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Letter

Selective binding of very hydrophilic $H_2PO_4^-$ anion by a hydrogen-bonding receptor adsorbed at the 1,2-dichloroethane–water interface

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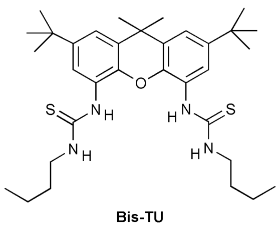
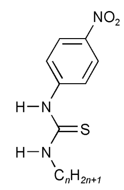
A thiourea-functionalized benzo-15-crown-5 (TU-B15C5), adsorbed at the 1,2-dichloroethane–water interface, can bind $H_2PO_4^-$ selectively over hydrophobic anions ($H_2PO_4^- > Cl^-$, ClO_4^-, Br^-, CH_3COO^-) *via* the formation of hydrogen bonds.

Due to the large differences in physical properties compared to bulk solutions,[1,2] studies on chemistry at the liquid–liquid (L/L) interface are of ongoing interest. Specific reactions of molecules (adsorbed) at the L/L interface have been reported in various systems such as photoinduced electron transfer reactions,[3a] organic synthesis,[3b] charge transfer,[3c] phase-transfer catalysis[3d] and molecular association.[3e] Our particular interest is hydrogen bond-mediated complexation at the L/L interface for specific analyte recognition.[4] We have recently studied electrochemical anion transfer across the L/L interface as facilitated by abiotic hydrogen-bonding receptors.[5] The receptor-assisted anion transfer process was successfully analyzed for the first time,[5a] indicating that, in spite of significant interference from anion hydration, complementary hydrogen bonding at phase boundaries is indeed effective for analyte recognition. However, due to limitations of this experimental technique, little is known about the characteristic features of hydrogen-bonding receptors *just* at the L/L interface.

Here we report on the anion binding behavior of a hydrogen-bonding receptor *adsorbed* at the 1,2-dichloroethane (DCE)–water interface. To analyze the interfacial phenomena, we have employed interfacial tensiometry,[6] which is widely used for the analysis of interfacial adsorption of various types of surfactants. It must be stressed that the interfacial tension decreases when molecules are adsorbed at the interface and as a result the concentration of the molecules at the boundary region increases compared with that in the bulk phase. This technique therefore has an intrinsic surface sensitivity, and thermodynamic and kinetic parameters of the interfacial adsorption can be obtained quantitatively. In the present study, we examined a complexation reaction at the L/L interface using three kinds of receptors (Bis-TU,[7] C_nH_{2n+1}-TU[8a] and TU-B15C5[8b]), all of which were previously shown to bind anions through hydrogen-bonding in bulk organic phases.[7,8] Although both Bis-TU and C_nH_{2n+1}-TU show essentially no surface activity irrespective of the presence or absence of guest anions,† thiourea-functionalized benzo-15-crown-5 (TU-B15C5), a bifunctional receptor for simultaneous binding of anions and sodium ions, shows a relatively strong surface activity and can work as a selective receptor for $H_2PO_4^-$ ($H_2PO_4^- > Cl^-$, ClO_4^-, Br^-, CH_3COO^-) at the L/L interface. To date, there have been only a few examples of receptor-based two-phase distribution systems such as ion-selective electrodes[9] and membrane transports[10] identified as exhibiting high selectivity for $H_2PO_4^-$ over hydrophobic anions. This is due to the difficulty in compensating large differences in Gibbs free energies of transfer between anions by highly selective complexation.[11] In contrast, the results of the present study suggest that selective binding of very hydrophilic $H_2PO_4^-$ by hydrogen-bonding receptors can be indeed obtained just at the L/L interface. Unlike bulk two-phase distribution systems, it is likely that complete dehydration of $H_2PO_4^-$ is not required for the interfacial binding event, which probably makes it possible to selectively recognize $H_2PO_4^-$.

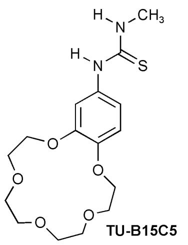


Bis-TU



C_nH_{2n+1}-TU

(n = 3, 8,12)



TU-B15C5

At first, the effect of NaH_2PO_4 on the interfacial adsorption of TU-B15C5 was examined qualitatively. For comparison, two counterparts of TU-B15C5, bezo-15-crown-5 (B15C5) and phenylthiourea (PTU), were also examined. Fig. 1 shows the decrease in the equilibrium interfacial tension, $\Delta\gamma(=\gamma_0-\gamma_e)$, (a) in the absence or (b) presence of 0.1 M NaH_2PO_4 in the aqueous phase. For PTU, which has no crown ether moieties, only a slight decrease in the interfacial tension was observed, and $\Delta\gamma$ did not change markedly irrespective of the presence or absence of NaH_2PO_4. This indicates that PTU has no ability to bind $H_2PO_4^-$ under the experimental conditions. Similar results were obtained for B15C5, which lacks the thiourea moiety. In contrast, even in the absence of NaH_2PO_4 a relatively large decrease in the interfacial tension was observed for TU-B15C5, indicating that this receptor molecule can adsorb at the DCE–water interface. Furthermore, in the presence of NaH_2PO_4 $\Delta\gamma$ was larger by 1.5 mN m^{-1} than in the absence of NaH_2PO_4. It should be noted that TU-B15C5 has no ability to extract the Na^+ and $H_2PO_4^-$ ion pair from the aqueous phase into the DCE phase.‡ Also, there are no changes in the distribution ratio of TU-B15C5 under the experimental conditions. Obviously, complex formation of TU-B15C5 with $H_2PO_4^-$ and/or Na^+ takes place just at the interface, accompanied by the interfacial adsorption of the complex.

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† Details of the interfacial phenomena of Bis-TU and C_nH_{2n+1}-TU will be reported elsewhere.

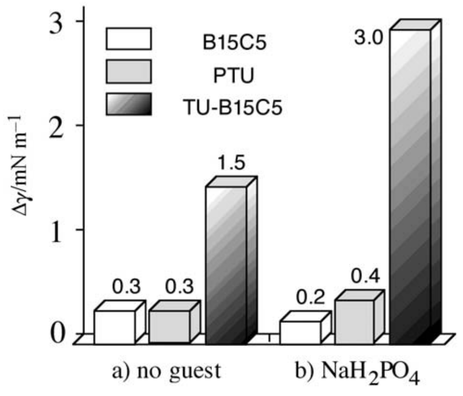

Fig. 1 Decrease in the interfacial tension at the DCE–water interface. Aqueous phase: (a) pure water or (b) 0.1 M NaH_2PO_4; DCE phase: 1.0 mM of a receptor (B15C5, PTU or TU-B15C5).

The effect of various anions on the adsorption behavior of TU-B15C5 was quantitatively analyzed according to the Gibbs plot. Fig. 2 shows typical Gibbs adsorption isotherms for TU-B15C5 (a) in the absence or (b) presence of 0.1 M NaH_2PO_4 in the aqueous phase. In this graph, the equilibrium interfacial tension γ_e is plotted as a function of the concentration of TU-B15C5 in the organic phase. As shown in Fig. 2, the interfacial tension decreases as the receptor concentration increases, indicating strong adsorption of TU-B15C5 at the DCE–water interface. The adsorption parameters can be evaluated by a non-linear fit with the following Szyszkowski equation:[12]

$$\gamma_e = \gamma_0 - \Gamma_{sat} RT \ln(1 + K_{ad}[\mathrm{TU-B15C5}])$$

where γ_0 is the interfacial tension without receptors, Γ_{sat} is the saturated interfacial concentration, and K_{ad} is the adsorption constant. The adsorption parameters of TU-B15C5 thus obtained are summarized in Table 1.

As can be seen from Table 1, $H_2PO_4^-$ is the only anion that induces significant changes in the adsorption parameters of TU-B15C5 at the DCE–water interface. While the adsorption constant – K_{ad} for CH_3COO^- (2200 ± 700), Br^- (2300 ± 400), ClO_4^- (3700 ± 1300) and Cl^- (6100 ± 2300) are almost equal within the experimental errors, the adsorption constant for $H_2PO_4^-$ (15 000 ± 3000) is indeed larger by a factor of 13 than that in the absence of these anions (1200 ± 100). Similarly, clear changes in the saturated interfacial concentration Γ_{sat} and the apparent molecular occupied area A_{occ} are observed only in the presence of $H_2PO_4^-$ in the aqueous phase. TU-B15C5 at the interface therefore shows high selectivity for $H_2PO_4^-$ over other anions ($H_2PO_4^- > Cl^-$, ClO_4^-, Br^-, CH_3COO^-). It is noteworthy that, among these anions, $H_2PO_4^-$ is the most hydrophilic one when one considers its end position in the Hofmeister series, which reflects the free energy of hydration of anions ($ClO_4^- > Br^- > Cl^- > CH_3COO^- > H_2PO_4^-$). If the strength of interaction between anions and TU-B15C5 is controlled only by the free energies of anion adsorption to the interface without specific binding, the selectivity should obey the Hofmeister series as has been found in the case of anion adsorption to hexadecyltrimethylammonium monolayers at the nitrobenzene–water interface ($Br^- > Cl^- > F^-$).[13a] It is thus clear that the observed dependence of the adsorption parameters on anion nature is indicative of interfacial binding between the anions and the thiourea moiety of TU-B15C5 *via* the formation of hydrogen bonds.

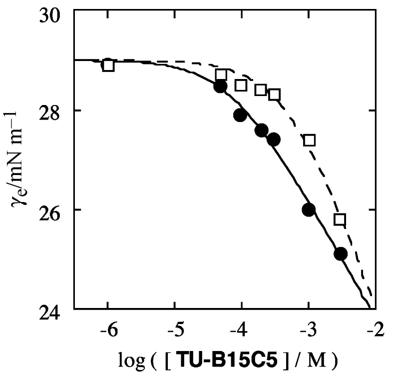

Fig. 2 Gibbs plot. Aqueous phase: (□) pure water or (●) 0.1 M NaH_2PO_4; DCE phase: 1.0×10^{-6}–3.0×10^{-3} M of TU-B15C5.

Interestingly, for the appearance of such anion binding ability of TU-B15C5 at the interface, the simultaneous binding of cations at the crown moiety is essential. In accordance with the optimal spatial fit to the crown cavity size, complex formation between TU-B15C5 and $H_2PO_4^-$ is observable only when Na^+ is present in the aqueous phase; no evidence for the binding with $H_2PO_4^-$ is obtained in the case of Li^+, K^+ and Rb^+ [K_{ad} (M^{-1}): LiH_2PO_4: 1000 ± 100; KH_2PO_4: 1200 ± 400; RbH_2PO_4: 840 ± 100]. The role of Na^+ binding to the crown moiety is ascribed to (*i*) enhancement of the hydrogen bond donation ability of the thiourea NH protons[8b] and/or (*ii*) neutralization of the negative charge of the TU-B15C5/$H_2PO_4^-$ complex to stabilize its adsorption.[13]

It is also of interest to note the changes in the apparent molecular occupied area A_{occ} upon interfacial complexation (Table 1). The A_{occ} of TU-B15C5 in the absence of anions is 210 ± 30 Å^2, which roughly agrees with the molecular area of 130 Å^2 (8.5 × 15 Å) as estimated from the CPK model by assuming that this receptor adsorbs horizontally at the interface. Upon interfacial binding with $H_2PO_4^-$, the apparent molecular area increases significantly to as high as 400 ± 30 Å^2. Such a complexation-induced change in the interfacial density is a characteristic phenomenon of surface-active molecules at the interface.

Table 1 Effect of anions on the adsorption behavior of TU-B15C5 at the 1,2-dichloroethane–water interface

Anion[a]	K_{ad}/M^{-1} [b]	$\Gamma_{sat}/10^{-6}$ mol m^{-2} [c]	A_{occ}/ Å^2 [d]
No guest	1200 ± 100	0.80 ± 0.1	210 ± 30
CH_3COO^-	2200 ± 700	0.60 ± 0.1	280 ± 50
Br^-	2300 ± 400	0.66 ± 0.06	250 ± 20
ClO_4^-	3700 ± 1300	0.68 ± 0.1	240 ± 40
Cl^-	6100 ± 2300	0.58 ± 0.09	290 ± 50
$H_2PO_4^-$	15 000 ± 3000	0.42 ± 0.03	400 ± 30

[a] 0.1 M solution of Na^+ salts. [b] The adsorption constant. [c] The saturated interfacial concentration. [d] The apparent molecular occupied area.

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‡ The distribution ratio of TU-B15C5, $[\mathrm{TU\text{-}B15C5}]_{DCE}/[\mathrm{TU\text{-}B15C5}]_{aq}$ ($[\mathrm{TU\text{-}B15C5}]_{DCE}$ and $[\mathrm{TU\text{-}B15C5}]_{aq}$ are the concentrations of all species of TU-B15C5 in the DCE and aqueous phases, respectively), was determined by UV-vis absorption spectrometry. While both the shape and position of the absorption spectrum of TU-B15C5 hardly changed after shaking a DCE solution containing the receptor with deionized water, a decrease in the absorbance was observed from which the distribution ratio was calculated to be 5.4. TU-B15C5 did not show any obvious spectral changes even in the presence of 0.1 M of alkali metal salts (NaH_2PO_4, KH_2PO_4, NaBr) in the aqueous phase, and the distribution ratio did not change at all, irrespective of the presence or absence of these salts. These results indicate that ion pair extraction of alkali metal ions and anions by TU-B15C5 did not occur under the experimental conditions. Also, it is likely that there are no significant changes in population of the receptor and alkali metal salts in bulk DCE and aqueous phases.

In summary, we have studied, for the first time, the binding properties of abiotic hydrogen-bonding receptors adsorbed at the L/L interface. Selective binding of $H_2PO_4^-$ in the aqueous solution is made possible by the use of TU-B15C5 just at the L/L interface; this finding should offer a novel approach to the sensing of very hydrophilic anions, which are difficult to detect by conventional receptor-based chemical sensors.

Experimental

The interfacial tension (mN m^{-1}) at the 1,2-dichloroethane (DCE)–water interface was measured by the dynamic drop volume method.[6,14] TU-B15C5 was dissolved in DCE. Droplets of an aqueous solution containing alkali metal salts (0.1 M) were sent upward, using a syringe pump, into the DCE solution from a glass capillary (0.705 cm o.d.) fixed in the cell. The dynamic interfacial tension $\gamma(t)$ was calculated from the volume of the droplets as a function of the introduction time, and then the equilibrium interfacial tension γ_e was obtained by plotting $\gamma(t)$ against $t^{-1/2}$.

Acknowledgements

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