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Chloride Transfer across the Liquid–Liquid Interface Facilitated by a Mono-Thiourea as a Hydrogen-Bonding Ionophore

Seiichi Nishizawa, Tomoyuki Yokobori, Ryo Kato, Takeshi Shioya, and Norio Teramae*

Department of Chemistry, Graduate School of Science, Tohoku University, Aoba-ku, Sendai 980-8578

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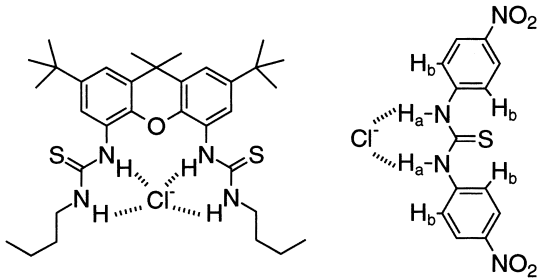
Applicability of a thiourea-based hydrogen-bonding ionophore **2**, *N*,*N′*-bis(*p*-nitrophenyl)thiourea, for amperometric anion sensors is presented. Chloride transfer across the nitrobenzene (NB)–water interface facilitated by this ionophore is studied by using ion transfer polarography. When **2** is present in the organic phase, a well-defined wave can be observed, indicating that the chloride transfer across the NB–water interface is facilitated by **2** via formation of hydrogen bonds. The analysis of ion transfer polarograms shows that the chloride transfer is assisted by 1 : 1 complexation between **2** and chloride, and that the transfer process is reversible and controlled by diffusion of **2** from the bulk NB phase to the interface. Despite its simple binding mode based on two point interactions, mono-thiourea **2** has a strong ability to facilitate chloride transfer, which is comparable to that obtained for a highly preorganized bis-thiourea ionophore **1**, 2,7-di-*t*-butyl-4,5-bis(*N′*-butylthioureylene)-9,9-dimethylxanthene, in which four hydrogen bonds are involved in the chloride binding.

The design and synthesis of hydrogen-bonding ionophores for biologically and/or chemically important anions are of current interest in host-guest chemistry.[1–4] Successful applications of hydrogen-bonding ionophores in potentiometric ion-selective electrodes (ISEs) have been reported.[5–11] By contrast, despite significant advantages[12–16] over traditional potentiometry with plasticized PVC membranes containing ionophores, considerably less progress has been made with ionophore-based amperometric sensors for sensing of anions. Shao et al.[17] investigated complex formation between a positively charged ionophore, 1,4-phenylenebis(methyleneiminoimidazolinium), and dicarboxylates in electrolyte-containing nitrobenzene (NB) and water by cyclic voltammetry. A voltammetric study of halide (I^-, Br^-, Cl^-) transfer by macrotricyclic quaternary ammoniums has also been reported.[18] For both cases,[17,18] the positively charged ionophore was soluble in both organic and aqueous phases. While the transfer of the free ionophore across the interface gave a voltammetric wave, the transfer of the complexed ionophore did not give the current response because of the neutralization of positive charges. Analyte anions in the aqueous solution were therefore detected by measurements of the suppressed peak current of ionophore transfer.

On the other hand, we have directly observed,[19] for the first time, the polarographic wave of ionophore-assisted anion transfer between ITIES (interface between two immiscible electrolyte solutions) by using ion transfer polarography. We have utilized a neutral hydrogen-bonding ionophore, α,α'-bis(*N′*-phenylthiourelene)-*m*-xylene,[20–22] to study facilitated anion transfer across the 1,2-dichloroethane (DCE)–water interface. When this ionophore is present in the organic phase, a clear wave due to the facilitated transfer of a very hydrophilic anion, SO_4^{2-}, is observed, whereas only positive shifts are observed for Cl^- and CH_3COO^-.[19] We have also shown that a bis-thiourea ionophore preorganized by a rigid spacer xanthene **1**, 2,7-di-*t*-butyl-4,5-bis(*N′*-butylthioureylene)-9,9-dimethylxanthene,[21,23,24] can effectively facilitate the transfer of various hydrophilic anions, such as Cl^-, CH_3COO^-, $H_2PO_4^-$, HPO_4^{2-}, and SO_4^{2-}, across the NB–water interface.[25] These results strongly suggest the potential use of neutral ionophores for amperometric anion sensors, in which anion detection would be based on the observation of the current response due to facilitated anion transfer. Indeed, Qian et al.[26] recently designed a micro ITIES array for detection of nitrate by facilitated ion transfer. They used a neutral tripodal amide-based ionophore, *N*-{2-[bis-[2-(4-*t*-butylbenzoylamino)ethyl]amino]ethyl-4-*t*-butylbenzamide, for nitrate binding, together with dibenzo-18-crown-6 as a co-ionophore for potassium ion binding. In their dual recognition system, the interaction between nitrate and the ionophore was successfully detected by observing the current response of facilitated nitrate transfer and/or potassium ion transfer. Therefore, studies on the electrochemistry of facilitated anion transfer by various types of neutral hydrogen-bonding ionophores would provide important insights into their applicability for novel amperometric anion sensors.

In this report, chloride transfer across the NB–water interface facilitated by a mono-thiourea ionophore **2**, *N*,*N′*-bis(*p*-nitrophenyl)thiourea, is investigated by using ion transfer polarography. This ionophore was designed and synthesized in the course of our previous work on anion-selective chromoionophores.[27–29] Due to the introduction of two *p*-nitrophenyl units into the thiourea moiety, ionophore **2** can recognize anions by a readily observable color change.[29] An application of **2** to the colorimetric determination of acetic acid in a commercially available brand of vinegar was also reported.[29] In the present work, we report on the applicability of this chromoionophore for amperometric anion sensors, and the quantitative analysis of complexation between **2** and Cl^- is carried out by electrochemical measurements[30–40] and ^1H NMR spectroscopy. Chloride is chosen as a primary anion because development of simple methods for the measurements of this analyte is required in clinical analysis and environmental monitoring.[6,23] Even though the mono-thiourea **2** makes a 1:1 complex with Cl^- via only two point interactions between two NH groups and Cl^- (cf. Fig. 1), this ionophore can effectively transfer Cl^- from the aqueous phase to the organic phase. The stability of the Cl^- complex for **2** in the NB phase is even comparable to that for a highly preorganized bis-thiourea **1** which binds Cl^- by the formation of four point interactions through hydrogen bonds (cf. Fig. 1). Unique binding behaviors of very simple mono-thiourea **2** are presented.



1 **2**

Fig. 1. Structure formulas of Cl^- complex of ionophore **1** or **2**.

Experimental

Reagents. The synthesis of ionophore **2** was described previously.[29] Analytical grade nitrobenzene (NB) was obtained from Kanto Chemical Co., Inc. (Tokyo, Japan) and purified by passing through a column of basic alumina before use. Dimethyl sulfoxide-d_6 (DMSO-d_6) from E. Merk (> 99.5%, Darmstadt, Germany) was dried over molecular sieves (4 Å). Sodium tetraphenylborate (NaTPB) from Dojindo Laboratories (Kumamoto, Japan) was used as received. Tetrabutylammonium chloride (TBACl) from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan) was purified by recrystallization from ethyl acetate/hexane. Tetraheptylammonium tetraphenylborate (THepATPB) was prepared by mixing an equimolar aqueous solution of NaTPB and a 1,2-DCE solution of tetraheptylammonium iodide (Tokyo Chemical Industry Co., Ltd.). It was recrystallized twice from 1,2-DCE/methanol. Water was doubly distilled and subsequently deionized (≥ 18.0 MΩ cm specific resistance) by a Milli-Q Labo system (Millipore Corp., Bedford, MA, USA), and used for all electrochemical experiments. The other reagents were commercially available analytical grade and were used without further purification.

Binding Studies by ^{1}H NMR Spectroscopy. Complexation of ionophore **2** and Cl^- in DMSO-d_6 was confirmed by ^1H NMR spectroscopy. ^1H NMR spectra were obtained on a JEOL α-270 spectrometer (270 MHz; JEOL Datum, Tokyo, Japan). All chemical shifts values (δ) are reported in parts per million (*ppm*), using the residual solvent signal (δ2.49) of DMSO as a reference. To determine the complexation constant, a series of DMSO-d_6 solutions which contain Cl^- (used as a TBA^+ salt) and ionophore **2** was prepared. The concentration of **2** was fixed as 1.0 mM, and the concentration of Cl^- ranged from 0 to 100 mM. The chemical shifts of selected hydrogens of the ionophore were plotted as a function of the Cl^- concentration. The resulting titration curves were analyzed by a non-linear regression based on a 1:1 binding isotherm model.[41]

Electrochemical Measurements. The ion transfer polarograms were recorded by potential-scan polarography[30,33,34,37] using an electrolyte solution dropping electrode.[30,31,33,34,37] The following electrochemical cell was used to study the transfer of Cl^- across the NB–water interface:

Ag/AgCl/0.5 M LiCl/0.05 M NaTPB + 0.5 M LiCl/(org.) 0.5 mM **2** + 0.05 M THepATPB/(aq.) 0.5 M LiCl/0.5 M LiCl/AgCl/Ag

The aqueous solution rises into the NB phase from a PTFE capillary (0.7 mm i.d.) at a flow rate which ranges from 10 to 27.5 mL h^{-1}. Potential difference between the aqueous and NB phases, $\Delta\phi$ ($= \phi_w - \phi_{NB}$), was controlled at a scan rate of 2.5 mV s^{-1} by a conventional four-electrode potentiostat (Hokuto Denko Co. Ltd., Tokyo, Japan, Model HA-501 G) and is expressed by

$$\Delta\phi = E - \Delta\phi_{\mathrm{ref}}$$

where E (mV) is the potential difference between two reference electrodes and $\Delta\phi_{\mathrm{ref}}$ (mV) is the sum of all potential differences involved in the cell. The ohmic potential drop of the cell was compensated by using an *i–R* compensation instrument (Hokuto Denko, Model HI-203). The values of the potentials ($\Delta\phi$) were standardized by measuring the half-wave potential $\Delta\phi_{1/2}$ of ClO_4^- (used as Na^+ salt, $\Delta\phi_{ClO_4}{}^\circ$: -0.091 V)[38–40] as a reference ion with the same reference electrode system. Negative current flows when anions are transferred from the aqueous phase to the organic phase. All experiments were carried out at 298 ± 0.5 K.

Results and Discussion

In a previous report,[29] we have shown that highly selective binding and sensing of CH_3COO^- over various monovalent inorganic anions can be achieved by **2** as a hydrogen-bonding chromoionophore in 1% water–99% CH_3CN (v/v). The stability of the acetate complex in this binary solvent is very strong (3.0×10^5 M^{-1}), and acetic acid in vinegar can be successfully determined by the complexation-induced chromogenic response of **2**. However, it seems likely that the selective binding of CH_3COO^- in a binary mixture of water and CH_3CN is partly ascribable to a solvation (hydration) effect. As usual in hydrogen bond-based molecular recognition systems,[42] the binding behavior of this type of ionophore is quite sensitive to environmental changes, and the presence of water will have an especially significant effect on anion binding events. It has also been demonstrated[21,43] that the binding selectivity for anions is strongly affected by the solvent. Thus, it is reasonable that, in appropriate organic media, ionophore **2** binds several anions that may act as hydrogen bond acceptors, such as $H_2PO_4^-$ and Cl^-, through the formation of hydrogen bonds.

In the present study, complexation of ionophore **2** and Cl^- was confirmed in DMSO-d_6 by ^1H NMR spectroscopy. Figure 2 shows the chemical shifts of hydrogens of ionophore **2** as observed in a titration with TBACl. Downfield shifts for both hydrogens of the thiourea moiety of the ionophore were observed upon complexation with Cl^-. The chemical shifts of the two NH protons in the complex were larger by 1.5 ppm than those in the free ionophore. A smaller shift by 0.3 ppm was also observed for the aromatic hydrogen adjacent to the thiourea moi-

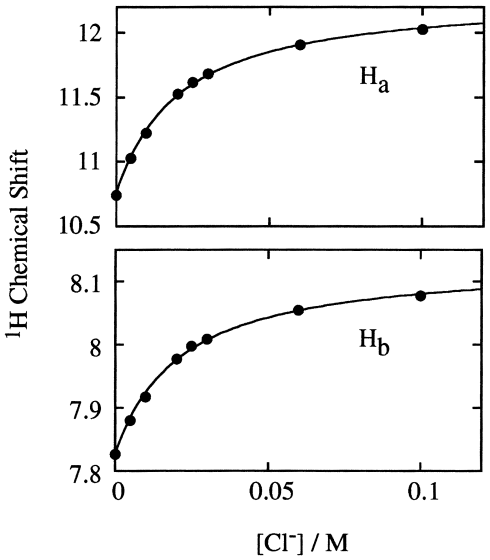


Fig. 2. ¹H NMR chemical shifts of the hydrogens in the thiourea moiety, H_a (cf. Fig. 1), and the aromatic hydrogens adjacent to the NH groups, H_b, in a titration with tetrabutylammonium chloride. [**2**] = 1.0 mM in DMSO-d_6 at 298 K. (●): Experimental data; (—): non-linear fitting based on the equation for a 1:1 complexation.

ety. A non-linear fitting shows that all these shifts can be explained by the formation of a 1:1 complex, and the association constant is obtained as 50 M^{-1}. While this shows a much weaker stability of the chloride complex of **2** as compared with that of bis-thiourea **1** (840 M^{-1} in DMSO-d_6),[21,23] mono-thiourea **2** in NB shows a strong ability to facilitate Cl^- transfer, which is comparable to that obtained for bis-thiourea **1**.

Ion transfer polarograms for Cl^- are shown in Fig. 3. While only a background wave due to the direct Cl^- transfer is observed in the absence of **2** (Fig. 3, curve a), a well-defined wave appears in its presence (Fig. 3, curve b). Obviously, the Cl^- transfer across the NB–water interface is facilitated by **2** via formation of hydrogen bonds.

Facilitated Cl^- transfer across the NB–water interface was analyzed according to theory.[30–36] When Cl^- is transferred by the formation of the complex having the stoichiometry 1:n (Cl^- to ionophore), the polarographic wave is given by[35]

$$\Delta\phi = \Delta\phi_{1/2} - (RT/F)\ln\{i/(i_l - i)^n\} \tag{1}$$

where $\Delta\phi_{1/2}$ is the reversible half-wave potential, i is the electrical current, and i_l is the limiting electrical current. As shown in the inset of Fig. 3, there is a linear relationship between $\Delta\phi$ and $\log\{i/(i_l - i)\}$ with a slope of −60 mV, revealing the transfer of monovalent anionic species through 1:1 complexation between **2** and Cl^-. The limiting current i_l is proportional to the square root of the flow rate of the aqueous solution, and also to the concentration of **2** in the NB phase (not shown). These results indicate that the transfer process of Cl^- across the interface is reversible and is controlled by diffusion of **2** from the bulk NB phase to the interface. The half-wave potential $\Delta\phi_{1/2}$ for the Cl^- transfer facilitated by **2** is evaluated as −0.142 V from the intercept of the regression curve in the inset of Fig. 3. The reversible half-wave potential for the transfer reaction is given by[32,33,35]

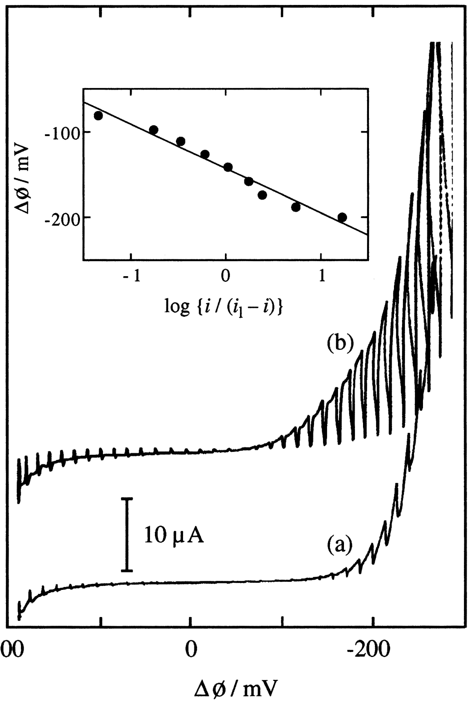


Fig. 3. Ion transfer polarograms of Cl^- across the NB–water interface. Aqueous phase: 0.5 M LiCl. Organic phase: 0.05 M $N(C_7H_{15})_4TPB$ and (a) 0 mM or (b) 0.5 mM **2**. Flow rate: 15 mL h^{-1}. Inset: Relationship between $\Delta\phi$ and $\log\{i/(i_l - i)\}$. Aqueous phase: 0.5 M LiCl. NB phase: 0.05 M $N(C_7H_{15})_4TPB$ and 0.5 mM **2**. Flow rate: 15 mL h^{-1}.

$$\Delta\phi_{1/2} = \Delta\phi_{Cl}{}^{\circ\prime} - (RT/2F)\ln(D_I/D_{IA}) + (RT/F)\ln(K_{11}[Cl^-]_W) \tag{2}$$

where $\Delta\phi_{Cl}{}^{\circ\prime}$ is the ion transfer formal potential for Cl^-, and K_{11} is the association constant in the NB phase. D_I and D_{IA} are the diffusion cofficients of the ionophore and the chloride complex, respectively. As expected from Eq. 2, the half-wave potential $\Delta\phi_{1/2}$ varies with the concentration of Cl^- in the aqueous phase $[Cl^-]_W$ (Fig. 4). In this figure, plotting $\Delta\phi_{1/2}$ against $\log[Cl^-]_W$ gives a straight line with a slope of −56.5 mV, in accordance with Eq. 2. On the assumption that D_I is nearly equal to D_{IA}, the association constant K_{11} of the 1:1 complex between **2** and Cl^- can be calculated as $3.8 \pm 0.4 \times 10^4$ M^{-1} from Eq. 2. Comparison with the case in the absence of ionophores (cf. $\Delta\phi_{Cl}{}^{\circ}$: −0.395 V; $\Delta G_{tr}{}^{\circ}$: 38 ± 2 kJ mol^{-1})[39,40] shows the Cl^- transfer across the NB–water interface is indeed stabilized by 26 kJ mol^{-1} through the binding with **2** in the NB phase. Significantly, as illustrated in Fig. 5, mono-thiourea **2** shows a striking ability to transfer Cl^- from the aqueous phase to the NB phase ($\Delta\phi_{1/2}$: −0.142 V; K_{11}: $3.8 \pm 0.4 \times 10^4$ M^{-1}), which is comparable to that obtained for highly preorganized bis-thiourea **1** ($\Delta\phi$: −0.140 V; K_{11}: $4.1 \pm 0.2 \times 10^4$ M^{-1}).[25]

We think it interesting to compare the binding behavior of mono-thiourea **2** with that of bis-thiourea **1**. ¹H NMR binding studies show that, in DMSO-d_6, bis-thiourea **1** binds Cl^- (840

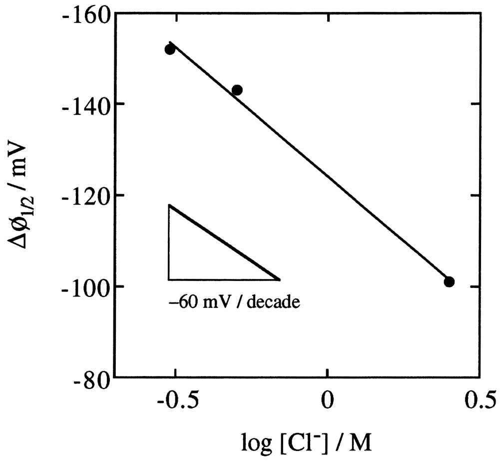


Fig. 4. Dependence of the reversible half-wave potential $\Delta\phi_{1/2}$ on the concentration of Cl$^-$ in the aqueous phase. NB phase: 0.05 M $N(C_7H_{15})_4TPB$ and 0.5 mM **2**. Flow rate: 15 mL h^{-1}.

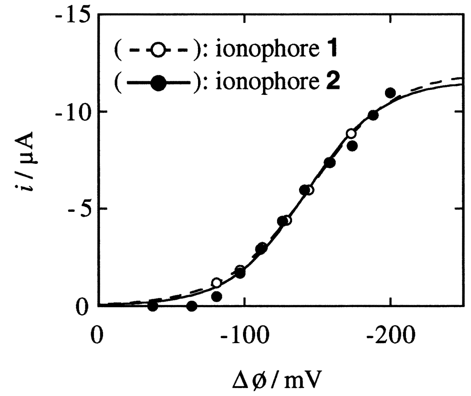


Fig. 5. Plot of i, corrected for the base current, against $\Delta\phi$ for the transfer of Cl$^-$ facilitated by ionophore **1** (○) or **2** (●). Aqueous phase: 0.5 M LiCl. NB phase: 0.05 M $N(C_7H_{15})_4TPB$ and 0.5 mM ionophore. Flow rate: 15 mL h^{-1}. (—) and (---): Non-linear fitting based on Eq. 1 for the reversible polarographic wave.

M^{-1}) more strongly than mono-thiourea **2** does (50 M^{-1}). DMSO is known to interfere with the complexation between ionophores and anions, since it forms hydrogen bonds to the ionophore, and solvates Cl$^-$ by ion-dipole interactions.[21,23] Hence, DMSO solvation should have a much more considerable influence on binding events of mono-thiourea **2**, which has an *open* binding site,[42] than on binding events of preorganized bis-thiourea **1**. The higher stability of the 1 : 1 complex between **1** and Cl$^-$ can therefore be explained by the formation of four hydrogen bonds and by the highly preorganized structure of the ionophore ascribed to the rigid spacer xanthene.[21,23]

On the other hand, electrochemical measurements show that the stability of the Cl$^-$ complex for mono-thiourea **2** ($3.8 \pm 0.4 \times 10^4$ M^{-1}) in the NB phase is indeed comparable to that for bis-thiourea **1** ($4.1 \pm 0.2 \times 10^4$ M^{-1}).[25] This indicates that, in spite of the simple binding mode via two point interactions, the Cl$^-$ complex stability can be significantly increased by using thiourea groups with acidity-enhancing substituents, and weakening the formation of the Cl$^-$ complex by NB solvation is not large even for mono-thiourea **2**. Thus, in this kind of organic solvent, mono-thiourea **2** can form a very stable complex with Cl$^-$, making it possible to facilitate Cl$^-$ transfer across the interface between two immiscible electrolyte solutions.

In summary, we have shown that a very simple hydrogen bond-forming ionophore **2** can effectively facilitate the transfer of Cl$^-$ across the NB–water interface. The stability of the Cl$^-$ complex for mono-thiourea **2** in the NB phase is indeed comparable to that for highly preorganized bis-thiourea **1**. This indicates that **2** might be a promising candidate for application in amperometric ISEs for the sensing of anions. Although only the formation of 1 : 1 complexes was observed under the present experimental condition ($[Cl^-]_W \gg [\mathbf{2}]$), other complex stoichiometries such as 1 : 2 (Cl$^-$ to ionophore) complex may occur if **2** is used in amperometric ISEs under the condition of $[\mathbf{2}] \gg [Cl^-]_W$. Further examination of various types of hydrogen-bonding ionophores[27,28,44] may lead to a new design of novel amperometric anion sensors; this work is now in progress in our laboratory.

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