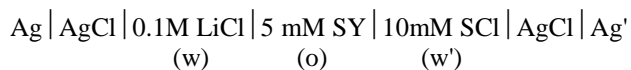


## Quasi-elastic light scattering and impedance study of electrical double layer at the polarised water|1,2-dichloroethane interface

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The main objective of this work was to apply the quasi-elastic light scattering (QELS) and impedance techniques to the study the electrical double layer at the water|1,2-dichloroethane (DCE) interface in a cell that can be represented by the scheme [1]:



where SY=bis(triphenylphosphoranylidene)ammonium tetrakis(4-chlorophenyl)borate (BTTPATPBCl), SCl = BTTPACl, (w) and (o) denote the aqueous and the DCE phase, respectively. An electrocapillary curve obtained from the QELS measurements is shown in Figure 1. The potentials are referred to the half-wave potential of the tetraethylammonium ( $\text{TEA}^+$ ) ion transfer, which was measured upon adding  $\text{TEA}^+$  ion to the aqueous phase. Electrocapillary maximum (potential of zero charge, PZC) is found at 0.03 V. The potential dependence of the double-layer capacity  $C$  evaluated by the fitting the impedance data to the Randles equivalent circuit is shown in Figure 2. Over a range of the potential differences around the PZC, the surface charge density obtained by integration of the capacity agrees well with that obtained by derivation of the interfacial tension. However, the ratio of these two charges starts to deviate significantly from unity close to the potential window limits, where the faradaic current associated with the transfer of the supporting electrolyte ions becomes more pronounced, and where the capacity shows a remarkable enhancement, cf. Figure 3. These results corroborate our previous experimental observations and conclusions [2], as well as earlier comparison [3] of the impedance and interfacial tension data [3,4] for the water|nitrobenzene interface. They all through doubts on the previous interpretation of the effect of electrolytes on the differential capacity close to the potential window in terms of the ion association [5-7], ion interpenetration [8], or specific ion adsorption [9]. In the potential range, where the capacity data can be reliably obtained, an effect of the nature of the organic electrolyte on both the interfacial tension and the differential capacity is observed, which can be ascribed to the change in the thickness of the inner (compact) layer due to a difference in the radius of the ions present.

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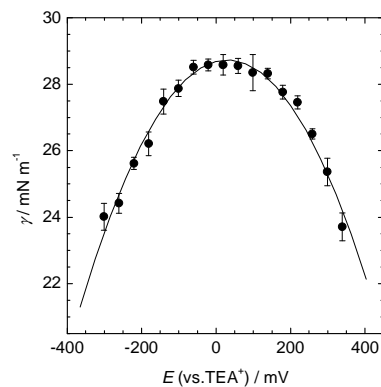
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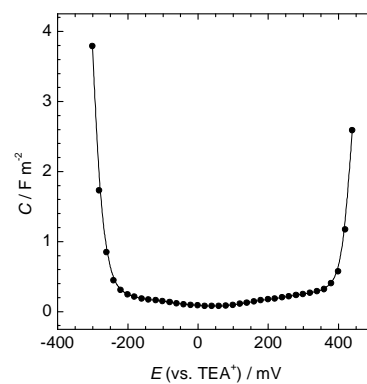
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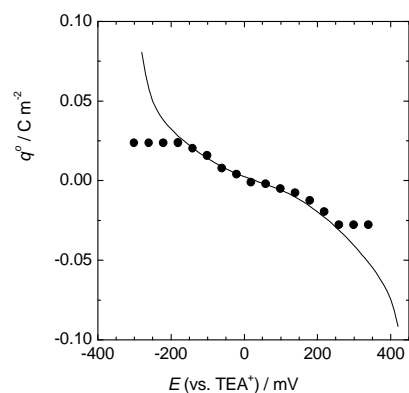
**Acknowledgements** This work was supported by Grant Agency of the Academy of Sciences of the Czech Republic (Grant no. IAA 4040407).



**Figure 1** Interfacial tension  $\gamma$  vs the potential  $E$  for the interface between 0.1 M LiCl in water and 5 mM BTTPATPBCl in DCE.



**Figure 2** Capacity curves for the interface between 0.1 M LiCl in water and 5 mM BTTPATPBCl in DCE.



**Figure 3** Surface charge density  $q^o$  on the organic side of the interface vs the potential  $E$  for the interface between 0.1 M LiCl in water and 5 mM BTTPATPBCl in DCE, as evaluated by a differentiation of the electrocapillary curves (points) or by an integration of the capacity curves (lines).