Experimental report

19/06/2023

Proposal:	**1-04-236**	**Council:**	4/2021
Title:	Structure of Ionic Liquids at the Electrode/Solution Interfaces		
Research area:	Chemistry		

This proposal is a new proposal

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Samples: Ionic Liquids - 1-alkyl-3-methylimidazolium bromide

Instrument	Requested days	Allocated days	From	To
FIGARO User-supplied	6	3	03/09/2021	06/09/2021

Abstract:

Electrochemical and thermal stability of ionic liquids make them perfect candidates as solvents and electrolytes for batteries, electrodeposition, lubrication and corrosion inhibition. Further development in these fields is tightly coupled with understanding solid/liquid interface phenomena.

Ionic liquids composed of imidazolium cations and bromide are reported to have corrosion inhibition effect on different metals through the formation of a protective layer on the metallic surface. Better corrosion inhibition is observed for longer alkyl chains. Increasing the alkyl chain length is also shown to be beneficial for Li-ion batteries and lubrication.

For the present proposal, MD simulations were performed in order to investigate IL layers formed at the metallic surface as a function of the electrical potential of the substrate. The corresponding expected reflectivity curves were calculated. As result of those simulations, we propose to use specular NR measurements to detect and characterize the layering of ionic liquids in proximity of a substrate. Our MD simulations indicate that a detectable difference in reflectivity is expected at Qz <0.3 Å-1

Report of experiment – Figaro 1-04-236

Structure of ionic liquids at the electrode/solution interface

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The purpose of this Figaro experiment was to understand the thickness and composition of ionic liquid layers (ILs) formed at the interface between an electrode and aqueous solutions of imidazolium based ILs. H/D contrast between the ILs and H2O/D2O was exploited to determine how imidazolium cation alkyl chain length influences the interfacial structure.

Materials/samples:

Five imidazolium bromide ionic liquids with different alkyl chain length (shortened as C_nC_1ImBr, where n = 4, 6, 8, 10, 12, Figure 1) with hydrogenated and deuterated side chains were synthesized.

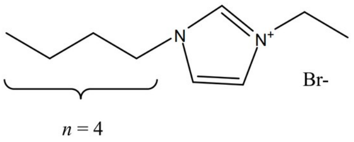

Figure 1. Structure of C_nC_1ImBr with n = 4

The concentrated aqueous solutions (~30 wt%) of hydrogenated ILs with D_2O and deuterated ILs with H_2O were prepared. The substrate was a polished single-crystal Si block n-doped (Phosphorous, specific resistivity 20 Ω cm, r.m.s. roughness ≤5 Å, dimensions: 8.0 × 5.0 × 1.5 cm^3, [100] oriented) obtained from Andrea Holm GmbH (Tann, Germany). About 2 ml of solutions was injected to the (electrochemical) cell built in-house.

Experiment and results

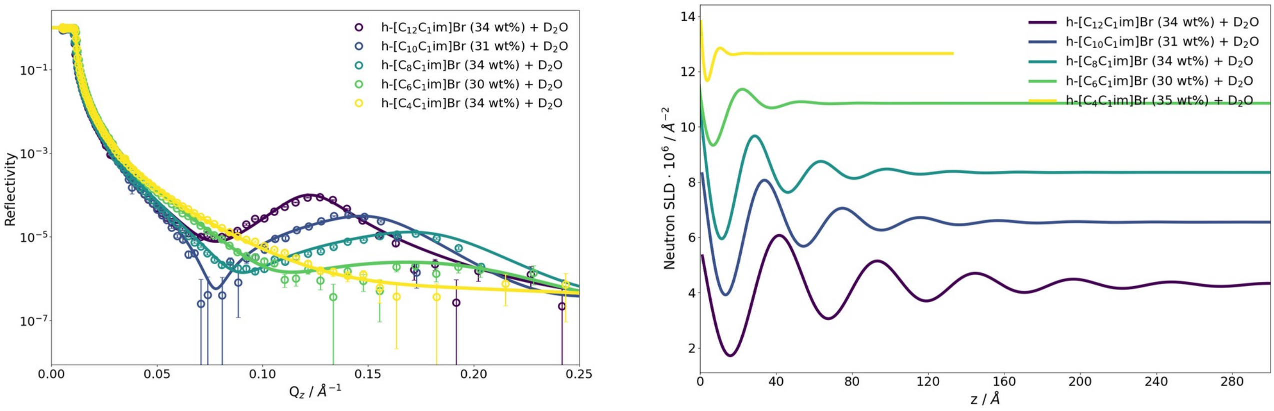

Figure 2. Left: Neutron reflectivity of five Si/(h-ILs + D_2O) interfaces at room temperature; Right: empirical SLD profiles used to fit the experimental NR.

Neutron reflectivity curves confirm ILs aggregation and layer forming at the interface as suggested by molecular dynamics simulations. However the structure of the interfacial layers and aggregates structure seem to be more complex than initially expected. The difference in layer thickness correlate well with the difference in the alkyl chain length. MD simulation data were not able to provide a direct fit and reasonable explanation. Empirical decaying oscillating functions fit the data but further investigation of the IL aggregates is needed.

Conclusions

The experiment confirms the existence of well defined layers at the interface between Si and IL solutions. A trend in interfacial layer thickness can be correlated with the alkyl chain length of the imidazolium cation, but the structure of IL aggregates is more complex then expected based on the available literature. This is extremely important discovery which requires performing new experiments (SANS, SAXS, TEM etc.). These experiments are needed to thoroughly understand aggregates/micellar structure at high IL concentrations, and fit the NR data. This Figaro experiment will provide a valuable contribution to understanding ILs at interfaces.