The tribological properties of monolayer KCl films on iron in ultrahigh vacuum: Modeling the extreme-pressure lubricating interface

F. Gao[a], G. Wu[a], D. Stacchiola[a], M. Kaltchev[a], P.V. Kotvis[b], and W.T. Tysoe[a]*

[a]*Department of Chemistry and Laboratory for Surface Studies, University of Wisconsin-Milwaukee, Milwaukee, WI 53211, USA*
[b]*Benz Oil, Inc., 2724 Hampton Avenue, Milwaukee, WI 53209, USA*

The friction coefficients of thin KCl films deposited onto clean iron in ultrahigh vacuum are measured using a tungsten carbide tip. A rapid decrease is found in the friction coefficient from ~ 2 for clean iron to 0.27 ± 0.03 after the deposition of ~ 40 Å of KCl. Based on previous contact resistance measurements, this was proposed to be due to the completion of the first layer of KCl. The first-layer KCl coverage was measured by adsorbing deuterium onto an iron surface partially covered by KCl, where deuterium selectively adsorbs onto the iron. This revealed that the first monolayer is complete after the deposition of ~ 40 Å of KCl and that the first-layer KCl film coverage $\Theta_{KCl}^{(1)}$ is given by $\Theta_{KCl}^{(1)} = 1 - \exp(-0.39 \pm 0.02t)$, where t is the film thickness. XPS data suggest that heating a KCl film to ~ 550 K causes it to wet the surface. This leads to decreases in the friction coefficients for thin KCl films in accord with the idea that friction is reduced by the first monolayer of KCl on iron. Temperature-programmed desorption data indicate that KCl in the first monolayer is ~ 5 kJ/mol more stable than the multilayer consistent with the wetting behavior. Finally, the kinetic data are analyzed to suggest that the first-layer film is ~ 2.6 Å thick.

KEY WORDS: KCl, iron, Auger spectroscopy, friction coefficient, deuterium adsorption, temperature-programmed desorption, X-ray photoelectron spectroscopy, extreme-pressure lubrication, ultrahigh vacuum tribometer

1. Introduction

Chlorinated hydrocarbons thermally decompose during extreme-pressure lubrication at the hot, lubricated interface to deposit a film that consists of $FeCl_2$ and carbon [1,2], where interfacial temperatures in excess of 1000 K can be attained [3]. The resulting interfacial coefficient of friction, measured using a pin and v-block apparatus, depended on the chlorinated hydrocarbon that was used as an additive, with films incorporating larger amounts of carbon apparently having larger coefficients. Raman spectroscopy revealed that the carbon was present, in these cases, as small (~ 50 Å) diameter particles [4]. Films that resemble those formed under tribological conditions can also be synthesized in ultrahigh vacuum, where a constant-flux beam of the chlorinated hydrocarbon is incident onto a clean, heated iron foil. In this case, the activation energies for reactions in ultrahigh vacuum, and the nature of the resulting films, are identical to those measured for reactions at high pressures [5–7]. The tribological properties of thin KCl films deposited onto clean iron in ultrahigh vacuum are studied in order to ultimately understand the relationship between the structure of these reactively formed films and their tribological properties. KCl was selected since it has a

relatively low hardness (H(Knoop) = 7.2 [110] and 9.3 [100]) and so should form a relatively low-friction coefficient film, and also since it will not react with iron.

It has been found previously that a very thin (~ 40 Å) film of KCl on an iron foil reduced the friction coefficient, measured in ultrahigh vacuum using a tungsten carbide pin, from ~ 2 for the clean surface to about 0.27 [8]. It was suggested, based on the observation that the contact resistance measured during rubbing increased at the same film thickness, that the reduction in friction coefficient to ~ 0.27 coincided with the complete coverage of the metal surface with KCl. This paper further explores this idea, where the first-layer KCl coverage is measured by titrating the metal using deuterium. This selectively adsorbs on iron, while it does not dissociatively adsorb on KCl [9,10], thus providing a straightforward method for determining when the surface has been completely covered by KCl.

2. Experimental

Experiments were carried out in two vacuum chambers, the first being an 8″-diameter ultrahigh vacuum chamber operating at a base pressure of 5×10^{-10} Torr that has been described in detail elsewhere [8]. This contained a vacuum tribometer for frictional and contact resistance measurements, an ion-bombardment source for sample cleaning, a quadrupole mass spectrometer for background gas analysis and leak checking,

* To whom correspondence should be addressed. e-mail: wtt@uwm.edu

and a single-pass, cylindrical-mirror analyzer for surface analysis using Auger spectroscopy. Frictional measurements were made using a tungsten carbide pin cut from a ball bearing (diameter 1.27 cm, Knoop hardness = 23.5 GPa). The height distribution of the tip, measured using AFM, was relatively Gaussian, with a width at half height of ~ 1500 Å [8]. Friction coefficients were measured using an applied load of 0.29 N at a sliding speed of 4 mm/s.

Temperature-programmed desorption experiments were carried out in a second chamber that has been described in detail elsewhere [11], which operated at a base pressure of 1×10^{-10} Torr following bakeout. This was pumped by means of a diffusion pump and also contained a single-pass, cylindrical-mirror analyzer and ion-bombardment source. The chamber also incorporated a Dycor quadrupole mass spectrometer which was located close to, and in line of site of, the sample, which was mounted onto a carousel geometry manipulator for temperature-programmed desorption studies.

An iron foil (0.1 mm thick for tribological experiments and 0.5 mm thick for temperature-programmed desorption studies, Johnson–Matthey, 99.99% purity, Knoop hardness $= 6.9 \pm 0.1 \times 10^8$ Pa) was mounted onto a vacuum-compatible manipulator allowing the sample to be moved in the x, y and z directions and rotated about its axis. The sample could be resistively heated and the temperature was monitored using a thermocouple spot-welded to the back of the sample.

The potassium chloride evaporation source was constructed based on a literature design [8,12] in which KCl (Aldrich, 99.9% purity) was placed in a small alumina tube (diameter 0.5 mm, 1 cm long) and wrapped by a tantalum heating wire.

The KCl film thickness was monitored using X-ray photoelectron spectroscopy in another chamber that has been described in detail elsewhere [13], or *in situ* using a quartz microbalance (Sigma Instruments, Model SQM-160).

3. Results

Figure 1 shows the friction coefficient, collected using a tungsten carbide tribopin, for a thin film of KCl deposited onto a clean iron foil in ultrahigh vacuum plotted versus the film thickness. The tribopin was cleaned by heating *in vacuo* using electron bombardment between each experiment. The different symbols in this plot (●, ■ and ▲) are for data from different experiments emphasizing the reproducibility of the friction coefficient measurements. This reveals that the initially high friction for the clean surface decreases to a value of 0.27 ± 0.03 after the deposition of ~ 40 Å of KCl (where film thicknesses are measured using the quartz microbalance). Figure 2 compares the film thicknesses as a function of deposition time measured using the micro-
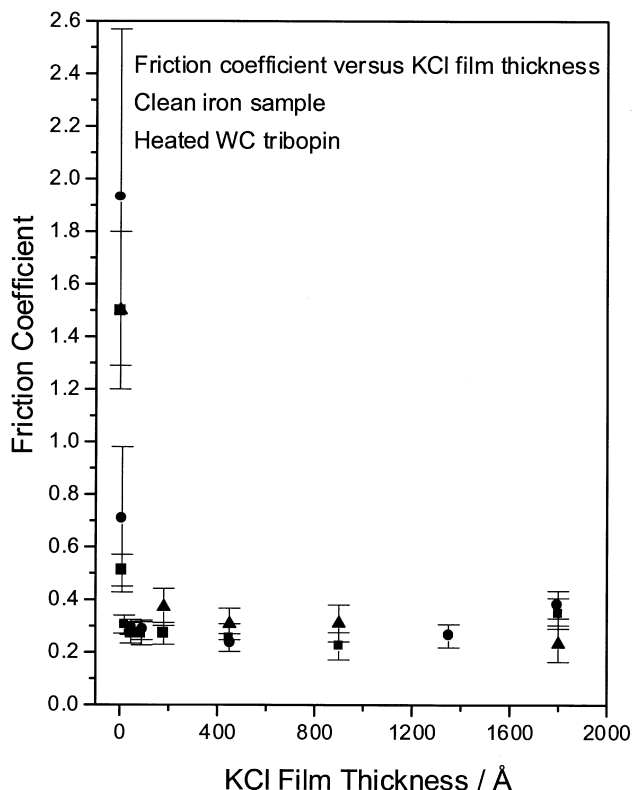

Figure 1. Plot of friction coefficient versus film thickness for KCl deposited onto clean iron at a sample temperature of 300 K.
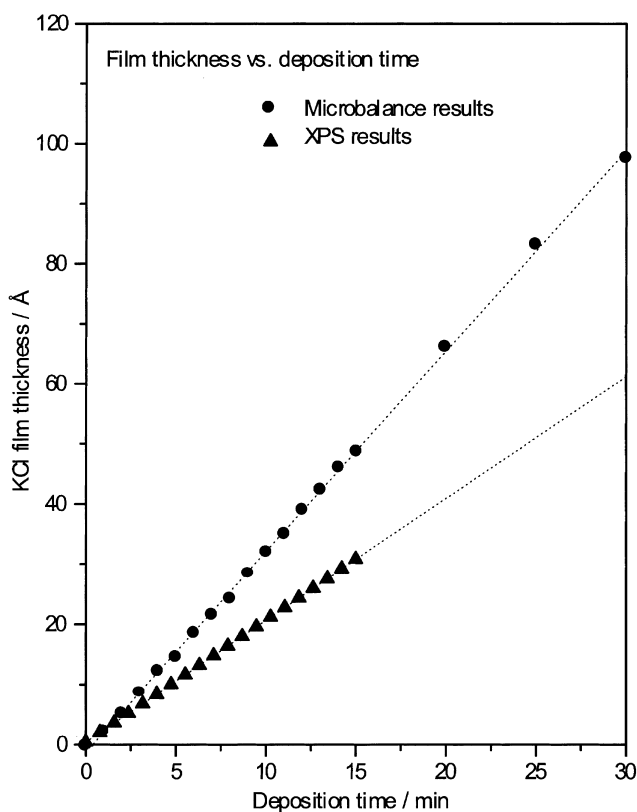

Figure 2. Plot of KCl film thickness versus deposition time, measured using X-ray photoelectron spectroscopy, using electron escape depths, assuming the formation of a uniform film (▲), and that using the quartz microbalance (●).

balance (●) with those calculated from the X-ray photoelectron spectrum (XPS) (▲) using electron escape depths [14] and assuming that the KCl is deposited as a uniform layer. It is clear that XPS substantially underestimates the KCl coverage. This is proposed to be due to the immobility of KCl deposited on the iron surface held at 300 K, so that any KCl that impinges onto a portion of the surface that is already covered by KCl is not sufficiently mobile to move to the bare metal, thus growing second and subsequent layers before the first layer has saturated. If this is the case, heating the surface should increase the mobility of the KCl and, if this adsorbs more strongly onto the metal, cause the KCl to wet the surface. Annealing should result in an apparent increase in the film thickness measured using XPS. The results of this experiment are displayed in figure 3, where the apparent film thickness increases as the sample is heated to 550 K, but then subsequently decreases when the sample is heated to 600 or 650 K. The increase on heating to 550 K is ascribed to wetting the surface and the formation of a more uniform film. The subsequent decrease at higher temperatures is due to KCl desorption.

This is confirmed by the temperature-programmed desorption data for KCl (detected at 35 amu, Cl) from a clean iron surface displayed in figure 4. Desorption spectra collected at 39 (K) and 74 (KCl) amu exactly mirror these profiles. This shows the appearance of a broad feature at a film thickness of 2 Å centered at ∼ 638 K. As the film thickness increases to 6 Å, a peak appears at lower temperatures (∼ 618 K), which continues to grow with increasing film thickness. This temperature coincides with the loss of KCl found in X-
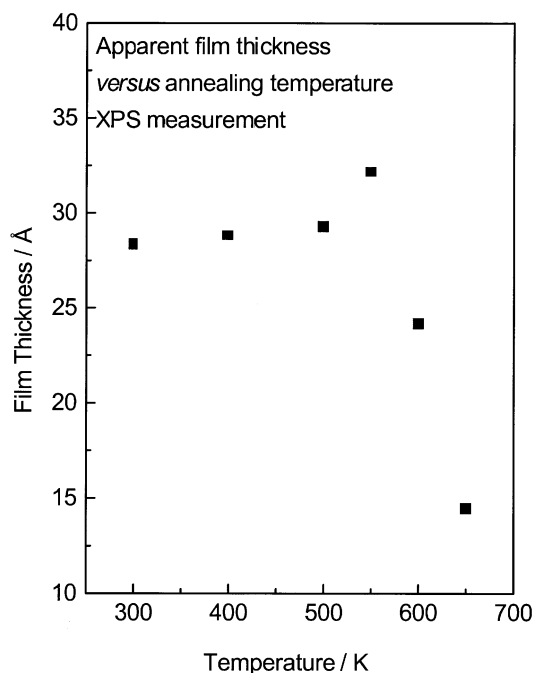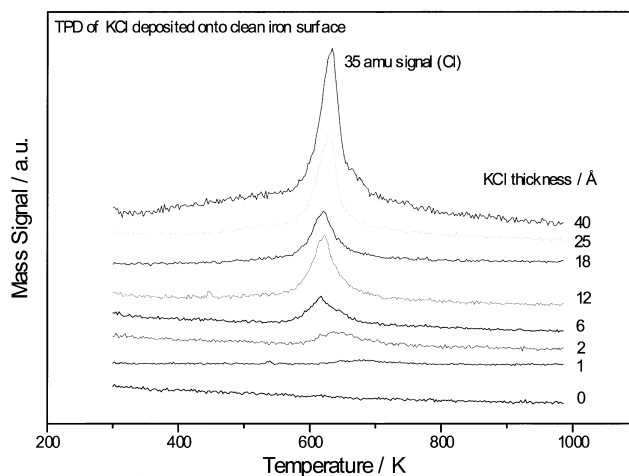

Figure 4. Temperature-programmed desorption spectra of KCl deposited on clean iron at 300 K as a function of film thickness. Film thicknesses are marked adjacent to the corresponding spectrum.

ray photoelectron spectroscopy (figure 3) and confirms that this is due to KCl desorption from the surface. The feature at 638 K, from a KCl film of ∼ 2 Å thickness, is assigned to desorption of KCl from the metal surface itself, and the appearance of the feature at ∼ 618 K, which continues to grow with the addition of further KCl, is assigned to desorption from second and subsequent KCl layers.

In order to gauge the proportion of bare metal in the presence of a film of KCl, the surface was exposed to 20 L (1 L = 1 × 10⁻⁶ Torr.s) of deuterium after the deposition of KCl films of various thickness. Deuterium was selected for this purpose since the detected mass for D_2 (4 amu) is not present in the background spectrum of the ultrahigh vacuum chamber, and it quantitatively desorbs from the surface at ∼ 400 K [9,10] so that the structure of the KCl film is not likely to be severely disturbed during the D_2 desorption sweep. Finally, and perhaps most important, D_2 absorbs selectively on the clean iron surface, but not on KCl [9,10]. Thus, the amount of D_2 desorbing from the surface, measured from the area under the desorption profile, is a direct measure of the relative coverage of the bare metal surface, Θ_{Fe} [15]. If the relative first-layer coverage of the KCl on the iron is given by $\Theta_{KCl}^{(1)}$, then

$$\Theta_{KCl}^{(1)} = 1 - \Theta_{Fe} \qquad (1)$$

and equation (1) allows the coverage of the first KCl monolayer on the iron surface to be measured directly. $\Theta_{KCl}^{(1)}$ (○) is plotted versus film thickness in figure 5, and compared with the value measured from the frictional data (____). This comparison will be discussed in greater detail below.

Finally, shown in figure 6 is the effect on the friction coefficient of annealing a KCl film, deposited on clean iron at 300 K, to 550 K for 30 s, and then cooling to
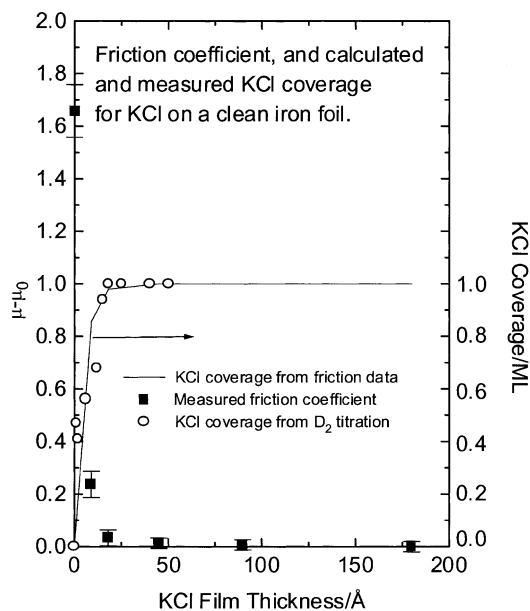

Figure 3. Plot of film thickness measured using X-ray photoelectron spectroscopy after annealing the surface to various temperatures.

Figure 5. Plot of $\mu - \mu_0$ *versus* film thickness (■) along with the first-layer KCl coverage predicted from these measurements (——) compared with values measured by titrating the bare surface using deuterium (○).

Figure 6. Plot of friction coefficient *versus* film thickness following deposition at 300 K (■), and after annealing at 550 K for 30 s (●).

300 K (●). Shown for comparison are the friction coefficients measured prior to annealing (■). Clearly, annealing causes a significant decrease in the friction coefficient of the film.

4. Discussion

The data of figure 1 demonstrate that a relatively small thickness of KCl deposited onto iron causes the friction coefficient to decrease substantially. The data of figure 2 suggest that the KCl film does not grow uniformly, but that the growth of the second and subsequent layers commences before the first layer is complete. This notion is corroborated by the data of figure 3, which implies that annealing the KCl film to ~550 K wets the surface, providing a more uniform film, leading to an apparently larger film thickness when measured using the electron escape depths. The decrease in film thickness at higher temperatures (≥ 600 K) is due to KCl desorbing from the surface and is in accord with the multilayer desorption state detected in temperature-programmed desorption (figure 4). In addition, another feature is detected at ~638 K for a film thickness of ~2 Å and is assigned to desorption of KCl adsorbed directly onto the metal surface. The activation energy for desorption from this state can be estimated using a Redhead analysis [15], assuming a preexponential factor of $1 \times 10^{13} \mathrm{s}^{-1}$ and a heating rate of 10 K/s, to be ~162 kJ/mol. A similar analysis for the multilayer feature at ~618 K leads to a value of 157 kJ/mol, so that KCl adsorbed on the metal surface is approximately
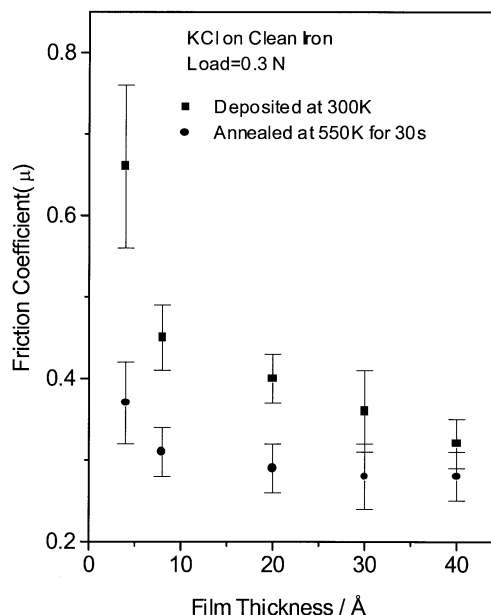
5 kJ/mol more stable than when adsorbed as a multilayer. This is in accord with the observation that heating a KCl film wets the metal surface.

It has been proposed previously that the initial drop in friction coefficient coincides with the completion of the first monolayer [8]. Confirmation of this idea came from a measurement of the contact resistance, which maintained a low value for film thicknesses below ~40 Å and started to rise for thicker films. This was taken to be due to the presence of some tip-metal contact prior to the completion of the first layer. The contact resistance did not immediately rise to large values due to some breakthrough of the thin film, but nevertheless provided some evidence that the formation of the first monolayer coincided with the minimum friction coefficient of 0.27 ± 0.03. It was assumed that the friction coefficient at intermediate coverages was proportional to the relative coverages of the first-layer KCl film and the bare iron surface so that, writing the first-layer coverage of KCl as $\Theta_{\mathrm{KCl}}^{(1)}$ where $0 \Theta_{\mathrm{KCl}}^{(1)} < 1$,

$$\mu = \mu_{\mathrm{KCl}}^0 \Theta_{\mathrm{KCl}}^{(1)} + \mu_{\mathrm{Fe}}^0 (1 - \Theta_{\mathrm{KCl}}^{(1)}), \qquad (2)$$

where μ_{KCl}^0 is the friction coefficient of the KCl monolayer and μ_{Fe}^0 is the friction coefficient of clean iron. Assuming that the rate of KCl adsorption onto the bare metal in the first layer is proportional to the area of the exposed metal surface yields a rate of adsorption proportional to $1 - \Theta_{\mathrm{KCl}}^{(1)}$, and is *via* Langmuir kinetics [16], where integration gives

$$\Theta_{\mathrm{KCl}}^{(1)} = 1 - \mathrm{e}^{-\alpha t}, \qquad (3)$$

where α is a constant. Substituting equation (3) into equation (2) yields:

$$\mu - \mu_{KCl}^0 = (\mu_{Fe}^0 - \mu_{KCl}^0)e^{-\alpha t}. \tag{4}$$

The data of figure 2 show that the film thickness is proportional to the deposition time, so that equation (4) represents the theoretical change in friction coefficient as a function of film thickness. The data of figure 1 are replotted in figure 5 as $\mu - \mu_{KCl}^0$ *versus* film thickness t (■), where μ_{KCl}^0 is taken to be 0.27 ± 0.03. In cases where more than one measurement of the friction coefficient was made for the same KCl film thickness in different runs, these values have been averaged and the resulting error bars included on the figure. A best fit to the function in equation (4) yields a value of $\alpha = 0.39 \pm 0.02 \, \text{Å}^{-1}$. The corresponding KCl coverage in the first layer from these tribological data is given by equation (3) and shown plotted as a solid line on this graph. This reveals that the predicted first-layer film thickness saturates when a total film thickness of $\sim 40 \, \text{Å}$ has been deposited. It should be emphasized that this just represents the coverage of the first layer, and that the second and subsequent layers are being formed at the same time. In order to directly measure the coverage of the first layer, we have taken advantage of the fact that hydrogen adsorbs strongly on bare metal surfaces, but not on KCl, and desorbs reversibly at $\sim 400 \, \text{K}$ [9,10]. Since the background gas in the ultrahigh vacuum chamber includes a small amount of hydrogen, the experiment was carried out using deuterium to allow it to be easily distinguished from background gases, while exhibiting identical chemistry. A clean iron surface was saturated with D_2 (using a 20-L exposure) [9,10] and a temperature-programmed desorption spectrum collected at a heating rate of $10 \, \text{K/s}$. Since the area under the desorption profile is proportional to coverage, the area under the clean-surface spectrum (collected at 4 amu) was used to normalize the saturation deuterium coverage on the clean surface to unity [15]. Various thicknesses of KCl were then deposited onto the surface. In this case, great care was taken to carefully outgas the dosing source prior to deposition to ensure that the iron surface was not blocked by gasses evolving from the hot source. The KCl-covered surface was then exposed to 20 L of D_2 and the 4-amu temperature-programmed desorption spectrum collected. The area under the desorption feature was normalized to that of the clean surface to yield the relative coverage of bare iron. Equation (1) allows the corresponding relative KCl coverage to be calculated directly as a function of KCl film thickness and the results plotted in figure 5 (○). Clearly the agreement between these measurements and the KCl coverage predicted from the tribological data (——) is extremely good. Thus, direct measurements of the first-layer KCl coverage are in accord with the

contact resistance measurements, indicating that the friction coefficient is well represented by equation (2).

These results reveal that the first monolayer is essentially complete when a film of $\sim 40 \, \text{Å}$ has been deposited, and that bare surface is present for lower coverages while, simultaneously, the second and subsequent layer growth has started. The data of figure 2 suggest that annealing the surface causes the KCl to wet the iron in accord with the temperature-programmed desorption data of figure 4, which show that KCl is more strongly bound to the metal surface than when it forms a multilayer. This implies that if a film less than $\sim 40 \, \text{Å}$ thick is annealed, it should wet the surface providing a more complete first monolayer with a concomitant reduction in friction coefficient. The results of these experiments are displayed in figure 6. The friction coefficient measured for the film following deposition at 300 K (■) decreases with film thickness and essentially reproduces the data shown in figure 1. However, when this film is annealed at 550 K for 30 s, below the KCl desorption temperature (figure 4), where XPS data suggest that the film becomes mobile (figure 3), the friction coefficient is significantly reduced (●). This result is in accord with the conjecture above and provides additional evidence for the importance of the first monolayer in reducing friction. It has been known for some time from experiments in ultrahigh vacuum that a chemisorbed overlayer on a metal surface can reduce its friction coefficient [17]. These results suggest that the first monolayer plays a similarly central role in reducing friction in the presence of thin films.

The kinetic data can be used to estimate the thickness of the first-layer KCl film. Equation (3) gives the first-layer KCl coverage (designated $\Theta_{KCl}^{(1)}$), so that the rate of change of coverage with film thickness for the first KCl layer is given by

$$\frac{d\Theta_{KCl}^{(1)}}{dt} = \alpha(1 - \Theta_{KCl}^{(1)}) \tag{5}$$

and is proportional to relative coverage of the bare metal. If the coverage of the second layer is designated $\Theta_{KCl}^{(2)}$, and if it is assumed that the adsorption kinetics into the second layer are identical to those into the first, the change in coverage of the second layer with thickness is proportional to the coverage of the bare surface in the first layer so that

$$\frac{d\Theta_{KCl}^{(2)}}{dt} = \alpha(\Theta_{KCl}^{(1)} - \Theta_{KCl}^{(2)}). \tag{6}$$

Analogously, adsorption into the n-th layer is given by

$$\frac{d\Theta_{KCl}^{(n)}}{dt} = \alpha(\Theta_{KCl}^{(n-1)} - \Theta_{KCl}^{(n)}). \tag{7}$$

The total rate of change of coverage, $d\Theta_{KCl}/dt$, with thickness is given by

$$\frac{d\Theta_{KCl}}{dt} = \sum_{n=1}^{\infty} \frac{d\Theta_{KCl}^{(n)}}{dt}. \qquad (8)$$

If the thickness of one layer is designated the $t_0\,\text{Å}/$ monolayer, then

$$t_0 = 1 \left/ \left(\frac{d\Theta_{KCl}}{dt}\right)\right. . \qquad (9)$$

From equations (7) and (8):

$$\frac{d\Theta_{KCl}}{dt} = \alpha \sum_{n=1}^{\infty} (\Theta_{KCl}^{(n-1)} - \Theta_{KCl}^{(n)}) = \alpha \qquad (10)$$

since, by definition, $\Theta_0 = 1$, and $\Theta_{KCl}^{(n-1)} > \Theta_{KCl}^{(n)}$. Combining equations (9) and (10) yields $t_0 = 1/\alpha$. From above, $\alpha = 0.39 \pm 0.02\,\text{Å}^{-1}$ giving $t_0 = 2.6 \pm 0.2\,\text{Å}$. The face-centered-cubic unit cell dimensions for KCl are $6.29\,\text{Å}$ [18], equal to a bilayer KCl film thickness if the (100) face is oriented parallel to the surface. A monolayer K plus Cl film would be half this value ($3.15\,\text{Å}$), in reasonable agreement with the thickness measured from the tribological and deuterium blocking data ($2.6 \pm 0.2\,\text{Å}$). Clearly, this is an approximate value since it relies on the assumption that all of the layers have an identical thickness and that the adsorption kinetics into each layer are identical. The film-growth data of figure 2 clearly indicate that the latter appears to be a reasonable assumption since growth is extremely linear.

It is evident from the data of figure 1 that the friction coefficient is essentially independent of film thickness as thicker films are deposited. Comparison of both the friction coefficient and wear scar area of bulk KCl with those of $\sim$2000-Å thick KCl films reveals that they are similar, indicating that films of $\sim$2000 Å or thicker behave like bulk KCl [8]. Coincidentally, the friction coefficient for bulk KCl ($\sim$0.3) is identical, within experimental error, to the limiting value of the monolayer (0.27 ± 0.03) found above. Further films are currently under investigation for which the monolayer and thick film friction coefficients may be different, thereby allowing the transition between these two types of behavior to be monitored.

5. Conclusions

The decrease in friction coefficient measured for a tungsten carbide tip sliding on KCl-covered iron in ultrahigh vacuum decreases from a value of $\sim$2 for the clean surface to $\sim$0.27 at the completion of the first layer of KCl, measured to be $\sim$2.6 Å thick. This layer saturates when approximately 40 Å of KCl have been deposited onto the surface indicating that the second and subsequent layers are present prior to the saturation of the first layer on iron. Temperature-programmed desorption indicates that KCl is more strongly bound to iron than to KCl. Heating KCl films thinner than $\sim$40 Å, where the first layer has not yet saturated, to $\sim$550 K wets the surface to provide a larger first-layer coverage, and results in a reduction in friction coefficient.

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