for the salt transfer to the organic phase, and therefore, potassium transfer is doubly facilitated by both the crown and the anion host. The current at 80 mV is corrected for the facilitated transfer at −280 mV. It should further be emphasized that the current at 80 mV cannot be due to Li⁺ transfer since addition of Li_2SO_4 produces no current increase.

From control experiments (cells I, III, and IV), we found that, without triamide in the organic phase, increasing nitrate concentration alone did not increase the potassium transfer, and without DBC in the organic phase, potassium transfer cannot be observed at 80 mV (voltammograms not shown). A linear relationship is observed up to 3.5 mM K⁺ concentration when only one receptor (dibenzo-18-crown-6) is present in the organic phase. Therefore, it is concluded that the current increase at an applied potential of 80 mV must be due to the cohosting effect of the dual host recognition system. The measurement can be made with a relative standard deviation of 3% (n = 5). However, these results show that facilitated transfer is more efficient than dual host transfer as the former yields currents that are a factor of 5 times higher.

The reasons for this difference are under investigation. Vapor pressure osmometry studies suggest no significant association between the DBC and the amide host and only weak self-association of the latter.[18]

CONCLUSIONS

This paper clearly illustrates that the interface between two immiscible electrolyte solutions can be used to measure aqueous phase anions by facilitated (host−guest) transfer. Furthermore, this analysis can be performed by both direct and indirect methods. In the former case, only anion transfer is facilitated by complexation with an appropriate receptor. In the latter situation, both anion and cation transfers are facilitated by a dual host system, in which receptors for both anion and cation are employed. Even though the binding constant for nitrate with the host TTB in aqueous solution is rather weak (log $K \cong 1.6-1.7$),[18] there is still a significant enhancement of transfer of nitrate and, when the dual system is applied, also potassium to the organic phase. Thus, the amide host receptor must help to compensate for the Gibbs transfer energy for nitrate ($\Delta G_{calc} = 34$ kJ/mol).[57] Additionally, the presence of the host for nitrate allows, as observed for the first time, for the current response to be shifted from the negative potential window edge, so that the problems of anion transfer masked by supporting electrolyte can finally be resolved. Last, the application of differential pulse voltammetry to the ITIES experiment is shown to be superior to the cyclic voltammetric monitoring of ion transfer. The application of ITIES to anion analysis and DPV to ITIES analysis are thus extended.

(57) Moyer, B. A.; Bonnesen, P. V. In *Supramolecular Chemistry of Anions*; Bianchi, A., Bowman-James, K., García-España, E., Eds.; Wiley-VCH: New York, 1997; p 14.