A Liquid/Liquid-Type Heteropolyanion Reference Electrode for Ion-Transfer Voltammetry

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A new liquid/liquid-type reference electrode for ion-transfer voltammetry with the nitrobenzene (NB)/water (W) interface has been developed. This reference electrode is expressed as Pt/1.8 mM α -[SiMo₁₂O₄₀]⁴⁻ + 0.2 mM α -[SiMo^V₂Mo₁₂O₄₀]⁴⁻ + 0.1 M H₂SO₄ (W)/0.3 mM α -[SiMo₁₂O₄₀]⁴⁻ + 0.02 M tetrahexylammonium tetraphenylborate (NB). The Galvani potential difference between the reference NB/W interface is determined virtually by the distribution equilibrium of the heteropolyanion (α -[SiMo₁₂O₄₀]⁴⁻), whereas the Pt electrode potential is determined by the redox equilibrium of the heteropolyanion couple. With this reference electrode, a potential window of about 0.4 V is available in a fairly negative potential region, where the transfer of hydrophilic inorganic anions (Br⁻, I⁻, SCN⁻, NO₃⁻, and ClO₄⁻) can be observed voltammetrically.

Keywords Reference electrode, ion-transfer voltammetry, 12-molybdosilicate, nitrobenzene/water interface

In recent years the electrochemical technique with the interface between two immiscible liquids, which we call "ion-transfer voltammetry", has been extensively applied to the study of ion-transfer processes in various fields.¹⁻⁴ A typical Galvani cell used in such measurements is shown in the following diagram:

where TBACl and TBATPB stand for tetrabutylammonium chloride and tetrabutylammonium tetraphenylborate, respectively. The nitrobenzene (NB)/water (W) interface (indicated by an asterisk) between phases II and III is polarizable, and when a "semi-hydrophobic" ion like tetramethylammonium ion is added to either phase, its transfer across the interface can be observed voltammetrically.⁵ As also seen in cell A, a Ag/AgCl electrode is usually used for the reference electrode in the W-phase side. On the other side, since there is no reference electrode which can be used in NB⁶, such a liquid/liquid (L/L) type reference electrode as in cell A is generally employed. The Galvani potential difference between phases I and II, $\Delta_{\text{II}}^{\text{I}}\phi$ ($\equiv \phi^{\text{I}} - \phi^{\text{II}}$), is determined by the distribution equilibrium of TBA⁺ between the two phases:^{5,7}

$$\Delta_{\text{II}}^{\text{I}}\phi = \Delta_{\text{NB}}^{\text{W}}\phi_{\text{TBA}^+}^{\circ} + \frac{RT}{F} \ln \frac{a_{\text{TBA}^+}^{\text{II}}}{a_{\text{TBA}^+}^{\text{I}}} \quad (1)$$

where $\Delta_{\text{NB}}^{\text{W}}\phi_{\text{TBA}^+}^{\circ}$ is the standard ion-transfer potential of TBA⁺, $a_{\text{TBA}^+}^{\text{I}}$ and $a_{\text{TBA}^+}^{\text{II}}$ are the activities of TBA⁺ in

phases I and II, respectively, and *R*, *T*, and *F* have their usual meanings. Since the Ag/AgCl electrode immersed in an aqueous solution (phase I) containing Cl⁻ shows a defined potential, the Ag/AgCl/0.1 M TBACl (W) electrode finally exhibits a Nernstian response to TBA⁺ in NB (phase II).

Although the above cell system has been frequently utilized, its polarizable potential range (so-called "potential window") is not very wide (*i.e.*, about 0.32 V), because the negative-current limit is determined by the transfer of TBA⁺ that is not sufficiently hydrophobic. Thus far, some attempts have been made to broaden the potential window by replacing TBA⁺ with more hydrophobic cations including Crystal Violet⁸⁻¹⁰, tetraphenylarsonium^{10,11}, tetrapentylammonium (TPenA⁺)¹², and tetrahexylammonium (THexA⁺)¹² ions. For example, the use of THexA⁺ broadens the polarizable potential range in the negative direction by as much as *ca.* 0.25 V.¹² In this case, however, such an L/L type reference electrode as shown in cell A is no longer available, because $\Delta_{\text{II}}^{\text{I}}\phi$ is not determined only by the distribution equilibrium of THexA⁺; Cl⁻ added initially to the aqueous phase (phase I) may be extracted to NB by THexA⁺ of extreme hydrophobicity. The $\Delta_{\text{II}}^{\text{I}}\phi$ of the interface should be elucidated on the basis of the concept of the mixed ion-transfer potential¹³⁻¹⁶, and from a practical point of view, it seems inappropriate to use such an interface for a reference interface.

In this paper we will propose a new L/L type reference electrode based on the distribution of a Keggin-type heteropoly molybdosilicate anion, *viz.* α -[SiMo₁₂O₄₀]⁴⁻, at the NB/W interface and its redox equilibrium at the platinum electrode surface. Figure 1 shows the scheme of the new reference electrode. In

Fig. 1 Scheme of the heteropolyanion reference electrode. To phase I, 2.0 mM α -H₄[SiMo₁₂O₄₀] was initially added, a part of which was then reduced by the addition of a mM ascorbic acid (usually, $a = 0.2$). To phase II, the heteropolyanion was added as the THexA⁺ salt.

this reference electrode system, $\Delta_{II}^I\phi$ is determined virtually by the distribution of α -[SiMo₁₂O₄₀]⁴⁻ between phases I and II:¹⁷

On the other side, the potential ($\Delta_{II}^I\phi$) of the platinum electrode immersed in the acidic heteropolyanion solution is determined by the equilibrium potential of the redox couple:^{18,19}

In this study the characteristics of the heteropolyanion reference electrode have been evaluated through the use in voltammetric measurements for the transfer of some hydrophilic inorganic anions.

Experimental

Chemicals

Based on TG-DTA, 12-molybdosilicic acid n -hydrate (α -H₄[SiMo₁₂O₄₀] $\cdot n$ H₂O; available from Wako Pure Chemical Industries, Ltd.) was dehydrated by heating at 120°C before use. The THexA⁺ salt, α -(THexA)₄ [SiMo₁₂O₄₀], was prepared as follows: 2 g of α -H₄ [SiMo₁₂O₄₀] (anhydrous) was dissolved in 44 ml of 1:1 (v/v) 1,4-dioxane–water containing 1.0 M sulfuric acid. After 15 h during which the β -isomer as an impurity was transformed into the α -isomer, 2 g of THexABr (Tokyo Kasei Kogyo Co. Ltd.) was added to the yellow heteropolyanion solution. The resulting yellow precipitates were collected by filtration and recrystallized from acetone. The salt was finally dried at 50°C under reduced pressure.

Tetrahexylammonium tetraphenylborate (THex-ATPB) was prepared as described previously.¹² Analytical-grade NB (Wako) was treated by activated alumina (200 mesh) for column chromatography before use. All other reagents were of analytical grade and

used as further purification.

Preparation of the heteropolyanion reference electrode

The aqueous heteropolyanion solution for phase I (Fig. 1) was prepared by dissolving 2.0 mM α -H₄[SiMo₁₂O₄₀] (anhydrous) in 0.1 M sulfuric acid, followed by addition of a mM ascorbic acid (usually $a = 0.2$) which reduced an equimolar amount of the heteropolyanion as shown in Fig. 1. After standing for at least 30 min, the resulting blue solution was loaded in a Luggin capillary, in which a platinum wire electrode was then inserted. Finally, the reference NB/W interface was formed around the end of the Luggin capillary.

Electrochemical measurements

All voltammetric measurements were performed with a micro-computer assisted system (laboratory-constructed). Unless otherwise noted, the three-electrode cell previously reported²⁰ was employed for ion-transfer voltammetry. For redox voltammetry with a platinum working electrode a conventional three-electrode cell system was used. Potentiometric measurements were performed with an Advantest (Model TR8652) electrometer. All the electrochemical measurements were carried out at 25±0.1°C.

Results and Discussion

Reversibility of the heteropolyanion redox couple

The reversible behaviors of the redox couple shown in Eq. (3) on the platinum electrode were observed by potentiometric measurements of the electrode potential in 0.1 M H₂SO₄ (air saturated) containing 2 mM α -H₄[SiMo₁₂O₄₀], to which an aliquot of an ascorbic acid solution (0.1 M) was added stepwise. As we would expect, the equilibrium electrode potential measured against Ag/AgCl(sat. KCl) was found to obey the Nernst equation :

$$E^c = E^{\circ'} + \frac{2.303RT}{2F} \log \frac{[\text{ox}]}{[\text{red}]} \approx 0.280 + 0.033 \log \frac{[\text{ox}]}{[\text{red}]} \quad (\text{in V}) \quad (4)$$

where $E^{\circ'}$ is the formal potential; [ox] and [red] are the concentrations of oxidized and reduced forms of the heteropolyanion. The value of $E^{\circ'}$ (=0.280 V) agreed with that obtained from cyclic and normal-pulse voltammetric measurements.

Ion transfer voltammetry of yellow and blue heteropolyanions at the NB/W interface

The interfacial transfer of the yellow (oxidized) heteropolyanion ($\alpha\text{-[SiMo}_{12}\text{O}_{40}]^{4-}$) has already been studied in rather detail.¹⁷ In this study, we investigated the transfer of the blue species, *i.e.*, the 2-electron reduced form ($\alpha\text{-[H}_2\text{SiMo}^{\text{V}}_2\text{Mo}_{10}\text{O}_{40}]^{4-}$), which may interfere with the distribution equilibrium of the yellow species in the reference electrode system in Fig. 1. In Fig. 2 the voltammogram of the transfer of the blue species is compared with that of the yellow species. As seen, the transfer potential of the blue species is almost identical with that of the yellow species. The midpoint potential E_{mid}^{21} (= 0.354 V) of the blue species was only 10 mV more negative than that of the yellow species.

Distribution behaviors of the heteropolyanion at the NB/W interface

In order to know if the reference NB/W interface (between phases I and II in Fig. 1) exhibits a Nernstian response to $\alpha\text{-[SiMo}_{12}\text{O}_{40}]^{4-}$, we have measured the *emf*

Fig. 2 Cyclic voltammograms of the transfer of (1) 0.2 mM $\alpha\text{-[SiMo}_{12}\text{O}_{40}]^{4-}$ (yellow) and (2) 0.2 mM $\alpha\text{-[H}_2\text{SiMo}^{\text{V}}_2\text{Mo}_{10}\text{O}_{40}]^{4-}$ (blue) at the 0.1 M TPenATPB(NB)/0.5 M MgCl_2 + 0.1 M H_2SO_4 (W) interface (area=0.127 cm²). The heteropolyanion was added to the W phase as the acid form. The blue species (2) was prepared through a reduction of the yellow species by ascorbic acid. Reference electrodes: a Ag/AgCl/0.02 M TPenACl + 0.1 M MgSO_4 (W) electrode was used in the NB phase, while a Ag/AgCl/0.5 M MgCl_2 + 0.1 M H_2SO_4 (W) electrode was connected to the W phase through a glass sinter. The cyclic potential scan was applied from 0.4 V in the cathodic direction at the rate of 50 mV s⁻¹.

(electromotive force) of the following cell :

where SCE stands for a saturated calomel electrode. The $\alpha\text{-[H}_2\text{SiMo}^{\text{V}}_2\text{Mo}_{10}\text{O}_{40}]^{4-}$ in phase I or III was prepared by reduction of the oxidized form using ascorbic acid. The concentration ($C_{\text{ox}}^{\text{III}}$) of $\alpha\text{-[SiMo}_{12}\text{O}_{40}]^{4-}$ in phase III was changed stepwise by adding the acid in the concentrated solution or its solid form. The concentration dependence of the *emf* is shown in Fig. 3. Considering the experimental error of ± 1 mV, the experimental *emf*-values (open circles), on the whole, were found to show a Nernstian response, although somewhat deviations were observed at lower and higher concentrations. The solid line in Fig. 3 shows the Nernstian response with the slope of 15 mV ($=2.303 \times RT/4F$) :

$$\text{emf} = \Delta_{\text{II}}^{\text{III}} \phi + \text{const.} = \Delta_{\text{NB}}^{\text{W}} \phi_{\text{ox}}^{\circ'} - \frac{RT}{4F} \ln \frac{C_{\text{ox}}^{\text{II}}}{C_{\text{ox}}^{\text{III}}} + \text{const.} \quad (5)$$

where $\Delta_{\text{NB}}^{\text{W}} \phi_{\text{ox}}^{\circ'}$ is the formal potential for the transfer of $\alpha\text{-[SiMo}_{12}\text{O}_{40}]^{4-}$ at the NB/W interface. Thus, at moderate concentrations ($0.4 \text{ mM} < C_{\text{ox}}^{\text{III}} < 2 \text{ mM}$), the NB/W

Fig. 3 Dependence of the *emf* of cell B on $\log C_{\text{ox}}^{\text{III}}$. The solid line is the Nernstian response with a slope of 15 mV; the dashed line is the calculated values of the mixed ion-transfer potential. With the concentration ($C_{\text{ox}}^{\text{III}}=1.8 \text{ mM}$) indicated by the arrow, the proposed reference electrode is prepared.

interface between phases II and III responds to $\alpha\text{-[SiMo}_{12}\text{O}_{40}]^{4-}$ in a virtually reversible manner. Accordingly, the proposed reference electrode should be prepared under these conditions (e.g., $C_{\text{ox}}^{\text{III}}=1.8$ mM). The deviation from the Nernstian response at lower concentrations ($C_{\text{ox}}^{\text{III}} < 0.4$ mM) may be ascribed to the interference from the reduced form ($\alpha\text{-[H}_2\text{SiMo}^{\text{V}}_2\text{-Mo}_{10}\text{O}_{40}]^{4-}$), which has the ion-transfer potential almost identical with the oxidized form ($\alpha\text{-[SiMo}_{12}\text{O}_{40}]^{4-}$) as shown above. The potential difference of such a NB/W interface should be elucidated in terms of the mixed ion-transfer potential ($\Delta\phi_{\text{mix}}$).¹³⁻¹⁶ The dashed line in Fig. 3 shows the relative change of calculated $\Delta\phi_{\text{mix}}$ -values based on the proposed theory¹³, which are in harmony with that of the experimental values. In the calculation of $\Delta\phi_{\text{mix}}$ the reported value¹⁷ of $D^{\text{NB}}=1.14\times 10^{-6}$ cm² s⁻¹ was employed for the diffusion coefficients of the oxidized and reduced forms in NB. Their diffusion coefficients in W were assumed to be $D^{\text{W}} = 2.07\times D^{\text{NB}}$ (Walden rule) = 2.36×10^{-6} cm² s⁻¹. Based on the present calculation, the theoretical deviation from the Nernstian response is only 0.2 mV at $C_{\text{ox}}^{\text{III}}=1.8$ mM. The deviation from the Nernstian response at higher concentrations ($C_{\text{ox}}^{\text{III}} > 2$ mM) is most possibly ascribed to the protonation effect¹⁷ due to the increase in the acidity of phase III which would have been caused by addition of the acid form of the heteropolyanion.

Ion-transfer voltammetry of the transfer of hydrophilic inorganic anions

In order to examine the characteristics of the heteropolyanion reference electrode, voltammetric measurements were performed for the transfer of X^- (= Br⁻, I⁻, SCN⁻, NO₃⁻, and ClO₄⁻) using the following cell:

The NB/W interface (indicated by an asterisk) between phases II and III is to be tested. The transferring ion, X⁻, was added to phase III as the lithium or sodium salt. To avoid appearance of a current maximum, Span® 20 (sorbitan monolaurate, Wako) was added to the NB phase.²² Phase III was contacted to phase IV through a salt bridge containing 0.5 M Li₂SO₄.

A typical cyclic voltammogram is shown in Fig. 4. A well-defined wave for the transfer of NO₃⁻ was observed around -0.6 V. At less negative potential (around -0.25 V), a reversible wave for the transfer of $\alpha\text{-[SiMo}_{12}\text{O}_{40}]^{4-}$ (ref. 17) also appeared. Thus, the high-

Fig. 4 Cyclic voltammogram of the transfer of 0.5 mM NO₃⁻ at the NB/W interface (area = 0.045 cm²). The cyclic potential scan was applied from 0.35 V in the cathodic direction at a rate of 30 mV s⁻¹.

er potential region (ca. 0.2 V) in the potential window was spoiled by the heteropolyanion transfer, but the potential window of ca. 0.4 V still remained to be available in the lower potential region. For anions other than NO₃⁻, well-defined waves due to their transfers were also observed in the potential window.

The wave of the transfer of X⁻ showed the characteristics of a reversible wave. The peak separation (ca. 60 mV at 30 mV s⁻¹) agreed well with the theoretical value (i.e., 57 mV) for a reversible wave. Accordingly, the midpoint potential, E_{mid} , between the cathodic and anodic peak potentials can be assumed to be the reversible half-wave potential, ($E_{1/2}^{\text{r}}$), that is given by⁵

$$E_{1/2}^{\text{r}} = \Delta_{\text{NB}}^{\text{W}}\phi_{\text{ox}}^{\circ} + \frac{RT}{zF} \ln \frac{\gamma^{\text{NB}}}{\gamma^{\text{W}}} + \frac{RT}{zF} \ln \frac{\sqrt{D^{\text{W}}}}{\sqrt{D^{\text{NB}}}} + \Delta E_{\text{ref}} \quad (6)$$

where z is the ionic valence (here, $z = -1$), γ^{W} and γ^{NB} are the activity coefficients of the transferring ion in W and NB, respectively, and ΔE_{ref} is the constant which is determined only by the reference electrode system employed.

The value of ΔE_{ref} was determined from the $E_{1/2}^{\text{r}}$ -value (= -0.257 V) of $\alpha\text{-[SiMo}_{12}\text{O}_{40}]^{4-}$, which was reproducible within the experimental error of ± 4 mV (95% confidence limit). According to the previous study¹⁷, the $E_{1/2}^{\text{r}}$ of the simple transfer of $\alpha\text{-[SiMo}_{12}\text{O}_{40}]^{4-}$ is also given by Eq. (6) with $z = -4$. The value of $\Delta_{\text{NB}}^{\text{W}}\phi_{\text{ox}}^{\circ}$ for the polyanion was then reported to be 0.066 V on the basis of the assumptions that $(\gamma^{\text{W}}/\gamma^{\text{NB}})=1^{23}$ and $(D^{\text{W}}/D^{\text{NB}})=2.07$ (Walden rule). In this study, we also used these assumptions to estimate ΔE_{ref} to be -0.321 V for cell C.

The stability of the heteropolyanion reference electrode was checked by pursuing the E_{mid} 's for I⁻ and $\alpha\text{-[SiMo}_{12}\text{O}_{40}]^{4-}$. As seen in Fig. 5A, the E_{mid} 's of these ions remained constant ($< \pm 2$ mV) for at least 6 h, although their slight changes with time were observed, especially in the initial 10 min. Thus, the present reference electrode exhibited comparatively high stability.

Fig. 5 Time dependences of (A) the E_{mid} 's of I⁻ and α -[SiMo₁₂O₄₀]⁴⁻ and (B) their difference, ΔE_{mid} . The time measurement was started immediately after preparation of the reference interface.

As shown in Fig. 5B, however, the difference in E_{mid} between the two ions, ΔE_{mid} , could be determined in a more reliable manner. This shows that α -[SiMo₁₂O₄₀]⁴⁻ is available for the internal standard. Although tetramethylammonium ion (TMA⁺) has often been used as an internal standard, α -[SiMo₁₂O₄₀]⁴⁻ seems to be superior to TMA⁺, since the E_{mid} of the tetravalent polyanion can be measured more accurately than that of the monovalent TMA⁺ ion (note that the theoretical peak separation for a tetravalent ion is as small as 15 mV). Further, the sharp wave of α -[SiMo₁₂O₄₀]⁴⁻ spoils the potential window to a lesser extent. It should be noted that the E_{mid} of the heteropolyanion is invariant when pH > 2.¹⁷

Standard Gibbs energies of the transfer of inorganic anions

The value of $\Delta_{\text{NB}}^{\text{W}}\phi^{\circ}$ can be obtained from $E_{1/2}^{\text{r}}$ using

Eq. (6) with the estimated value of ΔE_{ref} ($= -0.321$ V). However, in common with the L/L type reference electrodes prepared for ion-transfer voltammetry, some variability (*ca.* ± 5 mV) in the reference electrode potential was observed for different preparations. Accordingly, in order to obtain more accurate values of $\Delta_{\text{NB}}^{\text{W}}\phi^{\circ}$ (with an error less than ± 2 mV), the wave of α -[SiMo₁₂O₄₀]⁴⁻ was here employed as internal standard. Using Eq. (6), we can obtain the expression for ΔE_{mid} between X⁻ and α -[SiMo₁₂O₄₀]⁴⁻ as

$$\Delta E_{\text{mid}} = E_{1/2}^{\text{r}} - E_{1/2, \text{ox}}^{\text{r}} = (\Delta_{\text{NB}}^{\text{W}}\phi^{\circ} - \Delta_{\text{NB}}^{\text{W}}\phi_{\text{ox}}^{\circ}) - \frac{RT}{F} \ln \frac{\gamma_{\text{NB}}^{\text{NB}}}{\gamma_{\text{W}}^{\text{W}}} + \frac{RT}{4F} \ln \frac{\gamma_{\text{ox}}^{\text{NB}}}{\gamma_{\text{ox}}^{\text{W}}} - \frac{RT}{F} \ln \frac{\sqrt{D^{\text{W}}}}{\sqrt{D^{\text{NB}}}} + \frac{RT}{4F} \ln \frac{\sqrt{D_{\text{ox}}^{\text{W}}}}{\sqrt{D_{\text{ox}}^{\text{NB}}}} \quad (7)$$

In this equation the subscript "ox" represents α -[SiMo₁₂O₄₀]⁴⁻, and no subscript X⁻. Since the value of $\Delta_{\text{NB}}^{\text{W}}\phi_{\text{ox}}^{\circ}$ is known to be 0.066 V¹⁷, the value of $\Delta_{\text{NB}}^{\text{W}}\phi^{\circ}$ for X⁻ can be obtained from ΔE_{mid} using Eq. (7) provided that the terms concerning γ and D are evaluated. The activity coefficients of X⁻ were estimated by Davies' extended equation²⁴ of the Debye-Hückel theory, and the term $-(RT/F) \ln(\gamma_{\text{NB}}^{\text{NB}}/\gamma_{\text{W}}^{\text{W}})$ was then calculated to be 0.004 V. The term $-(RT/F) \ln(\sqrt{D^{\text{W}}}/\sqrt{D^{\text{NB}}})$ was calculated to be -0.009 V based on the assumption of $(D^{\text{W}}/D^{\text{NB}}) = 2.07$ (Walden rule). The remaining two terms for the heteropolyanion are as described above. Finally, the value of $\Delta_{\text{NB}}^{\text{W}}\phi^{\circ}$ can be given by $\Delta_{\text{NB}}^{\text{W}}\phi^{\circ} = \Delta E_{\text{mid}} + 0.069$ (in V). Table 1 shows the values of $\Delta_{\text{NB}}^{\text{W}}\phi^{\circ}$ thus-calculated for the inorganic anions. In Table 1 are also shown the standard Gibbs energies ($\Delta G_{\text{tr}}^{\circ, \text{NB} \rightarrow \text{W}}$) of their transfers at the NB/W interface being related to $\Delta_{\text{NB}}^{\text{W}}\phi^{\circ}$ as $\Delta G_{\text{tr}}^{\circ, \text{NB} \rightarrow \text{W}} = -zF\Delta_{\text{NB}}^{\text{W}}\phi^{\circ}$, which are compared with some literature values.^{10, 25-27} The present values have been found to coincide best with those reported by Koryta *et al.*²⁵ The literature values in ref. 26 are negatively larger by 1 – 5 kJ mol⁻¹ than the present ones. Table 1 also shows the value of $\Delta G_{\text{tr}}^{\circ, \text{NB} \rightarrow \text{W}}$ (26.7 kJ mol⁻¹) for TBA⁺, which has been determined in a similar manner with the present system. This value differs somewhat from Koryta *et al.*'s value (24.0 kJ mol⁻¹)²⁵, but agrees well with another literature value (26.5 kJ

Table 1 Standard potentials and Gibbs energies of transfer of some anions at the NB/W interface at 25°C

Ion	$\Delta_{\text{NB}}^{\text{W}}\phi^{\circ}/\text{V} (\Delta E_{\text{mid}}/\text{V})$	$\Delta G_{\text{tr}}^{\circ, \text{NB} \rightarrow \text{W}}/\text{kJ mol}^{-1}$				
		This study	Ref. 10	Ref. 25	Ref. 26 ^a	Ref. 27
Br ⁻	-0.288 (-0.357)	-27.8	-30	-28.4	-32.8	-30.5
I ⁻	-0.191 (-0.260)	-18.4	-18	-18.8	-20.3	-19.5
SCN ⁻	-0.164 (-0.233)	-15.8			-17.9	-16.5
NO ₃ ⁻	-0.261 (-0.330)	-25.2	-26		-27.9	-26.6
ClO ₄ ⁻	-0.082 (-0.151)	-7.9	-5	-8.0	-9.0	-7.4
TBA ⁺	-0.277 ^b (-0.336)	26.7		24.0		

a. Calculated from the reported values of $\Delta_{\text{NB}}^{\text{W}}\phi^{\circ}$. b. Determined in a similar manner, but with $\Delta_{\text{NB}}^{\text{W}}\phi^{\circ} = \Delta E_{\text{mid}} + 0.059$ (in V).

mol⁻¹).²⁸

In conclusion, the proposed heteropolyanion reference electrode appears promising for voltammetric studies of the transfer of ions with fairly negative ion-transfer potentials.

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(Received September 24, 1997)

(Accepted November 26, 1997)