Voltammetric Study of the Transfer of Fluoride Ion at the Nitrobenzene | Water Interface Assisted by Tetraphenylantimony

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The transfer of F⁻ ion assisted by an organometallic complex cation tetraphenylantimony (TPhSb⁺) across the polarized nitrobenzene | water (NB | W) interface has been studied by means of ion-transfer voltammetry. A well-defined voltammetric wave was observed within the potential window at the NB | W interface when tetraphenylantimony tetrakis(4-chlorophenyl) borate and F⁻ ion were present in NB and W, respectively. The voltammogram can be interpreted as being due to the reversible transfer of F⁻ ion assisted by the formation of the TPhSbF complex through the coordination of F⁻ to Sb atom in NB. The formal formation constant of TPhSbF in NB has been determined to be 10^{10.95±0.2} M⁻¹. No voltammetric wave due to the TPhSb⁺-assisted transfer of other anions such as Cl⁻, Br⁻, I⁻, NO₃⁻, CH₃COO⁻ and H₂PO₄⁻ ions has been observed within the potential window.

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Tetraphenylantimony fluoride TPhSbF was synthesized by mixing equimolar TPhSbBr and LiF in 1:1:3 (v/v/v) water + ethanol + acetone, and recrystallized from 1:3 (v/v) ethanol + acetone. Yield 40%. Anal. Calcd. for TPhSbF: C, 64.18; H, 4.49; Sb, 27.11; F, 4.23%. Found: C, 63.47; H 4.45; Sb, 28.50; F, 4.33%.

Lithium fluoride (99.9%) was obtained from Wako Pure Chemicals Industries, Ltd. and used as received. Other chemicals were of reagent grade and used as received.

Electrochemical measurements

The transfer of F⁻ ion across NB | W interface assisted by TPhSb⁺ has been studied by means of cyclic voltammetry using a three-electrode system. The electrochemical cell used for recording the cyclic voltammograms (CVs) can be represented by cell-I:

![cell-I diagram]

where M = mol dm⁻³. The polarized NB | W interface, that is, the test interface, is indicated by an asterisk. The applied potential, E, is defined as the terminal potential of RE1 referred to that of RE2. The solution resistance between the two reference electrodes was about 3 kΩ for cell-I. The E was controlled by a potentiostat furnished with a positive feedback iR compensation circuit. The E is related to the Galvani potential difference, $\Delta \phi$, across the NB | W interface, as given by:

\[ E = \Delta \phi + R_i \frac{i}{|i|} \]

Experimental

Chemicals

Tetraphenylantimony tetrakis(4-chlorophenyl) borate TPhSbTClPB was synthesized by mixing equimolar tetraphenylantimony bromide (TPhSbBr) and sodium tetrakis(4-chlorophenyl) borate in 1:1:3 (v/v/v) water + ethanol + acetone, and recrystallized from 1:3 (v/v) ethanol + acetone. Yield 60%. Anal. Calcd. for TPhSbBr: C, 64.98; H, 4.09; Sb, 13.72; Br, 15.98%. Found: C, 64.99; H 4.13; Sb, 13.00; Br, 15.95%.

Tetraoctylammonium tetrakis(4-chlorophenyl) borate (TOctATClPB) and tetrapentylammonium tetrakis(4-chlorophenyl) borate (TPnATClPB) and the purification of tetrapentylammonium chloride (TPnACl) and NB were described elsewhere.¹⁻¹⁴ Tetraphenylantimony fluoride TPhSbF was synthesized by mixing equimolar TPhSbBr and LiF in 1:1:3 (v/v/v) water + ethanol + acetone, and recrystallized from 1:3 (v/v) ethanol + acetone. Yield 40%. Anal. Calcd. for TPhSbF: C, 64.18; H, 4.49; Sb, 27.11; F, 4.23%. Found: C, 63.47; H 4.45; Sb, 28.50; F, 4.33%.

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Notes

Voltammetric study of the transfer of anions across organic solvent | water interface assisted by ionophores has been the subject of research interest by several authors. Teramae and coworkers studied the assisted transfer of anions, such as Cl⁻, CH₃COO⁻, H₂PO₄⁻, HPO₄²⁻, and SO₄²⁻ ions, by thiourea-based hydrogen-bonding ionophores.¹⁻⁴ Shao et al. studied the transfer of dicarboxylates by xylylenyl bis-iminoimidazorium.⁵ A voltammetric study of the transfer of halide by macrotricyclic quaternary ammonium has been reported.⁶

The synthesis and structure of the compounds of tetraphenylantimony (TPhSb⁺) with organic or inorganic anions have been reported by several authors.⁷⁻¹² In the majority of the compounds of the general formula, (C₆H₅)₄SbX (X is an anion), the Sb atom has the trigonal-bipyramidal coordination with the axial X⁻ ligand. In this study, we investigated the transfer of anion assisted by TPhSb⁺ at the nitrobenzene | water (NB | W) interface. The TPhSb⁺ was added as tetraphenylantimony tetrakis(4-chlorophenyl) borate (TPhSbTClPB) to the NB-phase. A well-defined voltammetric wave attributed to the transfer of F⁻ ion across the NB | W interface assisted by TPhSb⁺ was observed within the potential window. The voltammetric behavior is described in this note.
M Li₂SO₄ (W). The standard potential of the transfer of TMA + determined to be 0.399 ± 0.010 V by cyclic voltammetry with voltammetric wave obtained with the 0.50 mM TPhSbTClPB, tetramethylammonium (TMA +) ion at the NB interface between 0.050 and 0.50 mM at temperature (25˚C).

TOctATClPB (NB) observed within the potential window at the 0.1 M concentration of the electrolysis cell and instruments, see Ref. 13. Measurements were carried out at 25 ± 1˚C. For further details estimated to be 0.355 V for cell-I. All electrochemical measurements were carried out at 25 ± 1˚C. For further details concerning the electrolysis cell and instruments, see Ref. 13.

Results and Discussion

19 F NMR measurements

The 19 F NMR spectra were collected at 282.4 MHz on a Varian Mercury-300 spectrometer. The TPhSbF complex was dissolved in CDCl₃ containing 1.0% C₆F₆ as an internal reference for the chemical shift of C₂F₆ (δ = –162.9 ppm vs. CFCl₃). The NMR measurements were carried out at ambient temperature (25˚C).

The potential peak separation, ∆(EΦ), defined by ∆(EΦ) = EΦ– EΦref, where EΦ is extrapolated to zero, was determined to be 0.057 ± 0.007 V, which coincides well with the theoretical value of 57 mV for a reversible transfer of monovalent ion. The midpoint potential, EΦm, defined by EΦm = (EΦ + EΦref)/2, remained constant independently of ν as a function of ν and was determined to be –0.192 ± 0.006 V. The results indicate that the associated ion-transfer is reversible, or Nernstian, and is controlled by the diffusion of TPhSb + ion in the NB-phase toward the interface. Using the theoretical equation of the peak current of reversible CV, the diffusion coefficient of TPhSb + in the NB-phase, Dp, was determined to be Dp = (1.8 ± 0.3) × 10⁻⁶ cm² s⁻¹ from the i vs. ν¹/² plot.

Tetraphenylantimony fluoride TPhSbF is soluble in NB up to a few hundreds mM, but is practically insoluble in W, which is supposed by atomic absorption spectrophotometry of Sb in a saturated TPhSbF aqueous solution. The conductivity of 2 mM TPhSbF (NB) was lower than 0.1 μS cm⁻¹ at 25˚C, whereas that of 2 mM TOctATClPB and TPhSbBr (NB) was 36 and 32 μS cm⁻¹, respectively, indicating that the formation equilibrium of TPhSbF in the NB solution,

\[ \text{TPhSb}^+ + \text{F}^- \rightleftharpoons \text{TPhSbF} \]


![Image](554_ANALYTICAL_SCIENCES_MARCH_2004_VOL_20.jpg)

Figure 1 Cyclic voltammograms of the 0.1 M TOctATClPB (NB) | 10 mM LiF (W) interface in the (a) presence and (b) absence of 0.50 mM TPhSbTCIPB in NB. Scan rate, ν = 0.02 V s⁻¹. Curve c: (a) – (b).

\[ E = \Delta_{\text{e}} \Phi + \Delta E_{\text{ref}}, \]

where \( \Delta E_{\text{ref}} \) is determined by the reference electrode system in cell-I. The reversible half-wave potential of the transfer of tetramethylammonium (TMA⁺) ion at the NB | W interface was determined to be 0.399 ± 0.010 V by cyclic voltammetry with cell-I, in which phase III is replaced by 0.20 mM TMACl, 0.05 M Li₂SO₄ (W). The standard potential of the transfer of TMA⁺ ion at NB | W interface under the tetrphenylarsionium-tetraphenylborate assumption is reported to be 0.035 V. Therefore, based on an appropriate assumption, the \( \Delta E_{\text{ref}} \) was estimated to be 0.355 V for cell-I. All electrochemical measurements were carried out at 25 ± 1˚C. For further details concerning the electrolysis cell and instruments, see Ref. 13.

19 F NMR measurements

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The potential peak separation, ∆(EΦ), defined by ∆(EΦ) = EΦ– EΦref, when ν is extrapolated to zero, was determined to be 0.057 ± 0.007 V, which coincides well with the theoretical value of 57 mV for a reversible transfer of monovalent ion. The midpoint potential, EΦm, defined by EΦm = (EΦ + EΦref)/2, remained constant independently of ν as a function of ν. Therefore, based on an appropriate assumption, the \( \Delta E_{\text{ref}} \) was estimated to be 0.355 V for cell-I. All electrochemical measurements were carried out at 25 ± 1˚C. For further details concerning the electrolysis cell and instruments, see Ref. 13.

Results and Discussion

Figure 1 shows the CVs of the 0.1 M TOctATClPB (NB) | 10 mM LiF (W) interface in the presence and absence of 0.50 mM TPhSbTCIPB in NB at the scan rate ν = 0.02 V s⁻¹. No voltammetric wave due to the transfer of TPhSb + ion was observed within the potential window at the 0.1 M TOctATClPB (NB) | 5 mM Li₂SO₄ (W) interface in the presence of 0.50 mM TPhSbTCIPB in NB, indicating that the voltammetric wave obtained with the 0.50 mM TPhSbTCIPB, 0.1 M TOctATClPB (NB) | 10 mM LiF (W) interface can be attributed to the transfer of F⁻ or TPhSb + ions across the NB | W interface, assisted by the association of TPhSb + and F⁻ in the NB- or W-phases, respectively.

The cathodic peak current, i_c, of the CV after correction for the base current was proportional to the concentration of TPhSbTCIPB in the bulk of the NB-phase, \( c_{\text{TPhSb}} \), in the range between 0.050 and 0.50 mM at ν = 0.02 V s⁻¹, and to \( ν^{1/2} \) in the range of ν between 0.01 and 0.2 V s⁻¹ at \( c_{\text{TPhSb}} = 0.50 \) mM (Fig. 2). The cathodic and anodic peak potentials, \( ΔE_{\Phi_c} \) and \( ΔE_{\Phi_a} \), shifted to more positive and negative potentials, respectively, linearly with decreasing \( ν^{1/2} \), which may be ascribed to an uncompensated iR drop due to the solution resistance.
the NB-phase is negligible. The reversible half-wave potential, 
\( \phi_{\text{OW}} \), of the assisted transfer of F– ion by TPhSb+ is given under the condition (case I) that the concentration of F– ion in the bulk of the W-phase, \( *c_{\text{FW}} \), is much higher than \( *c_{\text{FW}} (\ast c_{\text{FW}} ^{\ast} > *c_{\text{FW}} ) \) and the condition (case II) that \( *c_{\text{FW}} ^{\ast} = *c_{\text{FW}} \), respectively, by

\[
\phi_{\text{OW}} ^{\ast} = \Delta \phi_{\text{c}i} + (RT) \ln K_{\text{FW}} ^{\ast} + (RT) \ln \frac{D_{\text{FW}}}{D_{\text{W}}}, \quad (\ast c_{\text{FW}} ^{\ast} > *c_{\text{FW}} ) \tag{3}
\]

and

\[
\phi_{\text{OW}} ^{\ast} = \Delta \phi_{\text{c}i} + (RT) \ln K_{\text{FW}} ^{\ast} + (RT) \ln \frac{D_{\text{FW}}}{D_{\text{W}}}, \quad (\ast c_{\text{FW}} ^{\ast} = *c_{\text{FW}} ) \tag{4}
\]

where \( \Delta \phi_{\text{c}i} \) is the formal potential of the simple, or non-assisted, transfer of F– ion by TPhSb+ across the NB | W interface were independent of \( *c_{\text{FW}} \) between 4 and 20 mM when \( *c_{\text{FW}} = 0.20 \) mM, whereas the \( \Delta \phi_{\text{c}i} \) values were shifted to more positive potentials with increasing \( *c_{\text{FW}} \) in the range tested. The \( \Delta \phi_{\text{c}i} \) vs. \( \log *c_{\text{FW}} \) plot gives a straight line (plot a in Fig. 4), which is expressed by

\[
\Delta \phi_{\text{c}i}/V = (-0.079 \pm 0.012) + (0.056 \pm 0.006) \log *c_{\text{FW}}. \tag{5}
\]

The result agrees with the prediction from Eq. (3). The standard potential of the transfer of F– ion at NB | W interface, \( \phi_{\text{OW}} \), is calculated to be \(-0.726 \) V with the reported value of 70 kJ mol\(^{-1}\) for the standard Gibbs energy of the transfer of F– ion from W to NB. By taking that \( \Delta \phi_{\text{c}i} = \Delta \phi_{\text{c}i} ^{\ast} \) and that \( \Delta \phi_{\text{c}i} ^{\ast} = \Delta \phi_{\text{c}i} = -0.726 \) V and \( D_{\text{FW}} ^{\ast}/D_{\text{W}} = 1 \), the formal formation constant of TPhSbF in the NB-phase is calculated to be \( \log K_{\text{FW}} ^{\ast} = 10.9 \pm 0.2 \).

Figure 5 shows the CVs of the 10 mM TPhSbTCIPB, 0.1 M TOctATCIPB | 0.05 M Li\(_2\)SO\(_4\) (W) interface in the presence and absence of \( 0.20 \) mM LiF in W. \( \nu = 0.02 \) V s\(^{-1}\). Curve (c) (b) – (b).

The \( i_{pc} \) values were independent of \( *c_{\text{FW}} \) between 5 and 40 mM when \( *c_{\text{FW}} = 0.20 \) mM, whereas the \( \Delta \phi_{\text{c}i} \) values were
shifted to more positive potentials with increasing $c_{\text{OTPhSb}}$ in the range tested. The $\Delta \phi_m$ vs. log $c_{\text{OTPhSb}}$ plot gives a straight line (plot b in Fig. 4), which is expressed by

$$
\Delta \phi_m = (-0.098 \pm 0.011) + (0.057 \pm 0.006) \log c_{\text{OTPhSb}}.
$$

The result agrees with the prediction from Eq. (4). From Eqs. (3) and (4), we have

$$
\Delta \phi_{\text{I}} - \Delta \phi_{\text{II}} = \left( \frac{RT}{F} \right) \ln \left( \frac{D_{\text{FW}}}{D_{\text{OTPhSb}}} \right) + \left( \frac{RT}{F} \right) \ln \left( \frac{c_{\text{FW}}}{c_{\text{OTPhSb}}} \right).$$

The right-hand term of Eq. (7) can be calculated to be $0.019 \pm 0.011$ V when $c_{\text{FW}} = c_{\text{OTPhSb}}$ with the values of $D_{\text{FW}}$ and $D_{\text{OTPhSb}}$ obtained above, which is in good agreement with $\Delta \phi_{\text{I}} - \Delta \phi_{\text{II}} = 0.021$ V calculated by Eqs. (5) and (6) when $c_{\text{FW}} = c_{\text{OTPhSb}} = 10$ mM.

No voltammetric wave due to the assisted transfer of anions by TPhSb$^+$ was observed with the 0.50 mM TPhSbTClPB, 0.1 M TOctATClPB (NB) | 10 mM LiX (X = Cl$^-$, Br$^-$, I$^-$, NO$_3^-$, and CH$_3$COO$^-$) and NaH$_2$PO$_4$ (W) interface within the potential window. Also, no voltammetric wave due to the transfer of F$^-$ ion was observed with the 0.1 M TOctATClPB (NB) | 10 mM LiF (W) interface in the presence of 0.50 mM triphenylstibine, tetraphenylarsonium tetrakis(4-chlorophenyl) borate, and tetraphenylphosphonium tetrakis(4-chlorophenyl) borate in the NB-phase.

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