



# Differential pulse stripping voltammetry of moderately hydrophobic ions based on hydrophobic ionic liquid membranes supported on the Ag/AgCl electrode

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## ABSTRACT

Differential pulse stripping voltammetry (DPSV) based on the ion transfer across the hydrophobic ionic liquid and an aqueous sample solution has been achieved for the analysis of moderately hydrophobic ions. The ionic liquid membrane was made of the double layers of gelled trioctylmethylammonium bis(nona-fluorobutanesulfonyl)amide ([TOMA<sup>+</sup>][C<sub>4</sub>C<sub>4</sub>N<sup>-</sup>]), a hydrophobic ionic liquid. The first [TOMA<sup>+</sup>][C<sub>4</sub>C<sub>4</sub>N<sup>-</sup>] layer containing trioctylmethylammonium chloride (TOMACl) was in contact with a AgCl layer of a planar Ag/AgCl electrode, and the second [TOMA<sup>+</sup>][C<sub>4</sub>C<sub>4</sub>N<sup>-</sup>] layer without containing TOMACl was in contact with a sample solution. The linearity between the DPSV peak and the concentration of analytes, tetrapropylammonium and tridecafluoroheptanoate, was found between 5 μmol dm<sup>-3</sup> and 200 μmol dm<sup>-3</sup> of these ions.

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## 1. Introduction

For electrochemical detection of non-redox-active ions, such as Na<sup>+</sup>, acetylcholine, and perchlorate, the partition of those ions between the two-immiscible solutions has been made use of in both potentiometric and amperometric ion sensing methods [1–9]. Stripping techniques, which have been well-established as anodic stripping voltammetry using mercury electrodes and its variants, have been applied for sensitive detection of non-redox-active ions [10–22]. In those foregoing studies employed mainly as the phase that is immiscible with water are molecular solvents, for example, nitrobenzene, 1,2-dichloroethane, 2-nitrophenyl octyl ether, and 2-fluoro-2'-nitrodiphenylether, in the form of a plasticizer or a bulk liquid membrane. All these molecular solvents are more or less volatile and are of limited use in view of long-term stability, in addition to possible health and environmental concerns. The negligible vapor pressure of ionic liquids (ILs) at room temperature under the atmospheric pressure is one of, and probably the most distinctive, features of ILs, in comparison with molecular organic solvents. This unique property widens the scope of the applications of two-phase systems, which has been limited as long as organic solvents are employed. For applying ILs to voltammetric methods, ILs have to

be very hydrophobic, so that a substantial polarized potential window is available when it is in contact with an aqueous phase. Using ionic liquids of varying degrees of hydrophobicity, cyclic voltammetry and other voltammetric measurements of ion transfer across the IL|water (W) interface have been reported [23–33]. This paper reports differential pulse stripping voltammetry (DPSV) based on a gelled hydrophobic ionic liquid, trioctylmethylammonium bis(nona-fluorobutanesulfonyl)amide ([TOMA<sup>+</sup>][C<sub>4</sub>C<sub>4</sub>N<sup>-</sup>]), layered on a planar Ag/AgCl electrode to detect moderately hydrophobic ions in water.

## 2. Experimental

### 2.1. Materials

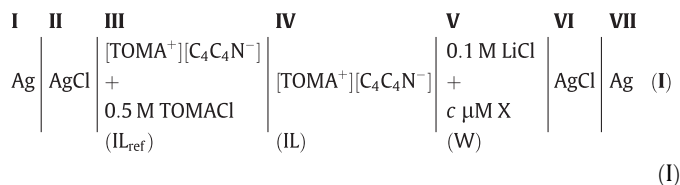
[TOMA<sup>+</sup>][C<sub>4</sub>C<sub>4</sub>N<sup>-</sup>] was prepared by mixing approximately equimolar amounts of trioctylmethylammonium chloride (TOMACl, Tokyo Chem. Ind.) and hydrogen bis(nonafluorobutanesulfonyl)amide (Wako Pure Chem. Ind.) in methanol. After the liquid precipitate was washed repeatedly with water to remove HCl and other water-soluble species, it was further purified using the method by Earle et al. [34]. Poly(vinylidene fluoride-co-hexafluoropropylene) (Aldrich), tetrapropylammonium chloride (Aldrich), and tridecafluoroheptanoic acid (Wako Pure Chem.) were used without further purification. Other chemicals used were of reagent grade.

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## 2.2. Methods

The electrochemical cell used for ion transfer voltammetry has the following configuration.



where X is either tetrapropylammonium chloride (TPrACl) or tridecafluoroheptanoic acid ( $\text{C}_6\text{F}_{13}\text{COOH}$ ) and M stands for  $\text{mol dm}^{-3}$ . The voltage applied to the cell across the two terminals of Cell (1) will be denoted  $E$ , where the value is referred to the left-hand side terminal. The current due to the transfer of cations from Phase V to Phase IV is taken to be positive.

### 2.2.1. Preparation of IL-coated Ag/AgCl electrodes

A half area of the one side of a rectangular silver plate of  $2 \text{ cm} \times 4 \text{ cm}$  with  $0.2 \text{ mm}$  thickness was first coated with aqueous  $\text{Ag}_2\text{O}$  paste. The  $\text{Ag}_2\text{O}$  coating was then decomposed at  $500^\circ\text{C}$ . The plate covered with a porous Ag layer was anodized in  $1 \text{ mol dm}^{-3}$  HCl for 45 min. TOMACl was dissolved in  $[\text{TOMA}^+][\text{C}_4\text{C}_4\text{N}^-]$  to prepare a  $0.5 \text{ mol dm}^{-3}$  TOMACl solution. The  $[\text{TOMA}^+][\text{C}_4\text{C}_4\text{N}^-]$  solution was mixed with poly(vinylidene fluoride-co-hexafluoropropylene) [35,36] by 2:1 ratio by weight in acetone. The Ag/AgCl plate was painted with this acetone solution and the acetone was allowed to evaporate. This painting-drying procedure was repeated, typically 10 times. Then, the plate was further painted with the acetone solution of  $[\text{TOMA}^+][\text{C}_4\text{C}_4\text{N}^-]$  without containing TOMACl. The total thickness of the two IL layers measured with a micrometer was  $0.3 \text{ mm}$ . The first layer (Phase II in Cell (1)) was introduced to improve the reversibility of the interface between Ag/AgCl and  $[\text{TOMA}^+][\text{C}_4\text{C}_4\text{N}^-]$  in Phase III.

We also tried a Ag/AgCl electrode coated with a single layer of AgCl-saturated  $[\text{TOMA}^+][\text{C}_4\text{C}_4\text{N}^-]$ . However, obtained cyclic voltammograms of ion transfer showed broader peak separation than those with the above two-layers substrate. The AgCl-saturated electrode appeared to have larger electrochemical polarizability, probably because of the low solubility of AgCl in  $[\text{TOMA}^+][\text{C}_4\text{C}_4\text{N}^-]$ ,  $0.85 \mu\text{mol dm}^{-3}$ , which we determined from atomic absorption spectroscopy.

### 2.2.2. Cell configuration

A conical glass cell, similar to the one that has been used for voltammetry of a flat Au electrode modified with a self-assembled monolayer [37], was mounted on the  $[\text{TOMA}^+][\text{C}_4\text{C}_4\text{N}^-]$ -coated Ag/AgCl electrode using an elastic O-ring whose inner diameter was  $4 \text{ mm}$ . An aqueous solution (Phase V) was filled in the glass cell and a Ag/AgCl electrode of a conventional spiral-wire type was inserted in the solution. The area of the IL|W interface was  $0.125 \text{ cm}^2$ .

### 2.2.3. Cyclic voltammetry and differential pulse stripping voltammetry

Cyclic voltammograms were recorded using a potentiostat with a two-electrode mode with the positive feedback for  $iR$  drop compensation at several dc-voltage scan rates ( $\nu$ ). For DPSV, first, the potential  $E_i$  was applied for a period of  $t_d$  for preconcentration, so that the target ions were accumulated in the IL membrane. The stripping of the ion was made with a differential pulse mode. A pulse of  $100 \text{ mV}$  height and  $0.1 \text{ s}$  duration was applied. The interval between two pulses was  $0.4 \text{ s}$ . The currents were sampled before the pulse was applied at the basal potential,  $E_j$  ( $j = 1, 2, \dots$ ), and at the end of the pulse to take the difference between the two cur-

rent values. This procedure was repeated with stepping  $E_j$  by  $1 \text{ mV}$  per step. The difference in the current was plotted as a function of  $E_j$ . The overall scan rate of  $E$  was  $2 \text{ mV s}^{-1}$ . All measurements were made at  $25 \pm 1^\circ\text{C}$ .

## 3. Results and discussion

### 3.1. Cyclic voltammetry of ion transfer

Fig. 1 shows cyclic voltammograms at the scan rate, 20 (curve a), 10 (curve b), and 5 (curve c)  $\text{mV s}^{-1}$ , when Phase V contained  $0.2 \text{ mmol dm}^{-3}$  TPrACl. The potential was scanned in the forward scan from  $E = 150 \text{ mV}$  to the positive direction of  $E$  to  $520 \text{ mV}$  and then scanned back. Curve d is a voltammogram in the absence of TPrACl in Phase V. The polarized potential window of about  $400 \text{ mV}$  in curve d is similar to that at the interface between non-gelled  $[\text{TOMA}^+][\text{C}_4\text{C}_4\text{N}^-]$  and  $0.1 \text{ mol dm}^{-3}$  LiCl [38].

The peaks in the middle of the potential window show the transfer of  $\text{TPrA}^+$  from the aqueous solution to the IL phase in the forward scan and the back transfer in the reverse scan. The peak separation was  $90 \text{ mV}$  when  $\nu = 5 \text{ mV s}^{-1}$ , which is greater than theoretical expected value,  $59 \text{ mV}$ , for diffusion limited transfer. Such peak broadening is not related to the slow kinetics of the  $\text{TPrA}^+$  transfer, as the peak separation did not appreciably depend on the scan rate, and the peak current was proportional to the square root of the scan rate. A similar broader peak was seen in ion transfer across the macroscopic, planar IL|W interface [24]. We believe that this broadening can mainly be ascribed to a large time constant of the cell determined by the double layer capacitance at IL|W, IL|IL and AgCl|IL interfaces and the uncompensated resistance, which remained even after the positive feedback compensation of the solution resistance. The mid-point potential for the transfer of  $\text{TPrA}^+$  was located at  $320 \text{ mV}$ .

The voltammograms for the transfer of  $\text{C}_6\text{F}_{13}\text{COO}^-$  are shown in Fig. 2. The applied voltage was first scanned from  $E = 450 \text{ mV}$  to the negative direction of  $E = 70 \text{ mV}$  and then the scan was reversed. The current increase in the middle of the potential window (curves a, b, and c) corresponds to the transfer of  $\text{C}_6\text{F}_{13}\text{COO}^-$ . The current was proportional to the square root of the scan rate. Although, again, the peak separation, ca.  $80 \text{ mV}$  at  $\nu = 5 \text{ mV s}^{-1}$ , is greater than that expected in a diffusion limited ion transfer, it is likely that the transfer of  $\text{C}_6\text{F}_{13}\text{COO}^-$  is electrochemically reversible, as is the transfer of  $\text{TPrA}^+$ .

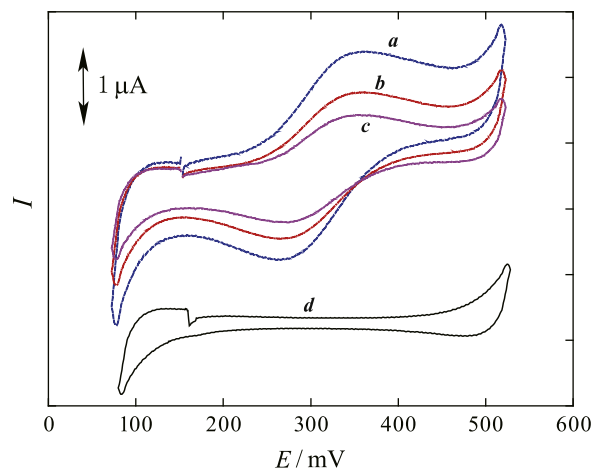


Fig. 1. Cyclic voltammograms at the interface between  $[\text{TOMA}^+][\text{C}_4\text{C}_4\text{N}^-]$  and aqueous  $0.1 \text{ mol dm}^{-3}$  LiCl solution in the presence (curves a–c) and in the absence (curve d) of  $0.2 \text{ mmol dm}^{-3}$  tetrapropylammonium chloride in the aqueous phase. The scan rates are 20 (curve a), 10 (curves b and d) and 5 (curve c)  $\text{mV s}^{-1}$ .

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