COMMUNICATION

ChemComm
www.rsc.org/chemcomm

# Atomic force microscopy studies of the KF (100) surface: formation of water-rich surface phases in moist *N,N*-dimethylformamide

**Gavin Macfie, Shelley J. Wilkins and Richard G. Compton***
*Physical and Theoretical Chemistry Laboratory, Oxford University, Oxford, UK OX1 3QZ.*
*E-mail: richard.compton@chemistry.ox.ac.uk*

*Received (in Cambridge, UK) 20th August 2001, Accepted 23rd November 2001*
*First published as an Advance Article on the web 21st December 2001*

**A water rich surface phase is observed in the system KF-DMF-$H_2O$ by atomic force microscopy; the effects on surface morphology and likely implications for halogen exchange reactions using KF are discussed.**

It has been observed that traces of water may enhance the rate of halogen exchange (Halex) reactions using solid KF.[1] In the absence or presence of tetramethyl ammonium chloride as phase transfer catalyst, the reaction of 3,4-dichloronitrobenzene with KF to form 3-fluoro-4-chloronitrobenzene in dimethyl sulfoxide does not proceed. Traces of water (0.2–0.3% w/w) are essential for effective transport of fluoride from the KF surface into the bulk organic phase.[2] A similar effect has been noted in the fluorination of aliphatic chlorides.[3]

More generally, it is well known that water plays a key role in determining the observed kinetics in reactions operating under conditions of phase transfer catalysis. The reaction of 1,4-dichlorobutane with solid sodium formate in chlorobenzene solvent using tetra-*n*-butylamonium hydrogen sulfate as phase transfer catalyst does not proceed in completely anhydrous conditions. The addition of trace amounts of water caused the rate to increase rapidly.[4] A maximum rate was observed where the solid salt contained 0.2% $H_2O$ by weight. A similar effect has been noted in cyanide displacement reactions of 1-halooctanes.[5]

It has been proposed that in the quaternary ammonium catalysed solid–liquid esterification of alkyl chlorides by alkali that the initial rate determining step is dissolution of formate into a thin liquid film surrounding the solid particle, followed by anion exchange with the quaternary ammonium salt in the organic phase.[6] Such catalysis has been termed ‘thin-layer phase-transfer-catalysis’.

Single crystals of several alkali halides have been imaged in air by AFM,[7] however KF was not included in this study. Adsorption of water from air onto the NaCl (001) surface has been studied by Shindo *et al.*[8,9] Spontaneous movements of monatomic steps were observed. Furthermore the growth of microcrystalline structures or ‘hillocks’ was observed. It was proposed that molecular water adsorption formed first a 2D gas state, second small islands of 2D liquid, third a network of 2D liquid and fourth islands of 3D water. The formation of the 3D water phase greatly enhanced ion mobility and hence ‘hillock’ formation. More recent work using IR spectroscopy at both cryogenic and ambient temperatures[10] has shown formation of a reversibly adsorbed layer at surface coverages of less than two monolayer thicknesses. Under ambient conditions higher coverages lead to dissolution of the solid surface and the formation of an ion-containing adlayer.

It is not clear whether such adsorbates or thin layers are formed on the surface of KF (100) and whether the formation of such phases may be responsible for the observed effect of water in solid–liquid Halex reactions using KF as a substrate. This prompted us to undertake an atomic force microscopy study of the uptake of water onto the KF (100) surface in dimethylformamide (DMF).

A Topometrix (Santa Barbara, CA) TMX 2010 Discoverer atomic force microscope, employing pyramidal silicon nitride tips (Topometrix AFM probe 1520) was used. Images were obtained with resolution of 200 × 200 data points per image and with a scanning rate of 10 Hz. For the *in situ* experiments a commercial Topometrix liquid cell was used, with modifications as described previously.[11] A gravity feed with adjustable stopcock allowed control of solution flow rate through the fluid cell in the range between 0.008 and 0.02 $cm^3 s^{-1}$.

The KF single crystals were supplied by H. Gallagher, Optical Materials Research Centre, University of Strathclyde, Glasgow. They were supplied immersed in silicone oil in order to prevent the deliquescent crystals from adsorbing water from the atmosphere and undergoing surface dissolution. Accordingly stringent efforts were made to isolate the samples from the atmosphere. A dry environment was provided by a two hand Atmosbag (Aldrich Techware) into which all items required to mount the crystals were placed. The bag was filled with argon and a small beaker of spray-dried KF (Aldrich) was used to strip the atmosphere of any residual traces of moisture. The samples were then removed from their protective silicone oil environment with tweezers and carefully wiped on a lens cleaning tissue to remove any residue of oil. A small quantity of a silicone adhesive compound (Dow Corning Q5-8401) was placed on an AFM sample holder and the sample placed on top.

After pressing gently into position with a lens cleaning tissue the mounted sample was transferred to a dessicater. The dessicator was then removed from the atmosbag and placed in an oven at 100 °C for 30 min in order to cure the adhesive. The sample was then returned to the atmosbag so that it could be mounted into the AFM flow cell. Dimethylformamide (puriss., $H_2O \leqslant 0.01\%$) was obtained from Fluka.

The samples were imaged first in static DMF. DMF was then flowed over the samples. Finally a solution of 2% w/w $H_2O$ in DMF was flowed over the sample. Images were acquired throughout in order that the introduction of water to the system was fully observed.

The (100) surface imaged in DMF appears to be relatively flat with a series of macrosteps with a few hillock growths on the surface as shown in Fig. 1(a). The steps are regular and typically 200 nm in height. The surface between the steps is featureless around the few growths. The growths are in a random orientation and location and are typically *ca.* 2 μm wide and 3 μm in height. In the flowing DMF solution there is minor change to the surface morphology however no net dissolution is observed. Hillocks on the surface are probably formed during sample preparation. The (100) plane is particularly hygroscopic and readily absorbs water if handled outside the argon atmosphere. Such water absorption could lead to the formation of a concentrated aqueous KF solution from which reprecipitation could subsequently occur.

As water is introduced the flat surface begins to fill out with irregular growths which surround a bunch of macrosteps typically 100–200 nm in height as shown in Fig. 1(b). These growths show irregular morphology, however, the steps occur in parallel and have kinks at an angle of 90°.

The image quality significantly deteriorates when the tip is retracted from the surface and then put in contact in a fresh imaging area. This suggests the surface layer has become soft and the tip consequently experiences difficulties in raster

DOI: 10.1039/b107466k

This journal is © The Royal Society of Chemistry 2002

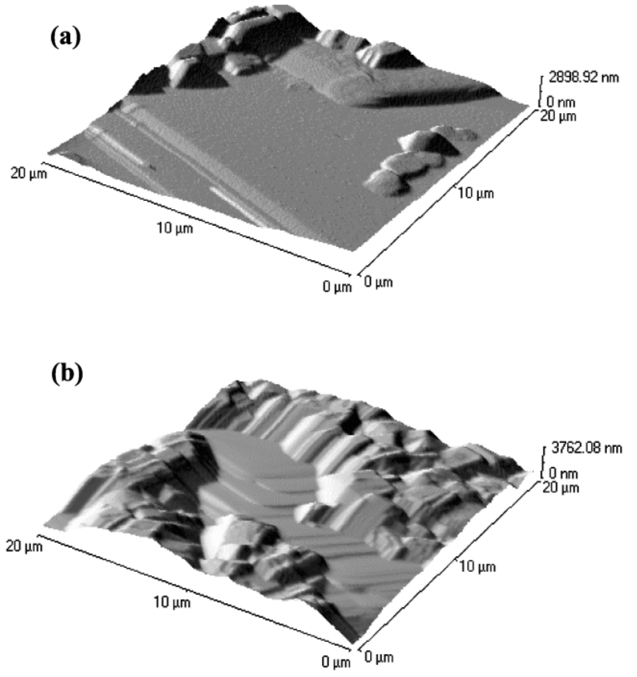

**Fig. 1** KF (100) surface imaged in DMF (a) and DMF containing 2% $H_2O$ w/w after 4 min of exposure (b).

scanning as the probe adheres to the surface. The morphology of the surface was monitored continuously over a 5 h period during exposure of the crystal to 2% w/w water in DMF. Fig. 2(a)–(c) show a sequence in time of the surface.

The surface remains soft as evidenced by the occasional poor quality of image recorded. In Fig. 2(a) recorded 8.5 min after exposure to the water solution the surface is rough with hillocks and macrosteps. A large step of 3500 nm can be seen on the lower left area of the image. The plane below the step consists of a bunch of macrosteps with few growths. The surface above the step is very rough with a series of hillocks which appear to have a regular shape and orientation with respect to each other.

The surface flattens out in time as the water–DMF solution is flowed over the crystal, the hillocks dissolve and re-precipitate filling in the voids and gaps in the surface. Fig. 2(b) shows the surface after 85 min. The step in the lower left of the image has been filled by small growths and only a small portion of the lower plane below the step is now visible. The surface above the step has become more even than in Fig. 2(a). In Fig. 2(c) recorded after 162 min a macrostep is no longer evident in the lower left of the image and the surface has flattened further. In order to confirm that the observed smoothing is the consequence of dissolution and reprecipitation, rather than a tip/surface interaction, the tip was translated to a different area where a similar morphology was observed.

Water absorption onto the KF (100) surface leads to the formation of a concentrated aqueous KF solution from which reprecipitation of KF occurs. We speculate that the formation of this water-rich surface phase may be essential for effective anion transfer to the organic phase in Halex reactions.

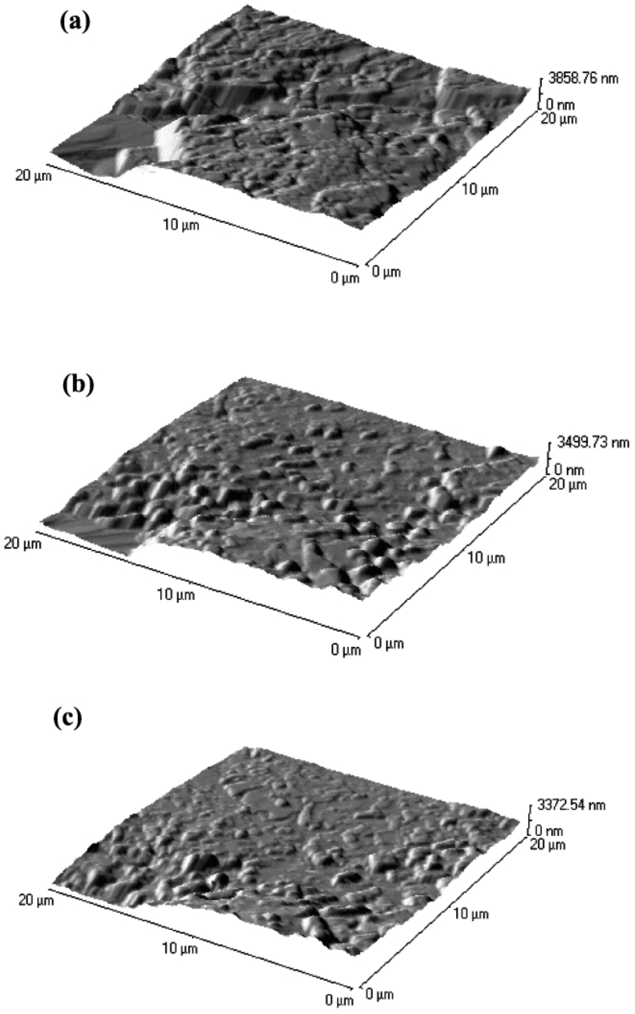

**Fig. 2** KF (100) surface imaged in DMF–2% $H_2O$ 8.5 min (a), 85 min (b) and 162 min (c) after introduction of water.

G. M. thanks EPSRC and Avecia, and S. J. W. thanks BBRSC and GlaxoSmithKline for CASE studentships.

## Notes and references

1 G. L. Cantrell, *US Pat. 4642398*, 1987.
2 Y. Sasson, S. Negussie, M. Royz and N. Mushkin, *Chem. Commun.*, 1996, 297.
3 S. Dermeik and Y. Sasson, *J. Org. Chem.*, 1985, **50**, 879.
4 H. A. Zahalka and Y. Sasson, *Chem. Commun.*, 1984, 1652.
5 C. M. Starks and R. M. Owens, *J. Am. Chem. Soc.*, 1973, **95**, 3613.
6 O. Arad and Y. Sasson, *J. Am. Chem. Soc.*, 1988, **110**, 185.
7 A. L. Shluger, R. M. Wilson and R. T. Williams, *Phys. Rev. B: Condens. Matter*, 1994, **49**,4915.
8 H. Shindo, M. Ohashi, O. Tateishi and A. Seo, *J. Chem. Soc.*, *Faraday Trans.*, 1997, **93**, 1169.
9 H. Shindo, M. Ohashi, K. Baba and A. Seo, *Surf. Sci.*, 1996, **111**, 357.
10 S. J. Peters and G. E. Ewing, *J. Phys. Chem. B*, 1997, **101**, 10880.
11 B. A. Coles, R. G. Compton, J. Booth, Q. Hong and G. H. W. Sanders, *Chem. Commun.*, 1997, 619.