12700 *J. Am. Chem. Soc.* **1998,** *120,* 12700−12701

Studying Ionic Reactions by a New Generation/Collection Technique

Yuanhua Shao, Biao Liu, and Michael V. Mirkin*

Department of Chemistry and Biochemistry
Queens College—CUNY Flushing, New York 11367

Received September 3, 1998

We describe here a new approach to studying ion-transfer (IT) reactions and homogeneous chemical reactions of ionic species in solution by a generation/collection technique. Simple IT of acetylcholine from water into 1,2-dichloroethane (DCE) and facilitated IT of K^+ by dibenzo-18-crown-6 (DB18C6) were probed using a novel dual-pipet device. The wave of direct transfer of potassium from water to DCE was observed for the first time.

Homogeneous and heterogeneous processes involving ionic reactants are of great fundamental and practical importance. Heterogeneous IT reactions are essential for many technological processes and biological cells.[1] A number of important organic reactions (e.g., S_N2-type processes[2]) involve ionic species. Charged metal complexes can activate organic molecules toward various transformations.[3] Valuable information about mechanisms of such reactions could be obtained from generation/collection (G/C) measurements. Electrochemical G/C techniques, e.g., time-of-flight measurements,[4a] rotating ring-disk electrode,[4b] and scanning electrochemical microscopy (SECM),[4c] have been successfully employed for studying kinetics of multistep reactions and probing mass/charge-transport in various media. In those experiments the species of interest were oxidized (or reduced) at one electrode ("generator") and the product of this reaction was detected by the second electrode ("collector"). Our work is aimed at developing an electrochemical G/C technique for studying ionic reactions which involve no oxidation/reduction steps.

The IT-based G/C experiments were carried out using novel dual-pipet electrodes. This device consists of two water-filled micrometer- or submicrometer-sized pipets whose orifices are separated by a submicrometer-thick band of glass.[5] If one of the pipets ("generator") contains a cation, it can be transferred to the outer organic solvent by biasing this pipet at a sufficiently positive potential (E_g). A significant fraction of ejected cations reaches the negatively biased second pipet ("collector") and gets transferred back into the aqueous phase (Figure 1A).

Figure 2 shows generator and collector voltammograms of simple IT of acetylcholine (ACh^+) between water and DCE phases.[6] The ACh^+ ejection is governed by quasi-linear diffusion of this ion inside the generator pipet.[7] Thus, at higher scan rates generator voltammograms are peak-shaped. A lower scan rate (e.g., $v = 5$ mV/s in Figure 2A) results in a quasi-steady state, sigmoidal voltammogram. The collector voltammograms (i.e., i_c vs E_g curves in Figure 2B) represent the reverse transfer of ACh^+ into the aqueous phase, and i_c closely follows i_g.

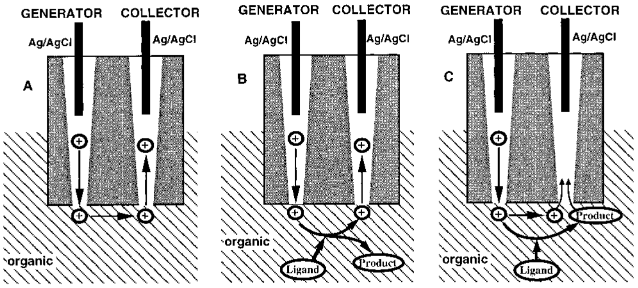

Figure 1. Probing ionic reactions with a dual-pipet device. (A) Simple transfer of a cation, (B) and (C) IT is followed by a chemical reaction in solution. (B) Only uncomplexed cation is collected. (C) Both the cation and the reaction product are collected.

The collection efficiency (Figure 2C) depends strongly on collector potential (E_c) and changes from 0 at $E_c = 0.5$ V to about 40% at $E_c = 0.1$ V (not shown in Figure 2). The theory developed recently for two identical coplanar disk electrodes acting as a generator and a collector predicts the maximum steady-state collection efficiency of about 36% for a close spacing of two electrodes (i.e., the edge-to-edge distance is much smaller than the disk radius).[8] A somewhat different geometry of θ-pipets (i.e., two halves of an ellipse separated by a very thin line of glass) results in a slightly larger maximum value of i_c/i_g. The collection efficiency remains practically constant over a wide range of E_g. Thus, the fraction of collected ions is independent of i_g and governed by device geometry. The increase in i_g at $E_g > 0.6$ V (Figure 2A) is due to transfer of $TPBCl^-$ from DCE into water. The collector voltammograms are not affected by this process. In this way one can separate parallel processes which often impair the studies of charge transfers at the liquid/liquid interface.[7a]

If some species contained in the outer solution ("ligand") can react with an ion ejected from the generator pipet, such a reaction affects the collection efficiency. Two possibilities are outlined in Figure 1B and C. In Figure 1B, the reaction product does not contribute to the collector current (i.e., either this product cannot be transferred into water or its diffusion coefficient is too small. Ion binding to high molecular weight DNA is a typical example of the latter). Hence, the collection efficiency decreases with increasing rate of ion complexation. If the product of the chemical reaction is transferred to water (Figure 1C), the collector voltammogram consists of the product and cation transfer waves occurring at different potentials. A well-studied reaction of this type is potassium transfer from water into DCE facilitated by dibenzo-18-crown-6 (DB18C6) which is used in a potassium sensor[9]

$$K^+(w) + DB18C6(DCE) \rightleftarrows [K^+DB18C6]\,(DCE) \qquad (1)$$

A typical steady-state voltammogram of this process at a generator pipet is shown in Figure 3A (curve 1, the left-hand current scale).[10] As expected, the current is limited by diffusion

---

[1] (a) Benjamin, I. *Chem. Rev.* **1996**, *96*, 1449. (b) Gennis, R. B. *Biomembranes*, Springer: New York, 1995.

[2] Shaik, S. S.; Schlegel, H. B.; Wolfe, S. *Theoretical Aspects of Physical Organic Chemistry. The S_N2 Mechanism*; Wiley-Interscience: New York, 1992.

[3] For example, see Harman, W. D. *Chem. Rev.* 1997, *97*, 1953.

[4] (a) Feldman, B. J.; Feldberg, S. W.; Murray R. W. *J. Phys. Chem.* **1987**, *91*, 6558. (b) Albery, W. J.; Hitchman, M. L. *Ring-Disc Electrodes*, Calrendon, Oxford, 1971. (c) Bard, A. J.; Fan, F.-R. F.; Mirkin, M. V. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Marcel Dekker: New York, 1994; Vol. 18, p 243.

[5] Dual pipet electrodes were made from borosilicate θ-tubing (OD = 1.5 mm, Sutter Instrument Co.) using a Sutter model P-2000 laser-based puller. A proper choice of pulling parameters yielded two very similar closely spaced pipets (edge-to-edge separation <1 μm). The pipets were filled with different aqueous solutions from the back using a small syringe. A 0.125-mm Ag silver wire coated with AgCl was inserted into each pipet from the back. The potentials of two pipets serving as working electrodes were controlled by a EI-400 bipotentiostat with respect to the organic reference [i.e., 0.125-mm Ag wire coated with AgTPBCl; TPBCl = tetrakis[4-chlorophenyl]borate]. The outer glass wall was silanized to prevent the formation of an aqueous film between two pipets and mixing of the filling solutions. For further details see ref 5b. (b) Liu, B.; Shao, Y.; Mirkin, M. V., to be submitted to *Anal. Chem.*

[6] The generator and collector pipets were as follows:

Ag/AgTPBCl/10 mM TBATPBCl//
outer DCE solution
0.4 mM AChCl + 10 mM LiCl/AgCl/Ag (generator)
generator pipet

Ag/AgTPBCl/10 mM TBATPBCl//10 mM LiCl/AgCl/Ag (collector)
outer DCE solution collector pipet

TBA = tetrabutylammonium.

[7] (a) Girault, H. H. In *Modern Aspects of Electrochemistry*; (Bockris, J. O'M., Conway, B. E., White, R. E., Eds.); Plenum Press: New York, 1993; Vol. 25, p 1. (b) Shao, Y.; Campbell, J. A.; Girault, H. H. *J. Electroanal. Chem.* **1991**, *300*, 415. (c) Shao, Y.; Girault, H. H. *J. Electroanal. Chem.* **1990**, *282*, 59.

10.1021/ja983154b CCC: $15.00

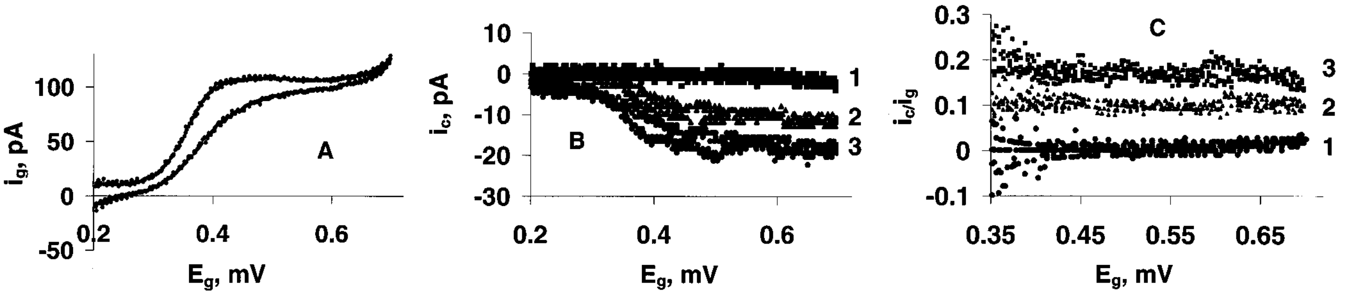

Figure 2. Dependencies of I_g (A), E_g (B), and collection efficiency (C) on E_g for the transfer of acetylcholine between water and DCE. E_c was: (1) 0.6, (2) 0.3, and (3) 0.2 V vs AgTPBCl. The effective radii of generator and collector pipets are $r_g = 7.5$ μm and $r_c = 6.0$ μm; $v = 5$ mV/s. For other parameters see ref 6. The shape of the generator voltammogram was practically independent of E_c.

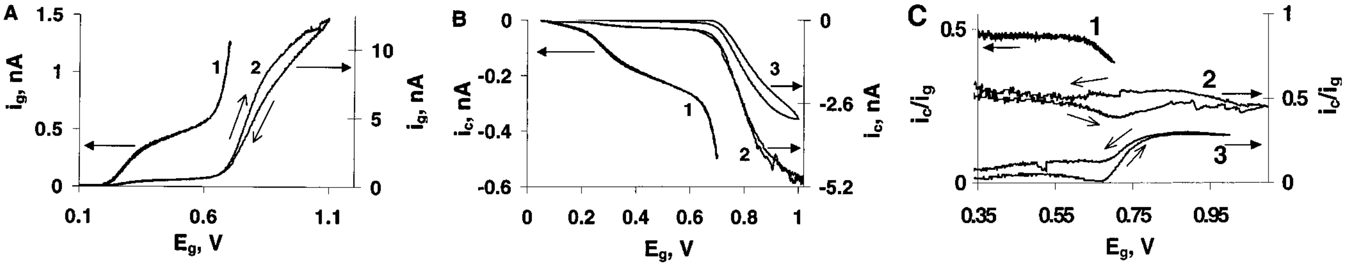

Figure 3. Generator (A) and collector (B) voltammograms and collection efficiency (C) for the transfer of K^+ between water and DCE containing DB18C6. $v = 20$ mV/s. $r_g = r_c = 4.5$ μm. Curves 1 correspond to the left-hand current scale, curves 2 and 3, to the right-hand scale. (B) and (C) E_c was: (1) 0.2, (2) 0.2, and (3) 0.6 V vs AgTPBCl. For other parameters see ref 10.

of DB18C6 in DCE as long as its concentration (c_{DB18C6}) is much lower than the potassium concentration inside the generator pipet (c_{KCl}).[9] The effective pipet radius calculated from the limiting current (4.5 μm) was in agreement with the value found by optical microscopy. The corresponding steady-state collector voltammogram (curve 1 in Figure 3B, the left-hand current scale) represents the reverse transfer of K^+ into water.[9] The collection efficiency changed from 0 to ~50% over the range of E_c from 600 to 200 mV and was practically independent of generator potential at $E_g < 0.6$ V (Figure 3C, curve 1). This indicates that generator current is produced by a single IT reaction, i.e., facilitated transfer of potassium. The same half-wave potential ($E_{1/2}$) value of 290 ± 10 mV was obtained from both generator and collector curves.

An increase in i_g at $E_g \geq 0.6$ V (Figure 3A, curve 1) is due to two simultaneously occurring processes, i.e., unassisted transfer of K^+ into DCE and the transfer of supporting electrolyte ($TPBCl^-$) into water.[11] Since $c_{KCl} \gg c_{DB18C6}$, the DB18C6 ligand is depleted in the proximity of the generator, and most ejected K^+ ions are uncomplexed. At $E_c = 0.2$ V (curve 2 in Figure 3B) both complexed and uncomplexed potassium ions are collected. Nevertheless, the i_c/i_g decreases at $E_g \geq 0.6$ V because the transfer of supporting electrolyte does not contribute to i_c (curve 2 in Figure 3C). The ratio of the collection efficiency at a given E_g to its plateau value (at $E_g < 0.6$ V) represents the fraction of i_g produced by potassium transfer. At $E_c = 0.6$ V (curve 3 in Figure 3B) only uncomplexed K^+ is collected (the interfacial dissociation of [K^+DB18C6] at this potential is slow). Unlike in curve 2, no initial wave of facilitated transfer is seen in curve 3.

The collection efficiency at $E_c = 0.6$ V (curve 3 in Figure 3C) is low when $E_g < 0.6$ V because almost all of the transferred potassium ions are in a complexed form. The steep increase in i_c/i_g at more positive potentials is due to ejection of uncomplexed K^+. The ratio of the limiting collection efficiency in curve 3 to that in curve 2 (~0.7) equals the fraction of uncomplexed K^+ in all potassium arriving at the collector and represents the extent of complexation reaction. A more quantitative characterization of this process is based on analysis of i_c/i_g vs c_{KCl} and c_{DB18C6} dependencies.[5b]

At $E_g \approx +1$ V, the potassium transfer reaches the diffusion limit. Accordingly, the i_g tends to level off and a plateau can be seen in curves 2 and 3 (Figure 3B). Unlike i_g, the i_c waves are only due to the transfer of K^+. To our knowledge, this is the first direct observation of the simple potassium transfer wave. The interfering transfer of organic anions into the aqueous phase greatly complicates conventional voltammetric studies of alkali metal transfers.[11] From both curves 2 and 3 in Figure 3B the half-wave potential of simple potassium transfer, $E_{1/2} = 770 \pm 10$ mV, can be extracted. The difference between this value and the $E_{1/2}$ of the facilitated transfer of potassium is about 480 mV, which corresponds to a very large association constant for reaction 1 of the order of 10^9 M^{-1}.

In summary, we have demonstrated the possibility of studying ionic reactions in solutions by a novel G/C technique. It allows quantitative separation of different charge transfer processes simultaneously occurring at the liquid/liquid interface (e.g., simple transfer of potassium, facilitated transfer of the same ion with a crown ether, and IT of the supporting electrolyte). In this way one can overcome potential window limitations and study numerous important reactions occurring at high positive or negative potentials (e.g., transfers of alkali metals from water to organic media). The new technique should also be useful for kinetic studies of fast homogeneous reactions involving ionic reactants or intermediates.

Acknowledgment. The support by the donors of the Petroleum Research Fund administrated by the American Chemical Society and a grant from PSC-CUNY are gratefully acknowledged.

JA983154B

---

[8] Phillips, C. G.; Stone, H. A. *J. Electroanal. Chem.* **1997**, *437*, 157.

[9] (a) Beattie, P. D.; Delay, A.; Girault, H. H. *J. Electroanal. Chem.* **1995**, *380*, 167. (b) Beattie, P. D.; Wellington, R. G.; Girault, H. H. *J. Electroanal. Chem.* **1995**, *396*, 317. (c) Shao, Y.; Mirkin, M. V. *J. Am. Chem. Soc.* **1997**, *119*, 8103.

[10] The generator and collector pipets were as follows:

Ag/AgTPBCl/0.5 mM DB18C6 + 10 mM TBATPBCl//
outer DCE solution
20 mM KCl/AgCl/Ag (generator)
generator pipet

Ag/AgTPBCl/0.5 mM DB18C6 + 10 mM TBATPBCl//
outer DCE solution
10 mM LiCl/AgCl/Ag (collector)
collector pipet

[11] (a) Samec, Z.; Marecek, V.; Colombini, M. P. *J. Electroanal. Chem.* **1988**, *257*, 147. (b) Shao, Y.; Stewart, A. A.; Girault, H. H. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 2593.