THE INTERACTION OF A FILM-FORMING AMINE WITH SURFACES OF A RECIRCULATING EXPERIMENTAL WATER LOOP

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ABSTRACT

Film-forming amines (FFAs) are receiving attention as additives in power plant coolants because their basicity and surface-active properties reduce corrosion. Preliminary experiments with bench-top apparatus have suggested that FFAs also mitigate corrosion product fouling of heat transfer surfaces. To understand how an FFA behaves on its addition to a typical coolant system, experiments have been performed with a recirculating water loop operating at high temperature and pressure. This loop, made mostly of stainless steel, circulates water coolant from a constant displacement pump through a heater to a test section designed to monitor corrosion in real time and returns it to the loop reservoir via a cooler and pressure-control valve. Experiments have been performed with single-phase water at 140°C and two-phase steam-water mixtures at 200°C. They involved injecting a commercial FFA into the loop and following its concentration with time by systematic sampling as it interacts with system surfaces. The results have been modelled assuming conventional adsorption/ desorption kinetics on the loop surfaces. At the same time, bench-top experiments at room temperature have provided complementary kinetic constants for adsorption onto stainless steel at room temperature. The derived kinetic constants may be used to predict the behaviour of the FFA in a loop dedicated to the study of fouling by corrosion products.

INTRODUCTION

Boiler systems, including nuclear steam generators, commonly have their water coolant dosed with an amine or combination of amines to raise the pH and generally reduce corrosion, as well as to combat the acidic effects of impurities that may enter the system from condenser leaks or from contaminated make-up. Examples of such amines are cyclohexylamine, ethanolamine and morpholine, and their combinations – including ammonia – depend upon their relative volatility and ability to be carried around a two-phase circuit. Such chemical control, labelled all-volatile treatment (AVT), can usually maintain the concentration of corrosion products dissolved and suspended in feedwater to the parts-per-billion (ppb – µg/kg) range. Nevertheless, even at such low levels, corrosion products such as magnetite (Fe_3O_4 – the oxide of iron ubiquitous in cooling-water systems) can foul heat transfer surfaces and lead to a loss of heat transfer efficiency, while deposits that build up to substantial thicknesses can harbour and concentrate cooling-water impurities and eventually generate corrosive conditions.

Measures to counteract fouling largely focus on periodic cleaning by chemical or mechanical means, or a combination of both, but there have been ongoing efforts to control corrosion product transport and deposition by dosing the coolant with chemical agents other than conventional pH additives. Polymeric dispersants such as polymethacrylate or polyacrylate have been effective in mitigating fouling in laboratory studies under low-temperature cooling water conditions [1] and in field trials with nuclear steam generators [2], while advanced amines such as dodecylamine have shown promise in mitigating fouling under nuclear steam generator conditions [3].

In the category of advanced amines for treating power-system coolants, film-forming amines (FFAs) are receiving increased attention. The most effective are aliphatic molecules of the family of oligo-alkyl-amino fatty amines having the general formula $R1\text{-}[NH\text{-}R2\text{-}]_n\text{-}NH_2$, where n is an integer between 0 and 7, R1 is an unbranched alkyl chain with 12 to 18 carbon atoms and R2 is a short alkyl chain with 1 to 4 carbon atoms [4]. The free electron pair of the amine nitrogen has a strong affinity for metals, so that a monoamine (n = 0) bonds to surfaces with the hydrocarbon chain sticking out, forming a hydrophobic film, while a polyamine attaches to surfaces at more than one point, forming a very strong bond, with the hydrocarbon chain somewhat parallel to the surface (see Figure 1).

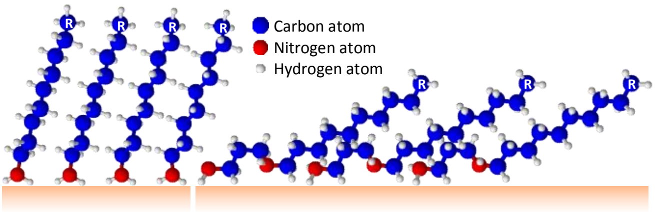

Fig. 1 Schematic representations of FFA films: monoamine (left), polyamine (right).

We are investigating the effectiveness of a commercial FFA, Cetamine®, in mitigating corrosion-product fouling in cooling-water systems and flow-accelerated corrosion (FAC) in feedwater and high-temperature steam-water systems. The laboratory experiments are carried out in water loops containing coolant simulating the temperature and chemistry conditions of industrial plant. The adsorption-desorption kinetics of the FFA on the surfaces of the loop and the corrosion products are important for understanding its influence on the fouling or corrosion process. They have been studied in conjunction with bench-top experiments at room temperature.

EXPERIMENTS

High-Temperature Loop

Figure 2 is a schematic representation of the loop used for the high-temperature studies. Made mostly of 9.5 mm (⅜") type 316L stainless steel tubing, it can operate at pressures up to 14 MPa and temperatures up to 310°C. A positive-displacement pump takes coolant from the 150-L reservoir at flow rates of the order of 1 L/min and directs it through the heaters, where it reaches the operating temperature, which typically for boiler feedwater studies is 140°C and for two-phase steam-water studies is 200°C. Steam-water mixtures are obtained by throttling the flow, which reduces the downstream temperature and pressure, so the maximum temperature for the two-phase experiments upstream of the throttling valve may be close to 300°C. The desired steam quality (voidage) in fact is obtained by adjusting the upstream single-phase conditions.

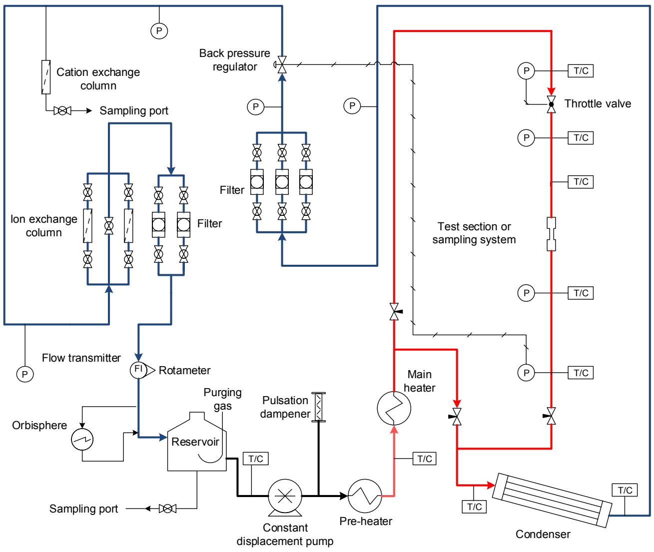

Fig. 2 High-pressure loop (hot section in red).

The coolant chemistry is governed by additions to the reservoir, which is usually sparged with an inert gas such as argon to eliminate air. Samples are taken from the bottom of the reservoir. The test section usually contains a probe for on-line corrosion measurements or a micro-sampling device for sampling fluid from the middle of the stream or from the liquid film next to the wall. From the test section, the coolant passes to a cooler/condenser before its pressure is reduced in a back-pressure control valve, after which it can be directed through an ion-exchange bed and filter before its return to the reservoir. The loop is instrumented with thermocouples (T/Cs), resistance-temperature detectors (RTDs), a high-temperature reference electrode for electrochemical measurements if required, pressure indicators/controllers, flow indicators, etc., and has an Orbisphere electrochemical sensor in a secondary loop to monitor dissolved oxygen.

The FFA was a component of Cetamine® V219, provided by BK Giulini GmbH, a company recently acquired by Kurita Water Industries. The product consists of a diamine FFA combined with cyclohexylamine (CHA) as the pH agent. After vigorous mixing it was injected into the loop as required via a syringe inserted through a septum at the entrance to the reservoir. Its concentration in coolant samples was determined via a colorimetric method based on rose Bengal as the indicator [5]. Sampling involved withdrawing 7.5 mL into a 10 mL glass vial, discarding the sample contents (to account for adsorption onto the sample vessel wall), then quickly taking another sample to be preserved for analysis.

The loop experiments began with a run involving single-phase water at 140°C in all of the hot section; this meant that the throttle valve remained fully open. The flow rate at the pump was 0.56 L/min. With no additive and with mixed-bed ion-exchange resin valved into the circuit, the coolant chemistry stabilised at neutral pH. After a week of steady operation, the ion-exchange was valved out and enough Cetamine® was added to give a concentration of 0.97 ppm (parts-per-million – mg/kg) and a $pH_{25^\circ C}$ of 9.2-9.3. After 12 days, the ion-exchange was valved in again to remove the Cetamine® and after a further 12 days it was valved out and CHA was added to give the original elevated $pH_{25^\circ C}$ value of 9.2 without the FFA. This condition was maintained until the end of the run, 35 days after the start. The measurements of FFA concentration and $pH_{25^\circ C}$, as determined from samples taken periodically throughout the run, are presented in Figure 3. It can be seen that, immediately after the injection of Cetamine®, the FFA concentration started to decrease towards an equilibrium value as it adsorbed on the walls of the loop yet the $pH_{25^\circ C}$ remained constant as there was no process to affect the CHA. After the valve-in of the ion-exchange, the FFA concentration dropped towards zero as it desorbed from the loop walls and was removed from the bulk liquid and the $pH_{25^\circ C}$ approached 7. The final period, when CHA was added, had a steady $pH_{25^\circ C}$ of 9.2 and no significant concentration of FFA.

Figure 4 shows the FFA concentrations and corresponding $pH_{25^\circ C}$ values in the loop as Cetamine® was added in a two-phase experiment lasting 54 days. The $pH_{25^\circ C}$ during the run was nominally 9.3 and the flow rate at the pump was 0.56 L/min. For the first four days the two-phase condition downstream of the throttle valve of 97% voidage at 200°C was established at neutral chemistry, necessitating a temperature upstream of the throttle valve of 297°C. An injection of Cetamine® to give an FFA concentration of 1.16 ppm gave a $pH_{25^\circ C}$ of 9.3, after which the FFA adsorbed on loop surfaces and its concentration declined during a series of voidage changes (from 97% to 80% to 60% – see Figure 4) while the pH remained constant. Each voidage at 200°C

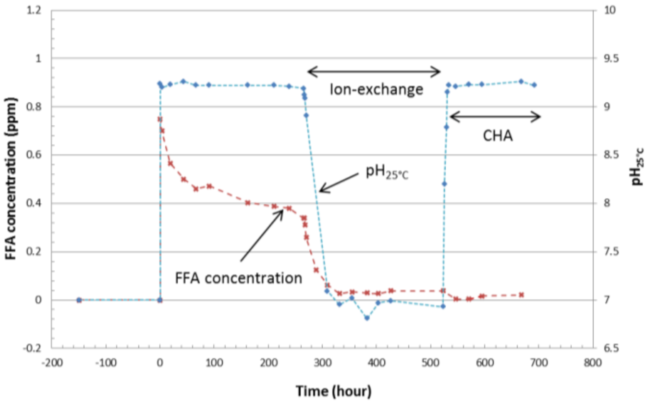

Fig. 3 FFA concentration and pH25°C in single-phase water run: all hot section at 140°C.

necessitated a specific temperature in the hot section upstream of the throttle valve, which therefore changed from 297°C to 220°C to 210°C. After 22 days of these successively decreasing voidages, Cetamine® was again injected to an FFA concentration of 1.05 ppm (giving a $pH_{25°C}$ of 9.35) and the voidage increased in steps from 60% to 80% and then 97%. The FFA concentration continually decreased to the end of the run.

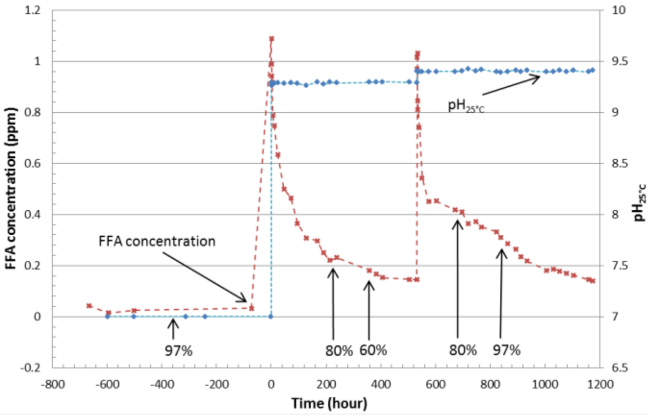

Fig. 4 FFA concentration and $pH_{25°C}$ in two-phase run: hot single-phase section to throttle valve at 297°C, 220°C and 210°C; two-phase section after throttle valve at 200°C and voidage respectively 97%, 80% and 60%.

The concentration changes of FFA were used to obtain the adsorption/desorption kinetics in the loop following the modelling shown below.

Bench-Top Experiments

The changes in FFA concentration as a Cetamine® solution was added to a 5 L beaker of type 316 stainless steel were measured by rapid sampling after addition and then after quickly replacing the equilibrated solution with fresh deionised water. The container had an outlet with a strainer and valve at the bottom for rapid drainage. An increased surface area of the stainless steel was obtained by putting 200 stainless steel type 316 ball bearings, each 6.4 mm diameter, into the bottom of the beaker.

An experiment began by adding 5 L of Cetamine® solution at a concentration of 1.5 ppm and pH 9.2 to the beaker, agitating to ensure good contact with the vessel surfaces, then sampling immediately and over the next four hours at fifteen-minute intervals for analysis of FFA concentration and pH. The solution was then drained and the beaker refilled with deionised water, after which sampling resumed for the next two or three hours. Figure 5 shows the evolution of concentration and pH throughout a typical experiment. The vertical scale is logarithmic to show the concentrations in the replaced liquid more clearly. Note that after three hours or so, absorption of CO_2 had caused the pH to fall, so more CHA was added to bring the pH back to 9.2 before the solution was drained.

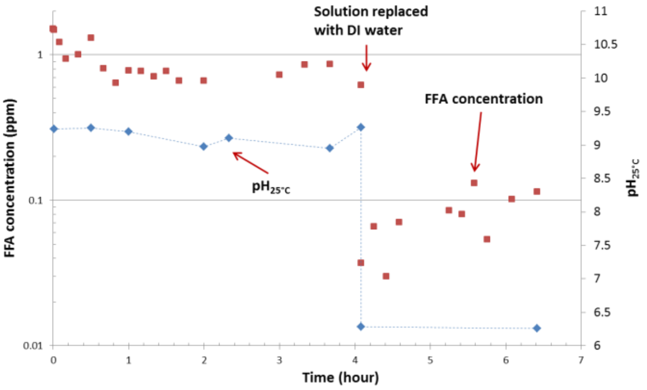

Fig. 5 FFA concentration and $pH_{25°C}$ in stainless-steel beaker experiment at room temperature.

DISCUSSION

Development of System Model

A recent study of the adsorption properties of mono-, di- and tri-amines on carbon steel, stainless steel and copper established adsorption isotherms for the different systems at several temperatures [6]. All three metals adsorbed the FFA readily, with stainless steel's generally having the lowest propensity at a third or so that of carbon steel. For solutions of oleyldiamine, the type of FFA studied in our experiments, in contact with stainless steel, the material of our loop, adsorption was characterised with the Henry adsorption model. This model postulates that the surface coverage at equilibrium, C_w^∞, is proportional to the equilibrium concentration in the coolant, C_b^∞. Thus:

$$C_w^\infty = K_H \cdot C_b^\infty \qquad (1)$$

where the Henry constant, K_H, was given as 45 L/m^2 for room temperature conditions. It was noted, however, that the surface became saturated for C_b values of about 4 ppm and above and the values of C_w and C_w^∞ roughly doubled as the temperature was increased from ambient to 60°C. A key finding that helped to explain the results in conjunction with those of earlier studies [7] was that the adsorption follows a two-step process, each with its own kinetics; the first is rapid, leading to small coverages, and the second is slower, leading to heavier coverages. This is consistent with the postulate that the surface is initially covered with a layer that is very adherent and survives removal of the solution and drying-out of the surface. In fact, hydrophobic surfaces are seen on steam-raising equipment treated with FFAs and subsequently opened for inspection [7], and we saw such behaviour in our fouling experiments [1].

The FFA behaviour illustrated in Figure 3 is interpreted the same way. Accordingly, as soon as the Cetamine® was added at t = 0, C_b began to decrease from 0.75 ppm as the FFA formed adsorbed layers until equilibrium was reached at a value of 0.38 ppm after about 240 h. It is of note that an on-line carbon-steel probe, which apparently interacted with the FFA similarly to the stainless steel of the loop, showed that corrosion was reduced to a fraction of its initial rate almost immediately after the addition, indicating that the rapid rise in pH had an effect but also suggesting that the first FFA layers to be formed afforded additional protection. The probe had a very small surface area compared with that of the rest of the loop and would have had a negligible effect on C_b.

When the loop ion-exchange was introduced at 270 h, C_b decreased as the labile layers of FFA were removed until there was virtually none left in the coolant (the very small concentrations shown are within the accuracy of the analyses). That there was some left on the surfaces, however, was indicated by the on-line probe that measured steady corrosion at less than a third the rate of that under neutral conditions at the start of the run. Interestingly, after a further 120 h or so, the probe indicated that those remnant layers were partially but not completely removed, with an increase in corrosion rate to another steady value that was still substantially below that measured in the initial period. Apparently, below the labile layers of FFA on the surface were adherent layers that released no measurable quantities of FFA to the de-ionised coolant but could be reduced step-wise to one or more thinner layers after prolonged exposures. It is of note here that the investigation reported in Reference 6 showed that the FFA films on stainless steel survived prolonged flushing with deionised water without releasing measurable amounts to the water.

To model the changes in the measured concentration of FFA in extracted samples (i.e., of C_b in the loop), we are concerned with the behaviour of the labile layers on surfaces, which are treated separately from the initial, adherent layers. The loop is considered as two connected systems. The high-temperature section is described as a simple straight length of pipe, diameter D (m), with plug flow of volumetric rate F (m^3/s). At a distance x (m) from the inlet and at time t (s) the concentration of FFA in the bulk water is C_b (kg/m^3) and of FFA adsorbed on the pipe wall is C_w (kg/m^2). The rate of deposition onto the wall is given by $a \cdot C_b$ (kg/m^2·s), where a (m/s) is the deposition rate constant, and the rate of release from the wall is given by $b \cdot C_w$ (kg/m^2·s), where b (/s) is the release rate constant. We note that a and b are phenomenological constants that reflect the observed behavior in the loop. Information on how they describe molecular adsorption-desorption processes will require more detailed investigations.

Material balances lead to the following Equations 2 and 3 relating C_b and C_w:

$$\frac{\partial C_b}{\partial t}\left(1+\frac{4a}{Db}\right)+\frac{4F}{\pi D^2}\cdot\frac{\partial C_b}{\partial x}+\cdots$$

$$\cdots\ \frac{4F}{\pi D^2 b}\cdot\frac{\partial^2 C_b}{\partial x.\partial t}+\frac{1}{b}\cdot\frac{\partial^2 C_b}{\partial t^2} = 0 \qquad (2)$$

$$\frac{\partial C_w}{\partial t}+b\cdot C_w-a\cdot C_b = 0 \qquad (3)$$

Initial and boundary conditions are: at t = 0 for $x \geq 0$, $C_b = C_w = 0$; at $t > 0$ for $x = 0$, $C_b = C_b^0$; at $t = \infty$ (i.e., at equilibrium) for $x \geq 0$, $C_b = C_b^\infty$ and $C_w = C_w^\infty$. Since measurements are made on C_b by sampling, we are mainly interested in Equation (2). The solutions of similar equations for first-order deposition and release processes in a flow system, involving the time variable t transformed to $p = t - x/u$, where u is the linear velocity of the coolant in the pipe, have been presented before [8]. We note, however, that the high-temperature section has a small volume compared with the rest of the loop and contains rapidly-flowing coolant. Those parameters for a typical experiment give a transit time averaging about three minutes, leading to a dynamic constant of ~5.3×10^{-3} /s.

From Figure 3, an approximate estimate of the rate of the adsorption-desorption processes averaged for the whole loop can be obtained by taking the slope of the concentration curve at t = 0 (i.e., when the Cetamine® is first added) and normalising (see Equation (6) below). The characteristic rate constant is 1.20×10^{-5} /s, indicating that the surface interactions by far dominate and that the variations with distance x in Equation (2) may be neglected. We then reduce Equation (2) to:

$$\frac{dC_b}{dt}\left(\frac{Aa}{V}+b\right)+\frac{d^2C_b}{dt^2} = 0 \qquad (4)$$

which is the equation for first-order adsorption and desorption processes in a cylindrical stirred tank with wetted surface area A (m^2) and volume V (m^3). In other words, our loop may be described as two stirred tanks connected via the coolant, one being the loop cold section with its large reservoir and the other the loop hot section tubing. However, to obtain the average behaviour for the whole loop, we approximate the system to one stirred tank and apply Equation (4) directly.

Equation (4) is easily solvable, and with the initial and final conditions that at t = 0, $C_b = C_b^0$, and at $t = \infty$ (i.e., at equilibrium), $C_b = C_b^\infty$, we derive Equation (5):

$$C_b = C_b^\infty + \left(C_b^0 - C_b^\infty\right)e^{-\left(\frac{Aa}{V}+b\right)t} \qquad (5)$$

We also have the relation at t = 0:

$$\left.\frac{dC_b}{dt}\right|_{t=0} = -\left(\frac{Aa}{V}+b\right)\left(C_b^0 - C_b^\infty\right) \qquad (6)$$

and at equilibrium, when $\frac{\partial C_w}{\partial t} = 0$, Equation (3) indicates:

$$C_w^\infty = \frac{a}{b}C_b^\infty \qquad (7)$$

A total balance on the system at equilibrium is:

$$VC_b^0 = VC_b^\infty + AC_w^\infty = VC_b^\infty + A\frac{a}{b}C_b^\infty$$

or:

$$\frac{a}{b} = \frac{V}{A}\left(\frac{C_b^0}{C_b^\infty} - 1\right) \qquad (8)$$

As noted earlier, from the initial slope of C_b when Cetamine® was added to the loop, we obtain the value of 1.20×10^{-5} /s for $\left(\frac{Aa}{V} + b\right)$ from Equation (6). Since A during the experiment was 2.37 m^2 and V was 0.150 m^3, we have:

$$(15.8a + b) = 1.20 \times 10^{-5} \qquad (9)$$

while from Equation (8) and the loop parameters and Figure 3 we get:

$$\frac{a}{b} = 0.0616 \qquad (10)$$

leading to: $a = 3.75\times10^{-7}$ m/s and $b = 6.08\times10^{-6}$ /s.

When the ion-exchange system was valved into the loop after 270 h, a removal process for the FFA was introduced at a rate given by $F \times C_b$ (in the experiments there was full-flow purification at the system flow rate F). The removal process includes a withdrawal of the FFA from the bulk by the ion-exchange, which lowers the FFA concentration in the flow, and in trying to maintain equilibrium release of the FFA from the deposit layer(s). The rate of change of C_b after the ion-exchange was introduced is given by:

$$\frac{dC_b}{dt} = \frac{Ab}{V}C_w - \frac{(Aa+F)}{V}C_b \qquad (11)$$

and, since at the time of valve-in (i.e., at $t = ix$, when the concentrations were at equilibrium) Equation (7) indicates $C_w = C_w^\infty = \frac{a}{b}C_b^\infty$, we have:

$$\left.\frac{dC_b}{dt}\right|_{t=ix} = -\frac{F}{V}C_b^\infty \qquad (12)$$

The loop flow rate was 0.56 L/min or 9.33×10^{-6} m^3/s, so from Equation (12) the slope of the FFA concentration curve in Figure 3 at 270 h should be -6.22×10^{-5} ppm/s – a value that falls reasonably within the scatter of the measurements (note: in accordance with the literature and for convenience we use ppm units rather than kg/m^3).

We see that from Equation (7) the Henry constant for our system is: $K_H = \frac{a}{b} = 0.0616$ m. As described earlier, the Reference 6 value for K_H measured at room temperature was 45 L/m^2 (or 0.045 m). Given that the value increases with temperature, ours measured with part of the system at 140°C is in good agreement. Moreover, the kinetic data from Reference 6 for the adsorption onto steel at 60°C indicates an overall rate constant [corresponding to our $\left(\frac{Aa}{V} + b\right)$] of 1.08×10^{-5} /s, in good agreement with our value of 1.20×10^{-5} /s; not enough information is supplied in the reference to provide separate values of a or b. From our values of C_b^0 and C_b^∞, we know that 0.113 g of FFA were added at the start of the loop experiment and that the coolant contained 0.057 g at equilibrium. The difference was the amount adsorbed on surfaces at equilibrium, averaging 0.023 g/m^2. This may be contrasted with the coverages on stainless steel reported in Reference 6 as 0.1 – 0.3 g/m^2, and in Reference 7 as 5×10^{-4} – 2×10^{-3} g/m^2. Such differences have been attributed to the different geometries of the experiments and also to the possible incompleteness of the supposed equilibria [6]. It is clear from Figure 3 that our experiment had achieved complete equilibrium.

The results of the two-phase experiment shown in Figure 4 indicate a rather different behaviour. The approach to an apparent equilibrium after the first addition of Cetamine® is uneven, possibly because of the changes in steam voidage in the hot section: there are indications of possible approaches to separate equilibria for the different voidage periods. Nevertheless, measuring the initial slope of the concentration curve and assuming initial and equilibrium values of C_b^0 and C_b^∞ of 1.16 and 0.14 ppm, respectively, we derive via Equation (6) the value of $\left(\frac{Aa}{V} + b\right)$ of 3.53×10^{-5} /s. Similarly, from Equation (8) and the same physical constants for the loop as before, the value of $\frac{a}{b}$ of 0.461 is derived, leading to: $a = 1.96\times10^{-6}$ m/s and $b = 4.26\times10^{-6}$ /s. While these kinetic constants are of similar order of magnitude to those from the first experiment, their ratio giving a K_H value of 0.461 m is different enough to indicate different behaviour. Indeed, after the second injection of Cetamine® to 1.05 ppm at 530 h, the FFA concentration decreased just as rapidly as before, fell to about the apparent previous equilibrium value and continued to fall, indicating that the behaviour immediately after the first injection was incompatible with that after the second. The hot section of the loop, now with the maximum water temperature varying between 297°C and 210°C and the two-phase length at 200°C containing a steam/water mixture travelling at high linear velocity, had clearly begun to influence the kinetics strongly. From the measured concentrations and the loop volume, we calculate that the first Cetamine® addition deposited FFA to a coverage of 0.0646 g/m^2 and the second added 0.0576 g/m^2, to give a total of 0.122 g/m^2, which is at the lower end of the range of coverages measured in Reference 6.

The bench-top experiments were done in the beaker, configured as a stirred tank, so Equations (5), (6) and (8) can be applied directly to Figure 5. The initial slope is 1.20×10^{-4} ppm/s, C_b^0 is 1.50 ppm and, at equilibrium, C_b^∞ is 0.73 ppm; we also have A as 0.164 m^2 and V as 0.005 m^3, so we get $a = 2.44\times10^{-6}$ m/s and $b = 7.58\times10^{-5}$ /s. The Henry constant for the system is: $K_H = \frac{a}{b} = 0.0322$ m. This value is in fair agreement with that from Reference 6, with the difference possibly arising from the different geometry and from a possibly different temperature. It supports the analysis of the data from the loop experiment with single-phase water at 140°C, and suggests that the treatment can be applied to other loop systems operating between room temperature and 140°C.

The behaviour of the FFA concentration after the clean water was added to the drained system in the beaker experiment, however, indicates the influence of the strongly-absorbed layers. Thus, when the solution with FFA concentration C_b^∞ of 0.73 ppm was decanted, the amount of FFA left in the system on surfaces was $(C_b^0 - C_b^\infty)V$, or 3.85×10^{-3} g. This gives a coverage of 0.023 g/m^2 (in excellent agreement with the equilibrium concentration of 0.023 g/m^2 in the 140°C loop experiment). The final equilibrium in the beaker, say at $C_w^{\infty 2}$ and $C_b^{\infty 2}$, is given by:

$$A\frac{a}{b}C_b^\infty = AC_w^{\infty 2} + VC_b^{\infty 2}$$

or:

$$C_b^{\infty 2} = \frac{Aa}{Aa+bV}C_b^\infty \qquad (13)$$

Applying the appropriate values in Equation 13 leads to a final equilibrium concentration of FFA of 0.375 ppm. Moreover τ, the "half-life" of the final calculated equilibrium (i.e., the time to the value of C_b of 0.187 ppm) is calculated via Equation 5 with $C_b^0 = 0$ and $C_b^\infty = C_b^{\infty 2}$:

$$C_b = C_b^{\infty 2}\left(1 - e^{-\left(\frac{Aa}{V}+b\right)t}\right) \qquad (14)$$

τ is 1.23 h. It is clear from Figure 5 that the data do not support these final equilibrium values. The removal of the equilibrium solution appears to have left mainly the non-labile or adherent inner layer or layers on the surfaces. The different kinetics of those layers seem to have little effect on the kinetics of the overall systems, either in the loop or in the beaker.

CONCLUSIONS

Experiments on the film-forming amine (FFA) Cetamine® in solution in water in a stainless steel circulating loop with a hot section at 140°C and in a stainless steel beaker at room temperature indicated that the overall behaviour of the systems on first addition of the FFA can be modelled on the postulate of a stirred tank having kinetic adsorption behaviour characterised by a first-order deposition constant and a first-order release constant. These kinetics are appropriate to the formation of labile surface layers that account for most of the observed changes in FFA concentration. Below these layers are tightly-bound layers that have their own characteristics. The behaviour observed in the experiments corresponded to that reported in the literature and the kinetic constants are appropriate for application to other stainless steel systems operating under similar conditions.

The tracking of FFA concentrations with time as the coolant in the loop was gradually diluted by clean water by circulating it through an ion-exchange system, or as the liquid in the beaker was decanted and replaced quickly with clean water, supported the postulate that the adherent or non-labile layers on the surfaces have kinetics that have little effect on the overall behaviour of the labile layers.

At higher temperatures with two-phase steam-water flows in the hot section of the loop, an apparent equilibrium was observed after an exposure period of 24 days; up to this time, there were indications of approaches to separate equilibria during periods of different steam voidage from 60% to 97% (and therefore different maximum temperatures between 210°C and 297°C). A second addition of Cetamine® on top of the equilibrium concentration caused further adsorption, so that over a further 27 days or so the FFA concentration fell to values below that of the first apparent equilibrium. The higher temperatures and flows in the hot section of the loop apparently led to different adsorption-desorption behaviour. The kinetic constants derived from the first part of the experiment, although supporting the conclusions of the lower-temperature studies, are therefore treated as tentative.

The kinetic parameters obtained from the lower-temperature loop and beaker experiments will be applied to experiments investigating the effects of FFAs on the fouling of heat-exchange surfaces by corrosion products.

NOMENCLATURE

A	wetted surface area (m^2)
a	deposition rate constant (m/s)
b	release rate constant (/s)
C_b	concentration of FFA in bulk (or coolant) (kg/m^3)
C_w	concentration of FFA on the wall (surface coverage) (kg/m^2)
D	pipe diameter (m)
F	volumetric flowrate (m^3/s)
K_H	Henry constant
t	time (s)
u	linear velocity of the coolant in the pipe
V	volume (m^3)
x	distance from the inlet (m)
FFA	film-forming amine
CHA	cyclohexylamine

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