The Facilitated Ion-Transfer of Lauryltrimethyl and Hexadecyltrimethylammonium Cations by Dibenzo Crown Ethers across the Water | 1,2-Dichloroethane Interface

Mandeep Singh Bakshi, Hidekazu Doe,* Norio Sakurada,† and Ryuichi Arakawa†
Department of Chemistry, Faculty of Science, Osaka City University, Sugimoto, Sumiyoshi-ku, Osaka 558
†*Department of Applied Chemistry, Faculty of Engineering, Kansai University, Yamatecho, Suita, Osaka 560*

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The transfer of lauryltrimethylammonium (LTA^+) and hexadecyltrimethyl-ammonium (HTA^+) cations facilitated by dibenzo-15-crown-5 (DB15C5), DB18C6 and DB21C7, from aqueous phase to 1,2-dichloroethane (DCE) phase were studied. In the presence of DB15C5, ambiguous wave was observed which became somewhat prominent in the presence of DB18C6 and then irreversible in the presence of DB21C7. Such waves have been attributed to the facilitated transfer of LTA^+ and HTA^+ cations across the interface in the form of surfactant ion-crown ether (CR) complexes. On the basis of electrospray ionization mass spectroscopy (ESI-MS) measurements, the stoichiometry of such a complex has been proposed to be 1:1. It has also been observed by interfacial tension (γ) measurements that the facilitated transfer becomes irreversible once the immiscible interface is fully occupied by the adsorption of amphiphilic surfactant monomers.

A lot of work has been carried out to understand the host-guest interactions particularly involving surfactants as guest molecules.[1-4] Most of these studies are related to encapsulation of the hydrophobic tail of a surfactant by a hydrophobic cavity as that of cyclodextrins.[1-4] There are also some examples of crown ether (CR)-surfactant interactions, in which rather than the hydrophobic tail, the counterion acts as a guest[3]. This is especially true in the case of anionic surfactants such as sodium dodecyl sulphate, since it has a Na^+ cation as a counterion and which has a strong affinity for an electronegative CR cavity. On the other hand, there are few studies related to the cationic surfactant-CR interactions in which only partially positively charged head group is vulnerable to interact with the CR cavity rather than the anionic counterion.[3] Such kind of association even becomes more interesting if the surfactant ion is facilitatively transferred across the immiscible interface by a totally hydrophobic CR. To achieve this goal, we have selected a series of dibenzo crown ethers such as DB15C5, DB18C6, and DB21C7 on the basis of their increasing cavity size so as to correlate this with an extent of host-guest interactions. This can be best evaluated by ion-transfer voltammetry across an immiscible interface as that of water | DCE.

The ion-transfer voltammetry measurements were carried out with the help of cyclic voltammetry using a gel electrode.[5] The voltammetric cell was the same as used in the previous study.[5] All measurements were carried out in an air conditioned room at 25 °C. The cell structure was as follows:

Ag	AgCl	0.125 M $MgCl_2$ 0.1 M LiCl	0.125 M Mg Cl_2	0.125 M $MgCl_2$ x M LTACl or HTACl

0.01M THATPB 5.0 x 10^{-4} M Crown Ether	0.01 M NaTPB 0.1 M LiCl	AgCl	Ag

where THATPB and NaTPB denote the tetraheptylammonium tetraphenylborate and sodium tetraphenylborate, respectively. The various concentrations studied for each surfactant in aqueous phase were 0.60, 1.2, 2.5, and 5.0 x 10^{-3} M, whereas, fixed concentration of 5.0 x 10^{-4} M was used for each CR in the DCE phase. All elec-

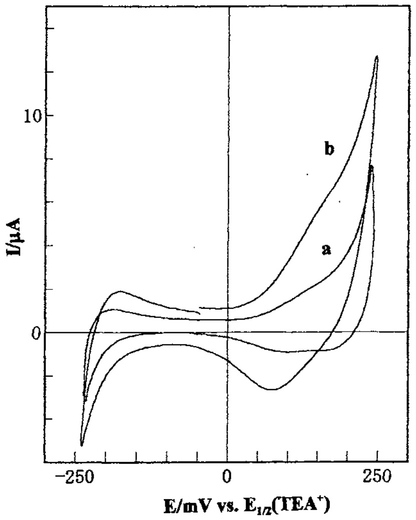

Figure 1. Cyclic voltammograms of facilitated ion-transfer of LTA^+ at the water|1,2-dichloroethane interface. Aqueous phase; 0.125 M $MgCl_2$ and (a) 0.60 x 10^{-3} M and (b) 1.2 x 10^{-3} M LTACl. Organic phase, 1.0 x 10^{-2} M THATPB and 5.0 x 10^{-4} M DB18C6. Scan rate, 0.050 V s^{-1}.

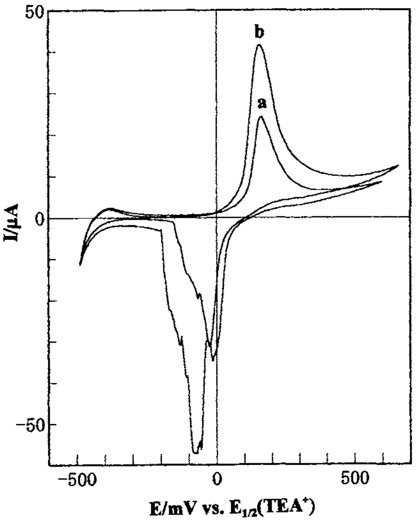

Figure 2. Cyclic voltammograms of facilitated ion-transfer of LTA^+ (a) and HTA^+ (b) at the water|1,2-dichloroethane interface. Aqueous phase; 0.125 M $MgCl_2$ and 1.2 x 10^{-3} M LTACl or HTACl. Organic phase, 1.0 x 10^{-2} M THATPB and 5.0 x 10^{-4} M DB21C7. Scan rate, 0.050 V s^{-1}.

trode potentials were referred to the half-wave potential of the tetraethylammonium (TEA$^+$) transfer from water to DCE phase.[5,6] A computer controlled apparatus described elsewhere[7] was used for cyclic voltammetric measurements.

In the absence of CR, we could not find any wave corresponding to the transfer of the present surfactant ions across the immiscible interface. However, in the presence of DB15C5, ambiguous waves appeared for both the ions close to the end of positive potential window (not shown). This became somewhat prominent in the presence of DB18C6 since it further shifted towards the positive potential (Figure 1). This suggests that the transfer is more facilitated in the latter case in comparison to the former case. However, in the presence of DB21C7, the facilitated transfer for both the ions became irreversible (Figure 2). Therefore, such a variation in the wave with respect to the increase in the cavity size may indicate that the facilitated transfer is associated with the extent of host-guest interactions. This is due to the fact that the association between a large surfactant polar head group and the smallest DB15C5 cavity will result in the weak host-guest interactions and which are expected to become stronger as the cavity size increases as in the case of DB18C6. Since DB21C7 has the largest cavity size, therefore, maximum host-guest interactions are expected. However, the irreversibility in the cyclic voltammogram in the latter case can be attributed to the strong host-guest interactions, which may lead to the adsorption of such a complex at the interface. This is only possible if the complex attains an amphiphilic character with sufficient hydrophobicity. Since, the outer surface of the CR is hydrophobic in nature[3] and hence, the larger CR such as DB21C7, will be having larger hydrophobic surface and thereby producing a stronger hydrophobic complex[3]. The hydrophilicity can be provided by the π-electron cloud of the aromatic rings, thus helping it to adsorb at the interface..

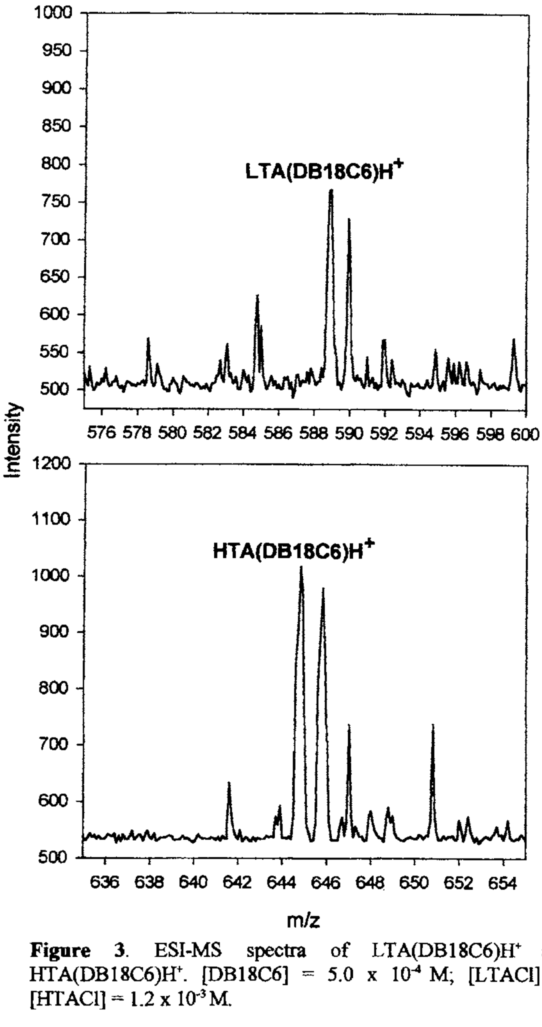

Figure 3. ESI-MS spectra of LTA(DB18C6)H$^+$ and HTA(DB18C6)H$^+$. [DB18C6] = 5.0 x 10^{-4} M; [LTACl] or [HTACl] = 1.2 x 10^{-3} M.

Apart from this, it is to be mentioned here that these wave were observed only at 0.60 and 1.2 x 10^{-3} M of each surfactant concentration, whereas at higher concentration, we could not get the reversible cyclic voltammograms. Although, HTACl has four extra methylene groups in the hydrophobic tail than LTACl, their electrochemical behavior remains predominantly identical, suggesting that the host-guest interactions are mainly between the identical polar head groups of the present unlike surfactants and the electronegative cavity of the respective CR.

In order to support the above results and to determine the stoichiometry of surfactant ion-CR complex, the ESI-MS measurements were performed. These measurements were carried out under the same experimental conditions as those for voltammetric studies and the DCE phase was used for these measurements. The details of the ES ion source were reported elsewhere.[8] The ESI-MS spectra for the present systems are shown in Figure 3. Again, we could not find any ESI-MS peak corresponding to 1:1 stoichiometry for LTA(DB15C5)$^+$ or HTA(DB15C5)$^+$. which may be due to the extremely low stability of this complex in the solution phase as is observed from the voltammetric studies. On the other hand, peaks corresponding to 1:1 stoichiometries for LTA(DB18C6)H$^+$ and HTA(DB18C6)H$^+$ at m/z equal to 589 and 645.0, and for LTA(DB21C7)H$^+$ and HTA(DB21C7)H$^+$ at m/z equal to 632.9 and 689.1, respectively, were observed. However. no peak corresponding to (host)$_2$(guest)$^+$ or host(guest)$^{2+}$ stoichiometries were observed. These results support the transfer of surfactant ion-CR complex across the immiscible water | DCE interface.

In order to observe the nature of immiscible interface with respect to the change in surfactant concentration, the interfacial tension (γ) measurements were carried out for the above mentioned systems (Wilhelmy plate, tensiometer model TD1, Luda, Germany). Such measurements revealed that γ value decreases with the increase in LTACl or HTACl concentration and approaches to zero around 2 x 10^{-3} M and then it remains almost constant (not shown). This may indicate that the surfactant monomers fully occupy the interface around 2 x 10^{-3} M concentration and which may be responsible for the irreversible transfer of the surfactant ions.

Therefore, from the above results it can be said that it is indeed possible to facilitate the transfer of cationic surfactant ions across an immiscible interface as long as it is not fully occupied by the surfactant monomers due to their amphiphilic adsorption.

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References and Notes

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