Experimental Report

02/01/2014

Proposal:	**9-10-1291**	**Council:**	10/2012

Title: Connecting the adsorbed structure of a model additive, hexylamine, with its exceptional anti-corrosion behaviour on nickel oxide.

This proposal is a new proposal

Researh Area: Chemistry

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Samples: Nickel oxide (on a nickel-coated silica substrate): NiO
Water: H2O
Deuterated water: D2O
Sodium nitrate: NaNO3
Nitric acid: HNO3
Sodium hydroxide: NaOH
Hexylamine: C6H15N

Instrument	**Req. Days**	**All. Days**	**From**	**To**
D17 He3 Spin Filter	3	3	06/07/2013	09/07/2013

Abstract:

This proposal seeks to characterise the adsorbed structure of a simple amine such as has been long used in additive systems for anti-corrosive applications at the nickel oxide / aqueous interface. With little work yet done towards understanding the structural and composition characteristics of adsorption on nickel oxide from solution, neutron reflection offers an unprecedented and unique opportunity to illuminate this molecular layer under different environmental conditions.

Characterising corrosion inhibitors for nickel – Experimental Report

D17 8th – 10th July 2013, Exp. No. 9-10-1291

Background and Aims

At low pH, the renowned resistance of nickel surfaces to corrosion is vastly reduced, and defects such as pitting develop. As nickel has uses in many applications that require exposure to an acidic environment (for example electrowinning), numerous additives have been proposed to protect the surface from these effects. Neutron reflectivity is an ideal way to improve our understanding of such systems, as it generates quantitative information about layer thicknesses and can thus be used to monitor any loss of the metal layer and growth of the oxide layer, as well as the adsorbed surfactant. It also yields the surface roughness, a key parameter in the study of corrosion.

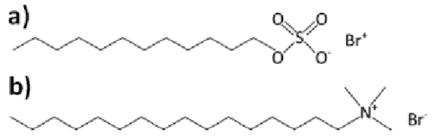

Figure 1. a) SDS – sodium dodecyl sulfate b) DoTAB – dodecyltrimethylammonium bromide

Two corrosion inhibitors that have been proposed to protect nickel in the electrowinning process at acidic pHs are sodium dodecyl sulfate (SDS)[1]-[3] and dodecyl trimethylammonium bromide (DoTAB)[4] (figure 1) Both surfactants are purported to act by adsorbing to the nickel surface, preventing diffusion of the corrosive species to the surface and also increasing wetting of the electrolyte so that the probability of pits developing is reduced. Zeta potential measurements have shown the nickel surface to be positively charged at pHs lower than 6.9, and so whilst it is understandable that the negatively-charged SDS strongly adsorbs, it seems surprising that DoTAB, a cationic surfactant, should have any affinity for the surface.

As Nickel has a high scattering length density (9.2×10^{-6} Å^{-1} for up-spin neutrons and 7.3×10^{-6} Å^{-1} for down-spin neutrons), by using either 100 % deuterated or protonated solvent, we could contrast-match to either the surface (and thus view the adsorbed layer) or to the surfactant (and thus view the effect on the surface) respectively. Hence, two sets of measurements were taken to give an overall picture of the inhibitor action.

Results

Both substrates were first characterised at neutral pH under D_2O and H_2O in order to determine the metal and oxide layer parameters.

SDS

A solution of 5 mM SDS (in 0.01 M $NaNO_3$) at pH 6 (neutral) was then added and a layer seen to adsorb to the surface as expected. Solutions of 5 mM SDS in both D_2O and H_2O at pHs 4 and 2 were measured, with little difference seen in the reflectivity profiles (figure 2), indicating that SDS was proficient in its protection of the nickel surface. Some roughening of the surface at pH 2 was evidenced in the heightened background and lessened distinction of the fringes.

The cell was then flushed through with pure H_2O at pH 2 (i.e. no further SDS) and measured over a 10 hour period, but still did not show any significant damage to the surface, although some nickel was lost, as seen in the increased fringe width for the H_2O measurements. However, it was clear that the SDS was bound strongly enough to the surface to continue protecting it even when flushed through with acidic solution over an extended time period.

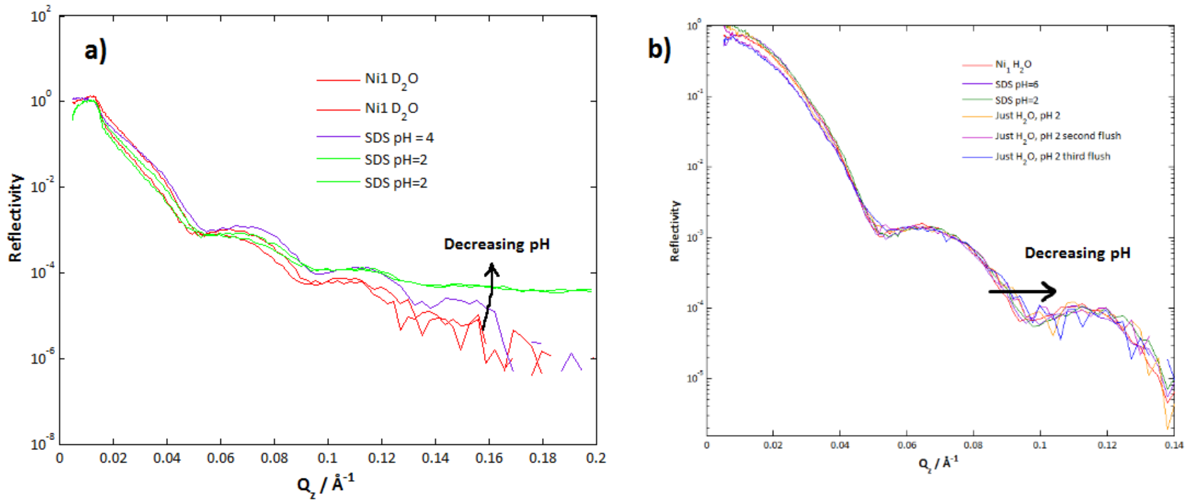

Figure 2:a) The measurements under D_2O (down-spin only shown) show an increasing roughness but that the layer thickness of the SDS does not change significantly. b) Under H_2O little effect is seen at the nickel surface even when flushed through at pH 2 (up-spin only shown).

DoTAB

The same experiments were repeated for the second nickel substrate but using 5 mM DoTAB solutions (in 0.01 M $NaNO_3$). For the H_2O measurements, some slight roughening of the surface was seen at pH 4, but then, in stark contrast to the SDS system, when the pH was reduced to 2, the DoTAB was seen to offer essentially no protection to the nickel surface - two back-to-back measurements were taken for 5 mM DoTAB at pH 2 in H_2O, with corrosion clearly increasing with time. The fringe spacing flattened out and magnetic splitting was gradually lost, indicating near complete loss of the entire nickel layer (figure 3).

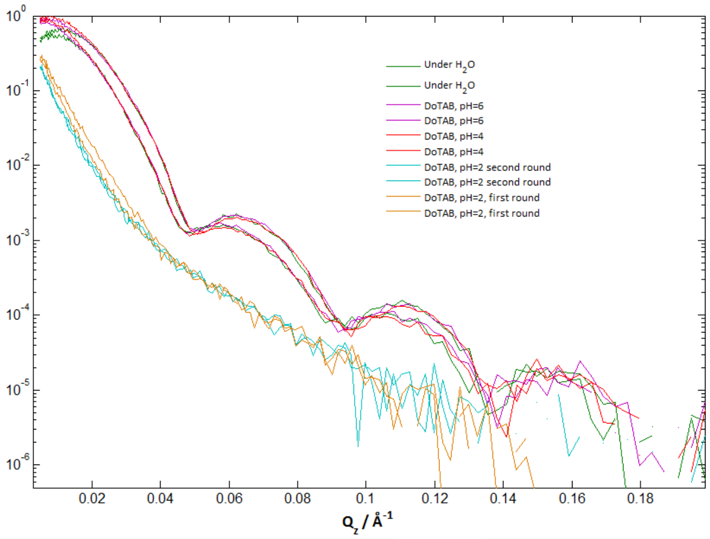

Figure 3: The measurements under H_2O for DoTAB. At pH 2 (orange and light blue) the nickel layer is almost entirely destroyed.

The D_2O data for DoTAB showed a significantly smaller, more diffuse layer of the surfactant is formed than for SDS. This layer remains intact at pH 4, though a decreased nickel layer thickness is seen. At pH 2, of course, it becomes impossible to discern the surfactant layer at all, so great is the roughness (figure 4).

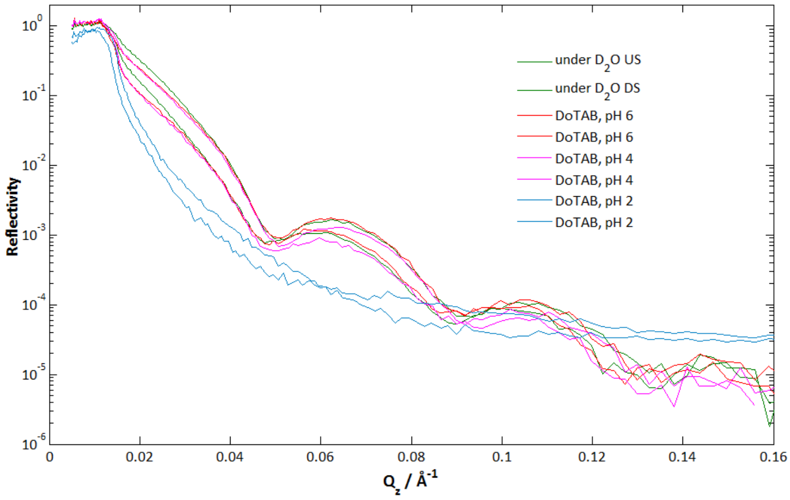

Figure 4: The measurements under D_2O for DoTAB. A small surfactant layer is seen (red) which remains intact at pH 4 (pink).

Offspecular

As well as the specular reflectivity profiles, offspecular data was monitored for both systems and clearly shows the difference between the two – an example of each is shown in figure 5.

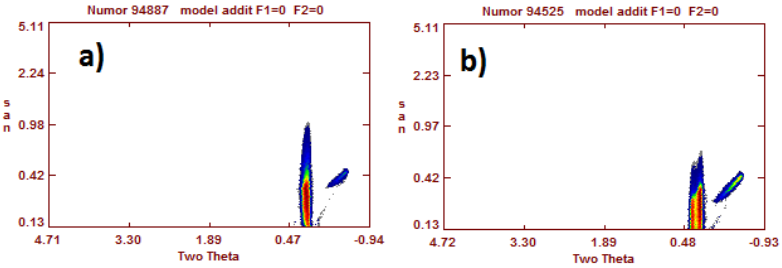

Figure 5: Offspecular plots for pH = 2 for a) SDS and b) DoTAB systems.

Both these plots were taken for the pH 2 systems, and the increased roughness is evident in the DoTAB system, whereas the plot for the SDS system shows little difference compared to the one for pH 6.

Conclusions

SDS protects the surface effectively at low pHs, and clearly binds strongly to the surface as it is not washed off even when flushed through with just pH 2 water and no further inhibitor. As was thought, and in contrast to the cited literature, DoTAB is considerably less effective at protecting the nickel surface, which is essentially completely destroyed at low pH.

Use of contrast matching and offspecular data meant that a complete picture could be built up of these systems. This experiment shows the great potential for neutron scattering in studies of corrosion and its inhibition.

References

[1] Jing, L.; Yang, Q.; Zhang, Z. *Trans. Nonferrous Met. Soc. China*, **2010**, *20*, s97
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[3] Mohanty, U. S.; Tripathy, B. C.; Das, S. C.; Sing, P.; Misra, V. N. *Hydrometallurgy*, **2009**, *100*, 60
[4] Chen, Y. C.; Kuo, S. L.; Lee, J. L.; Ke, S. T.; Wong, C. H.; Ger, M. D. *Key Engineering Materials*, **2008**, *364-366*, 346