



EFFECT OF CORROSION INHIBITOR ON WATER WETTING & CO₂ CORROSION IN AN OIL-WATER TWO PHASE SYSTEM

Chong Li, Sonja Richter and Srdjan Nešić

Institute for Corrosion and Multiphase Technology
Department of Chemical and Biomolecular Engineering
Ohio University
342 West State Street
Athens, OH 45701

ABSTRACT

Internal pipeline corrosion is primarily associated with the presence of free water, particularly when it acts in combination with CO₂, H₂S and organic acids. Corrosion inhibitors are surface active chemicals which can lower both corrosion rates and oil-water interfacial tension, which affects the oil – water flow pattern and the wettability of the steel surface. This paper proposes a methodology to estimate these inhibitive effects in an oil-water two phase system for a given corrosion inhibitor. By using this methodology, an inhibitor is put through tests to determine the corrosion inhibition, oil-water interfacial tension and the wettability. The results can be used to estimate the effectiveness of the inhibitor in oil-water pipe flow.

Two generic, “quaternary” and “fatty amino” inhibitors have been tested according to this methodology. A significant reduction of oil-water interfacial tension was found if only a relatively low concentration of corrosion inhibitor was applied and the steel surface became hydrophobic as a result. The performance of corrosion inhibition by the oil soluble/water dispersible “fatty amino” inhibitor was enhanced after the carbon steel surface was periodically wetted by the oil phase.

Key words: corrosion inhibitor, water wetting, CO₂ corrosion, inhibition, carbon steel, two phase, wettability, interfacial tension.

Copyright

©2009 by NACE International. Requests for permission to publish this manuscript in any form, in part or in whole must be in writing to NACE International, Copyright Division, 1440 South creek Drive, Houston, Texas 777084. The material presented and the views expressed in this paper are solely those of the author(s) and are not necessarily endorsed by the Association. Printed in the U.S.A.

Government work published by NACE International with permission of the author(s). The material presented and the views expressed in this paper are solely those of the author(s) and are not necessarily endorsed by the Association. Printed in the U.S.A.

INTRODUCTION

Carbon steel has been commonly selected as building material for oil and gas transportation pipelines. Internal corrosion has been encountered with carbon steel for many years in oil and gas production¹. Internal pipeline corrosion is primarily associated with the presence of free water, which is potentially corrosive with the existence of corrosive species, like CO₂, H₂S, organic acids, etc. If the water phase is fully entrained in the flowing oil phase, problems due to internal corrosion can be avoided. It is important to find whether the corrosive water phase will be in contact with the steel surface and cause internal corrosion in an oil-water pipe flow under various flow conditions². In the past, water wetting and CO₂ corrosion in oil-water flow in pipelines have been considered only in a qualitative sense³⁻⁵. The first comprehensive experimental and numerical study² of water wetting and CO₂ corrosion in large diameter oil-water pipe flow was carried out in 2005 by Institute for Corrosion and Multiphase Technology of Ohio University. The effects of crude oil property, pipe inclination and flow regime on water wetting and CO₂ corrosion have been extensively investigated⁶. During that experimental study^{2,6}, a series of comprehensive phase wetting map were obtained for model and crude oils with brine at different pipe inclinations. Figure 1 shows a phase wetting map obtained with model oil-brine in horizontal 4" pipe. Three types of phase wetting regimes were detected: oil wetting, intermittent wetting and water wetting. A complete absence of corrosion was observed under oil wetting regime. The corrosion rates measured under intermittent wetting regime were almost half of those measured under water wetting. These results confirm that water wetting is a complex phenomenon which has a large influence on the corrosion rate under oil-water pipe flow. A mechanistic water wetting model has been proposed by Cai et al⁷⁻⁸ to predict flow pattern and phase wetting regimes for oil-water pipe flow. Very good agreement has been achieved between experimental results and the model prediction as shown in Figure 1¹.

Control of internal corrosion of carbon steel pipeline can be achieved by the injection of corrosion inhibitors¹. Corrosion inhibitors are surface active compounds that, in small quantities (ppm level), produce a reduction in metal loss due to corrosion. Vast majority of corrosion inhibitors are made up of molecules which are composed of separate hydrophilic head and hydrophobic tail. It is this combined hydrophilic/hydrophobic nature that causes an inhibitor to partition between oil and water phases in pipe flow. No studies have been performed on the effects of an inhibitor on phase wetting and flow regimes in an oil-water two phase system, which is very important in order to understand water wetting and CO₂ corrosion under realistic flow conditions. It was found that a significant portion of the inhibitor adsorbs at the oil-water interface, which results in a lowering of the oil-water interfacial tension⁹. Oil-water interfacial tension is a key parameter indicated in the water wetting model⁷⁻⁸, which affects flow regimes and phase wetting regimes in oil-water pipe flow. It has also been known that by lower the oil-water interfacial tension by adding corrosion inhibitors may promote the formation and the stabilization of oil-water emulsions especially at high concentration of corrosion inhibitor at high flow rate⁵. The wettability of the carbon steel becomes an important factor to determine the risk of internal corrosion in oil-water pipe flow during transition between stratified flow with mixing layer approaching the bottom of pipeline and full dispersion of water-in-oil. The changes of wettability of the steel surface due to a corrosion inhibitor molecule adsorption layer¹⁰ can be a key factor for understanding surface phase wetting and inhibitive effects in oil-water two phase flow.

Understanding the effect of corrosion inhibitor on water wetting and corrosion inhibition is one of the most important missing links in our current overall understanding of controlling internal corrosion of transportation pipelines made from carbon steel. This paper proposes a methodology to estimate these inhibitive effects in an oil-water two phase system for a given inhibitor. By using this methodology, an inhibitor is put through tests to determine the corrosion inhibition, oil-water interfacial tension and the

wettability. Two generic, “quaternary” and “fatty amino” inhibitors have been tested according to this methodology. The results can be used to estimate the effectiveness of the inhibitor in oil-water pipe flow in a laboratory prior to implementation in a real system.

EXPERIMENTAL PROCEDURE

Inhibitor formulation and materials

The brine phase in all tests consists of de-ionized water with 1 wt.% NaCl salt added. Before each test, the brine phase was continuously purged with CO₂ until saturated and was adjusted to pH 5.0 with NaHCO₃. The tested oil phase is a refined model oil. The density and viscosity of the model oil are 825 kg/m³ and 2 cp, respectively. Two generic inhibitor packages, “quaternary ammonium chloride” and “fatty amino” were tested through the developed methodology. The formulations of two inhibitor packages are shown in Table 1 and Table 2 as received from the vendor. Details of their chemical structure, chemical name are not available as received. The concentration of inhibitor package used for tests was from 0 to 200 ppm.

The test coupons used for corrosion inhibition tests conducted in a glass cell are carbon steel (C1018) cylindrical coupons. The test coupons used for wettability tests employed in a goniometer are carbon steel (X65) flat coupons. The composition of C1018 and X65 is shown in Table 3 and Table 4, respectively. The carbon steel test coupons were polished with 400 and 600 grit SiC paper, cleaned with isopropanol in an ultrasonic bath for 30 seconds, rinsed with isopropanol and quickly dried with a dryer before each corrosion inhibition and wettability test.

Corrosion inhibition

The corrosion inhibition performance of corrosion inhibitors was tested in a glass cell with rotating cylinder working electrode (carbon steel, C1018). The carbon steel coupon is 1.18 cm in diameter, 1.46 cm in length and has 5.41 cm² exposed area to the test solution. All corrosion inhibition experiments were conducted with constant coupon rotation speed 1000 rpm which gives 2.2 Pa shear stress (the shear stress was calculated with rotation speed and diameter of test coupon) on the test coupon. Three test series were conducted, using three different techniques, LPR, EIS and potentiodynamic sweeps:

1. Only the brine phase was present in the glass cell. The performance of corrosion inhibition was observed with different concentrations (5, 20, 60, 100 and 200 ppm) of corrosion inhibitor. It is referred to as **pure corrosion inhibition** in this research.
2. Test coupon was immersed in the brine phase. After the injection of corrosion inhibitor into the brine phase by syringe, model oil was immediately added on the top of the brine phase. The volume ratio of model oil to brine is 1:9 in the 2 liters glass cell. The concentration of corrosion inhibitor was calculated based on the total liquid volume. During experiments, the test coupon was periodically lifted up and stayed in the oil phase for 5 minutes with keeping 1000 rpm rotation speed, then was returned to the brine phase. Corrosion measurements were carried out immediately after the test coupon was back to the brine phase. Since the test coupon was wetted by oil phase during lifting up process, it is referred as **direct oil wet** in this research. The periodical direct oil wet experiments were conducted at different concentrations (1, 5, 20 and 60 ppm) of corrosion inhibitor.

3. Model oil was added on top of the brine phase after the injection of corrosion inhibitor, similar as test series 2, but the test coupon was not lifted up during the experiments. i.e. the carbon steel coupon was not directly exposed to the oil phase. This test series is referred as **partitioning** in this research.

For corrosion rate measurements, linear polarization resistance (LPR) technique was used. The scanned potential range for LPR measurements is from -5 mV to +5 mV vs. the open circuit potential with scanning rate 0.1 mV/s. Solution resistance was measured by electrochemical impedance spectroscopy (EIS) technique to compensate the measured polarization resistance by LPR. Potentiodynamic sweeps were conducted at the end of corrosion measurements to study the inhibition mechanism. The cathodic sweep was conducted first starting at the open circuit potential and ending 400 mV or 500 mV lower. The anodic sweep was conducted after the open circuit potential had stabilized. The anodic sweep was finished with 150 mV over the open circuit potential. The scanning rate for potentiodynamic sweeps was 0.125 mV/s.

Oil-water interfacial tension

Corrosion inhibitor package was added to a test tube which contained model oil - brine mixture. The total volume of mixture was 30 mL and water cut is 50% (i.e. the volume of the brine was 15 mL). The concentration of corrosion inhibitor ranged from 0 to 200 ppm, based on the total volume of mixture. An illustration of the test tube with model oil - brine mixture and corrosion inhibitor is shown in Figure 2. To control the water chemistry of the brine phase, a glove bag with CO₂ purging was used. The samples used for oil-water interfacial tension measurements were all prepared in the glove bag. After adding the corrosion inhibitor package to model oil - brine mixture in the test tube, the test tube was shaken by hand for a few minutes and then was placed in a container at constant temperature 25°C for a period of 1 day to ensure adequate partitioning time. At the end of this period the sample was moved by syringe to a small glass cup which was used for model oil - brine interfacial tension measurements with a tensiometer. Figure 3 shows a real view picture of tensiometer employing a platinum ring to measure oil-water interfacial tension of the samples after 1 day inhibitor partitioning. Before each test, the platinum ring was cleaned with acetone, isopropanol and was heated to dry. The ring was immersed in the brine phase first and slowly pulled up to the oil-brine interface until the maximum interfacial force reached. The oil-water interfacial tension is in units of dyne per centimeter (dyne/cm) read from the tensiometer, which is equivalent to milliNewtons per meter (mN/m). The measurements were repeated five times. Between each individual measurement, the glass cup for holding the oil-water mixture and the platinum ring were cleaned with acetone, isopropanol and dried with heat.

Wettability (contact angle)

The wettability of steel surface was characterized by contact angles of oil/brine droplets on steel surface immersed in a continuous brine/oil phase. In this research, a contact angle of 90° or greater for an oil droplet in a continuous brine phase indicates the steel surface is hydrophilic. A contact angle of 90° or less indicates that steel surface is hydrophobic.

The contact angle measurements were carried out at room temperature in a goniometer, which was designed and built at the Institute for Corrosion and Multiphase Technology of Ohio University. Figure 4 shows a real view picture of the goniometer. Two types of contact angle can be measured in the goniometer, contact angles of oil droplets in a continuous brine phase and water droplets in a continuous oil phase. The continuous phase was first added in the goniometer. CO₂ gas purging was then applied to

avoid oxygen contamination during testing after which the pH was adjusted to 5.0 with NaHCO_3 . If the continuous phase was brine. A flat X65 carbon steel coupon was polished with 400 and 600 grade SiC paper and placed on a Teflon sample holder in the continuous phase contained in the goniometer. A baseline test without corrosion inhibitors was carried out first after which the corrosion inhibitor package was injected into the continuous phase and the concentration was increased in steps. Droplets were placed on the steel surface by 10 microliter syringe. Both videos and images were taken for angle measurements. For each concentration of corrosion inhibitor the contact angle measurements were repeated 4 times. The goniometer was cleaned with acetone and isopropanol after testing was complete..

RESULTS

Corrosion inhibition

Pure corrosion inhibition: In pure corrosion inhibition tests, corrosion rate and open circuit potential were monitored for different concentrations of corrosion inhibitor. Figure 5 and Figure 6 show the pure corrosion inhibition test results for “quaternary ammonium chloride” and “fatty amino”, respectively. Results show that “quaternary ammonium chloride” can not efficiently inhibit CO_2 corrosion for up to 20 ppm of inhibitor concentration. A higher concentration such as 60 to 100 ppm is required to reduce CO_2 corrosion to 90% inhibition efficiency in brine phase. Open circuit potential shifted to the positive potential direction with increasing corrosion inhibitor concentration.

It was found that “fatty amino” inhibitor package gave 85% inhibition efficiency when only 2 ppm inhibitor was injected in the brine phase (Figure 6). Inhibition efficiency over 90% can be obtained for inhibitor concentration of 5 ppm and higher. It took shorter time to reach steady corrosion inhibition than for the “quaternary ammonium chloride” inhibitor. Addition of “fatty amino” inhibitor also increased the open circuit potential as found for “quaternary ammonium chloride”.

Potentiodynamic sweeps were done at the end of pure corrosion inhibition tests. Figure 7 and Figure 8 show the potentiodynamic sweeps for “quaternary ammonium chloride” and “fatty amino”, respectively. It can be seen that both anodic and cathodic reactions are inhibited with the addition of corrosion inhibitor. At low concentration of “quaternary ammonium chloride”, such as 20 to 30 ppm, the inhibition effect was not obvious. This is also confirmed with LPR measurements. Only the anodic reaction was further inhibited with “fatty amino” concentration above 5 ppm.

Direct oil wet: Figure 9 shows direct oil wet test results for “quaternary ammonium chloride” at 20 and 60 ppm injection concentration. The dotted black line shows the inhibitor injection point (1.5 hours after beginning of each test). After corrosion inhibitor injection into the brine phase, the model phase was quickly introduced on the top of the brine phase by syringe. The test coupons were lifted up to the oil phase four times during each test. The straight lines show the direct oil wet points in time domain. Only a slight effect was observed on the corrosion rate for “quaternary ammonium chloride” inhibitor for both 20 and 60 ppm concentration compared to the pure inhibition test. The corrosion rate of the test containing 20 ppm inhibitor stabilized at the rate of 0.85 mm/yr for 25 hours after the first direct oil wet was done. Compared to the test results from pure corrosion inhibition at the same concentration, the corrosion rate only drops about 0.2 mm/yr. For 60 ppm inhibitor concentration, the first direct oil wet decreasing the corrosion rate temporarily, but after the second direct oil wet the corrosion rate returned to the pure inhibition value. No obvious improvement of inhibition performance was found for “quaternary ammonium chloride” inhibitor with the test coupon directly exposed to model oil phase and back to the brine phase.

Figure 10 shows results for direct oil wet test for “fatty amino” inhibitor at 1 and 5 ppm. The test coupon was lifted up into the model oil phase for three times in each test, at 6.4 hours, 18.4 hours and 24.9 hours for the 1 ppm test and 5.2 hours, 11.4 hours and 23.3 hours for the 5 ppm inhibitor concentration. When the coupon was put back into the brine phase the open circuit potential was immediately monitored. The open circuit potential was unstable during the first 30 minutes after the direct oil wet and during that time, LPR measurements could not be conducted. An obvious drop in the corrosion rate was found when the open circuit became stable and LPR measurement was conducted after the first direct oil wet. The second and third direct oil wet were done in both experiments. Only a slight drop in the corrosion rate was seen following the second direct oil wet and no further decrease of corrosion rate was observed for the third direct oil wet. Two possible explanations can be deduced from these results. The “fatty amino” inhibitor package is oil soluble and water dispersible and the additional source of inhibitor molecules in the model oil phase can give better surface coverage during the exposure to oil phase and thus improve the inhibition performance in the brine phase. Another explanation is that the wettability of steel surface changed from hydrophilic to hydrophobic after inhibitor molecules adsorbed at the steel surface, forming a thin oil film. The obvious enhanced corrosion inhibition was found with “fatty amino” inhibitor after the first direct oil wetting. However, the improvement could not be enhanced with further periodic direct oil wetting.

Partitioning: Figure 11 shows the result from the partitioning test for 5 ppm “fatty amino” inhibitor concentration. For this test, the oil phase was absent. The dotted straight line in Figure 11 indicates the inhibitor injection point at 6 hours. After the corrosion inhibitor was injected, the corrosion rate measurements were conducted in the same way as pure corrosion inhibition tests. The model oil was added into the glass cell with a 5 mL syringe (indicated by a solid line in Figure 11). After the addition of model oil, the test coupon was kept in the brine phase. It showed that the addition of the 5 mL model oil on the top of the brine phase did not affect the corrosion rate. The corrosion rate remained steady until the end of the experiment, with a second model oil addition by 20 mL applied at 23 hours. The corrosion rate from the partitioning test with 5 ppm “fatty amino” is identical to the results from the pure corrosion inhibition test. Partitioning tests were conducted and repeated with injection of 5, 20 and 60 ppm “fatty amino” and 20, 60 ppm “quaternary ammonium chloride”, respectively. In all partitioning tests, there was no improvement of corrosion inhibition found for two different inhibitor packages with model oil addition.

Oil-water interfacial tension

The interfacial tension of model oil - brine with no inhibitor added was measured as 40 dyne/cm. Figure 12 shows that the addition of an inhibitor resulted in a reduction in the oil-water interfacial tension.

The inhibitor concentration at the breakpoint of oil - water interfacial tension is called critical micelle concentration (CMC). When CMC is achieved the oil - water interface has become saturated with inhibitor molecules. With increasing the inhibitor concentration above the CMC, micelles form in oil/water phase and oil - water interfacial tension becomes stable. The critical micelle concentrations were found for two inhibitor packages shown in Figure 12. It can be seen that very low concentrations of “fatty amino” and “quaternary ammonium chloride” caused a great initial drop in oil - water interfacial tension. The breakpoints occurred for 3 ppm “fatty amino” and 5 ppm “quaternary ammonium chloride”.

Oil - water interfacial tension is a key factor to determine the flow regime and phase wetting regime for oil - water pipe flow. With the addition of corrosion inhibitor, a reduction of oil - water interfacial tension occurs which makes the water entrainment easier at lower oil flow rate. Once the water is

entrained in the flowing oil phase, internal corrosion can be avoided. Figure 13 shows the model oil – brine flow regime prediction by the water wetting model for the transition line between fully dispersed flow and stratified flow in a 4” pipe flow. In the graph, the area on the left side of the transition lines represents the stratified flow region and the right side area represents the dispersed flow region. The black line is the predicted transition line between two flow regimes for oil – water pipe flow without the addition of corrosion inhibitor. By lowering the oil - water interfacial tension causes the transition line to shift to lower values of oil – water mixture velocity at given water cut. In other words at given mixture velocity more water can be entrained and thereby greatly inducing the risk of corrosion. By adding 3 ppm of “fatty amino”, water cut up to 15% can be entrained compared with only 6% without inhibitor.

For a given inhibitor package, it is important to measure oil – water interfacial tension at desired inhibitor concentration with proper sample preparation as described above. The water wetting model developed at Institute for Corrosion and Multiphase Technology of Ohio University can be used to predict the flow regimes of oil – water pipe flow with the known value of oil – water interfacial tension as well as other fluid properties and flow conditions.

Wettability of steel surface (contact angle)

Model oil droplets-in-continuous brine phase (oil-in-water): Oil-in-water tests were conducted by placing oil droplets on the test coupon surface which was immersed in the continuous brine phase contained in the goinometer. Baseline test was employed first without inhibitor and then increasing concentration of inhibitor was added. The images of oil-in-water tests are shown in Figure 14 for “fatty amino” inhibitor. In all images, the top black area is a part of the carbon steel coupon. Model oil droplets were placed on the surface of the test coupon by a syringe. The lines on each image indicate the contact angle of oil-in-water. The contact angle of oil-in-water was measured as 158° with no inhibitor added in the brine phase, meaning that the wettability of carbon steel surface is hydrophilic (favors water). With the addition of inhibitor the contact angle decreased below 90° and the steel surface became hydrophobic (favors oil) At high concentrations of inhibitor, the model oil droplet immediately adsorbed on the surface and formed a very small contact angle.

A series of oil-in-water contact angle tests were also conducted with “quaternary ammonium chloride”. Figure 15 is a plot of the measured values of oil-in-water contact angle with increasing “quaternary ammonium chloride” inhibitor concentration in the brine phase. It is clear that addition of “quaternary ammonium chloride” had the similar effect as “fatty amino” which made the steel surface change wettability to hydrophobic.

Brine droplets-in-continuous model oil phase (water-in-oil): A series of water-in-oil tests with “fatty amino” were employed. The brine droplets were placed on top of a carbon steel coupon, which was immersed in the model oil phase. Figure 16 shows images of water-in-oil contact angle measurement results. The angle was measured as 70° without inhibitor addition indicating that the steel surface is hydrophilic. By adding “fatty amino” inhibitor into the model oil phase, the angles increased. Up to 200 ppm inhibitor addition, the contact angle of water-in-oil became 150° which showed the model oil phase has a higher affinity to the steel surface. Since “quaternary ammonium chloride” inhibitor used in this research is ionic type inhibitor (i.e. water soluble only), experiment for water-in-oil with “quaternary ammonium chloride” was not performed.

A summary plot Figure 17 shows contact angles from both oil-in-water and water-in-oil tests with different concentrations of “fatty amino” inhibitor. The dots on the figure represent the data from water-in-oil tests and the yellow dots represent the data from oil-in-water tests. It is clear to see that the contact

angles of oil-in-water decreased and the contact angles of water-in-oil increased with increasing the “fatty amino” inhibitor concentration. The wettability of steel surface was greatly affected by the two corrosion inhibitors tested in this research.

CONCLUSIONS

The effect of corrosion inhibitor on water wetting and CO₂ corrosion in an oil – water two phase system was studied. Some main points from this research were summarized as:

- the performance of corrosion inhibition with selected inhibitor in oil – water system can be enhanced when the steel surface is periodically wetted with oil phase
- oil – water interfacial tension is greatly reduced with addition of corrosion inhibitor. It affects the transition from stratified flow to fully dispersed flow under certain flow conditions
- the wettability of carbon steel surface may change from hydrophilic to hydrophobic when inhibitor is added..

In this project, it was also found that different formulations of the inhibitor package can have different inhibitive effects under an oil – water two phase flow, e.g. direct oil wetting did not enhance the performance of “quaternary ammonium chloride” inhibitor. To estimate the inhibitive effects in an oil-water two phase system for a given corrosion inhibitor package, a methodology was proposed in this research. Two inhibitor packages were tested according to the developed methodology:

- testing corrosion inhibition in a glass cell
- testing oil – water interfacial tension with a tensiometer
- testing oil-in-water and water-in-oil contact angles with a goniometer

REFERENCES

1. L. Smith, “Control of Corrosion in Oil and Gas Production Tubing”, British Corrosion Journal, vol 34, pp 247-253, 1999.
2. C. Li, X. Tang, F. Ayello, J. cai, S. Nestic, C.T. Cruz and J.N. Khamis, “Experimental Study on Water Wetting and CO₂ Corrosion in Oil-Water Two-Phase Flow”, Corrosion / 06, paper no.06595, (Houston, TX: NACE International, 2006).
3. J.P. Brill and H.D. Beggs, “Experimental Study of Oil-Water Flow in Inclined Pipes”, Journal of Energy Resources Technology, pp 56-66, March, 1981.
4. A.P.A. Kurban, P.A. Angeli, M.A. Mendes-tatsis and G.F. Hewitt, “Stratified and Dispersed Oil-Water Flows in Horizontal Pipes”, Multiphase 95, pp 277-291, 1995.
5. H.Shi, “A Study of Oil-Water Flows in Large Diameter Horizontal Pipelines”, Ph.D Dissertation, Ohio University, 2001.
6. F. Ayello, C. Li, X. Tang, J. Cai, S. Nestic, C.T. Cruz and J.N. Khamis, “Determination of Phase Wetting in Oil-Water Pipe Flows”, Corrosion / 08, paper no. 08566, (Houston, TX: NACE International, 2008)
7. J. Cai, S. Nestic and C. de Waard, “Modeling of Water Wetting in Oil-Water Pipe Flow”, Corrosion / 04, Paper No.04663, (Houston, TX: NACE International, 2004).
8. S. Nestic, J. Cai and K.J. Lee, “A Multiphase Flow and Internal Corrosion Prediction Model for Mild Steel Pipelines”, Corrosion / 05, paper No.05556, (Houston, TX: NACE International, 2005)

9. T. Moon and D. Horsup, “Relating Corrosion Inhibitor Surface Active Properties to Field Performance Requirements”, Corrosion / 02, paper no. 02298, (Houston, TX: NACE International, 2002).
10. G. Schmitt, “Wettability of Steel Surface at CO₂ Corrosion Conditions 1. Effect of Surface Active Compounds in Aqueous and hydrocarbon Media”, Corrosion / 98, paper no. 28, (Houston, TX: NACE International, 2004).
11. M.J. Rosen, Surfactants and Interfacial Phenomena (New York, John Wiley and Sons, 1989)

Table 1 Compositions of fatty amino inhibitor package (as received from the vendor)

| Substance | Weight (%) | Solubility |
|----------------------|-------------------|---------------------------------|
| fatty amino compound | 60 – 80 | Oil soluble / water dispersible |
| acetic acid | 10 – 30 | |
| methanol | 5 - 10 | |

Table 2 Compositions of “quaternary ammonium chloride” inhibitor package (as received from the vendor)

| Substance | Weight (%) | Solubility |
|------------------------------|-------------------|-------------------|
| quaternary ammonium chloride | 60 – 80 | Water soluble |
| methanol | 10 – 30 | |

Table 3 Chemical composition of X65 carbon steel coupon (wt.%)

| C | Si | P | S | Mn | Al | Fe |
|------|------|------|------|------|------|---------|
| 0.21 | 0.38 | 0.09 | 0.05 | 0.05 | 0.01 | balance |

Table 4 Chemical composition of C1018 carbon steel coupon (wt.%)

| C | Si | P | S | Mn | Cr | Cu | Ni | Mo | Al | Fe |
|------|------|-------|-------|------|-------|-------|-------|-------|-------|---------|
| 0.05 | 0.31 | 0.013 | 0.002 | 1.32 | 0.042 | 0.019 | 0.039 | 0.031 | 0.032 | balance |

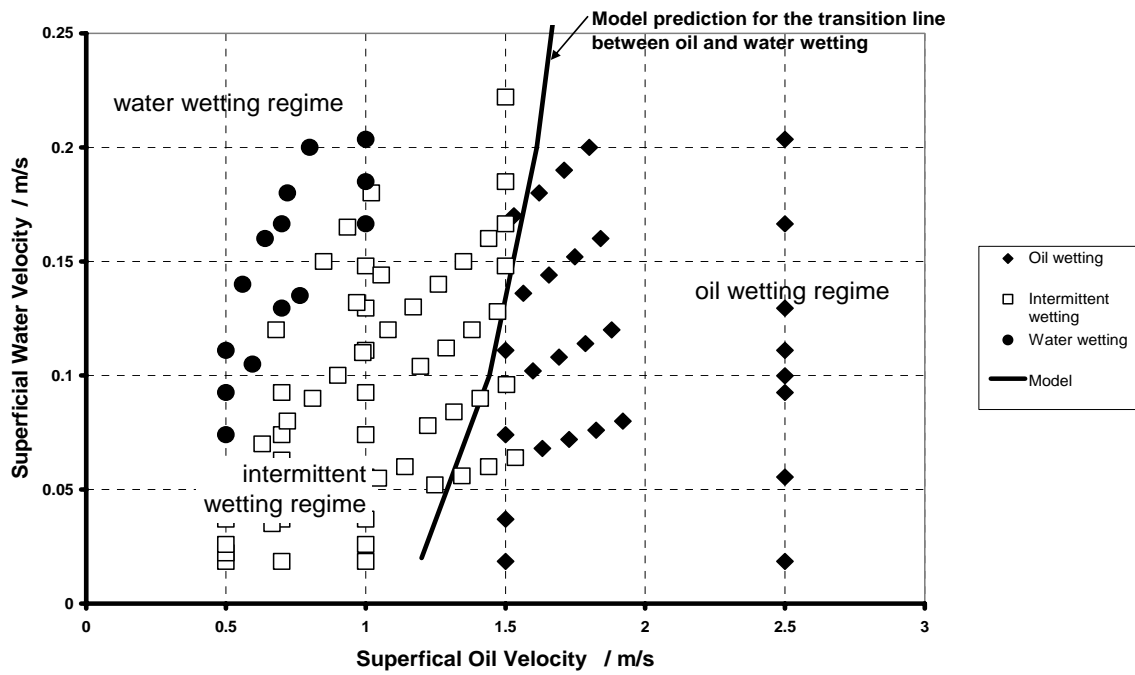


Figure 1 Phase wetting map based on superficial oil and water velocities in horizontal model oil - water 4" pipe.

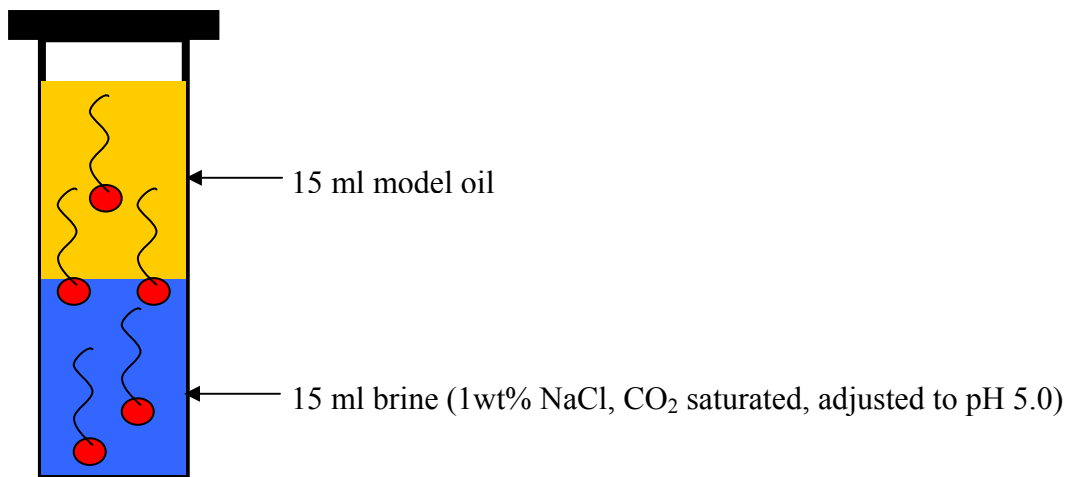


Figure 2 Illustration of sample preparation for model oil - brine with different concentrations of corrosion inhibitor in interfacial tension measurements



Figure 3 Tensiometer used for model oil - brine interfacial tension measurements



Figure 4 Goniometer used for contact angle measurements

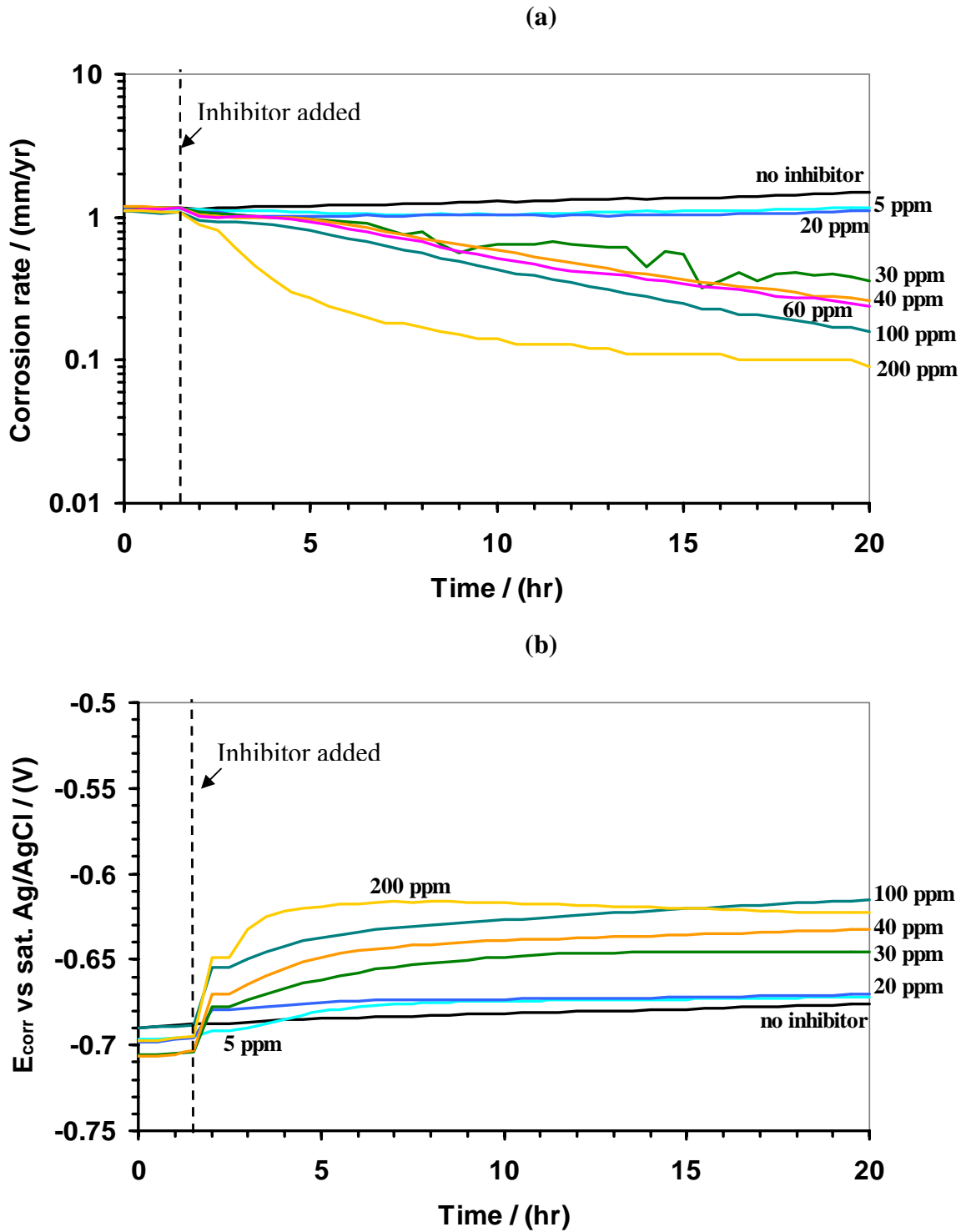


Figure 5 Corrosion rate (a) and open circuit potential (b) vs. test time in pure corrosion inhibition tests for “quaternary ammonium chloride” at different inhibitor concentrations

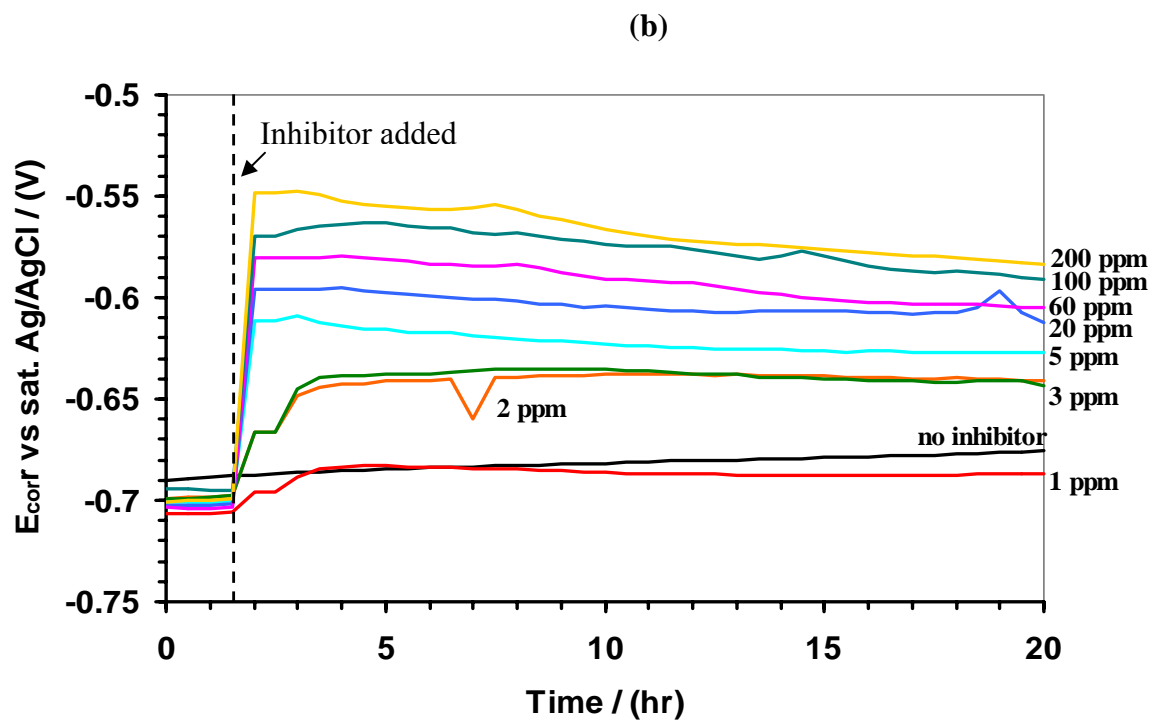
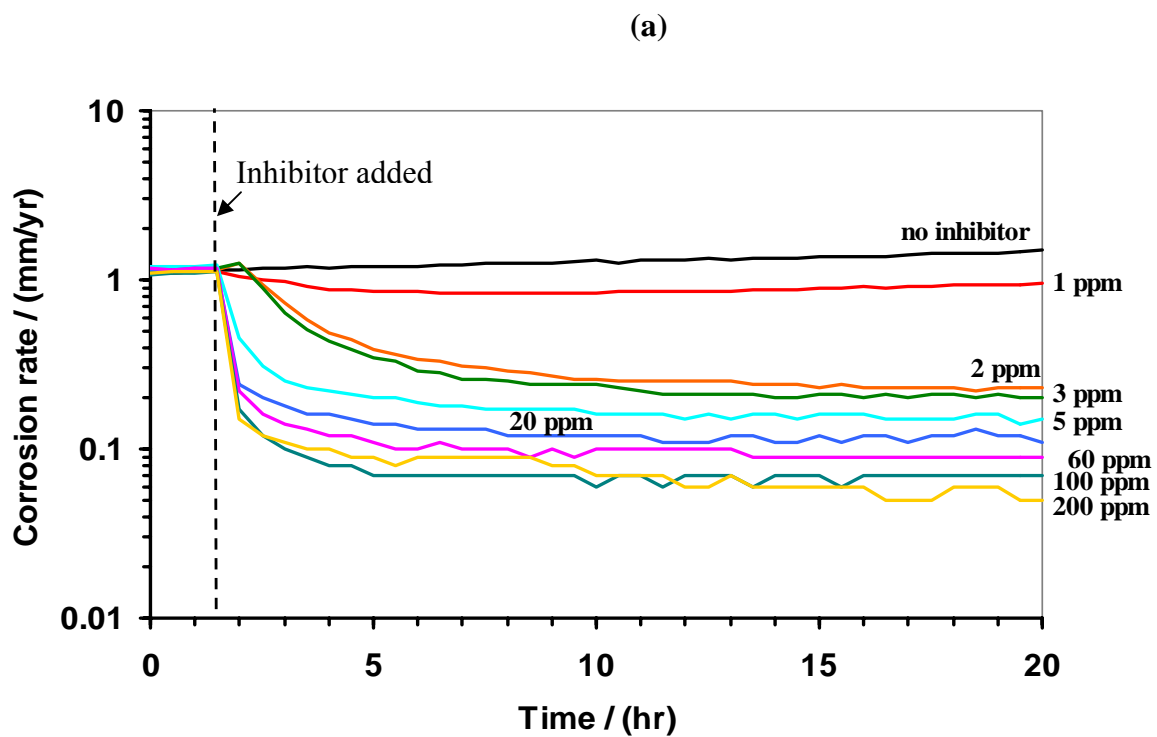


Figure 6 Corrosion rate (a) and open circuit potential (b) vs. test time in pure corrosion inhibition tests for “fatty amino” at different inhibitor concentrations

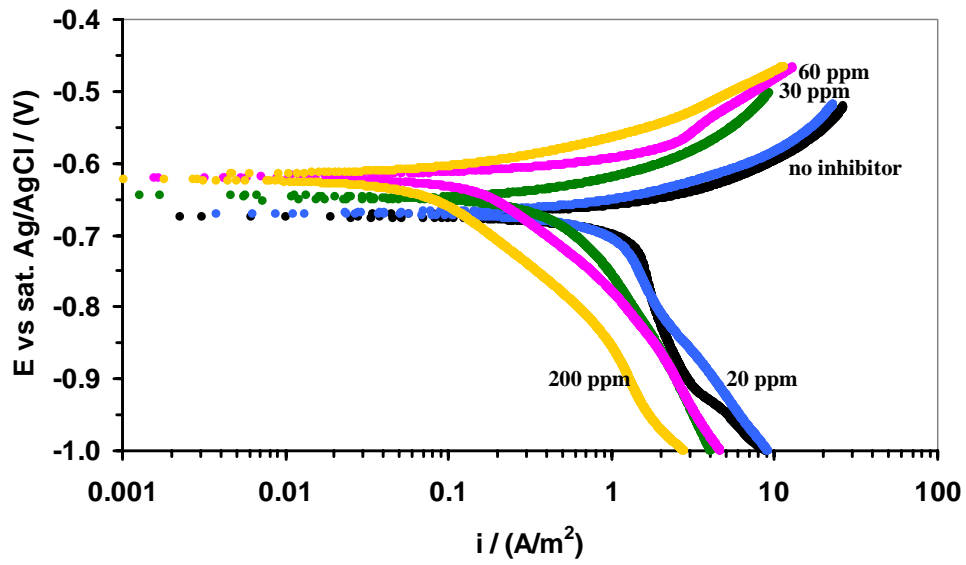


Figure 7 Potentiodynamic sweeps for “quaternary ammonium chloride” inhibitor.

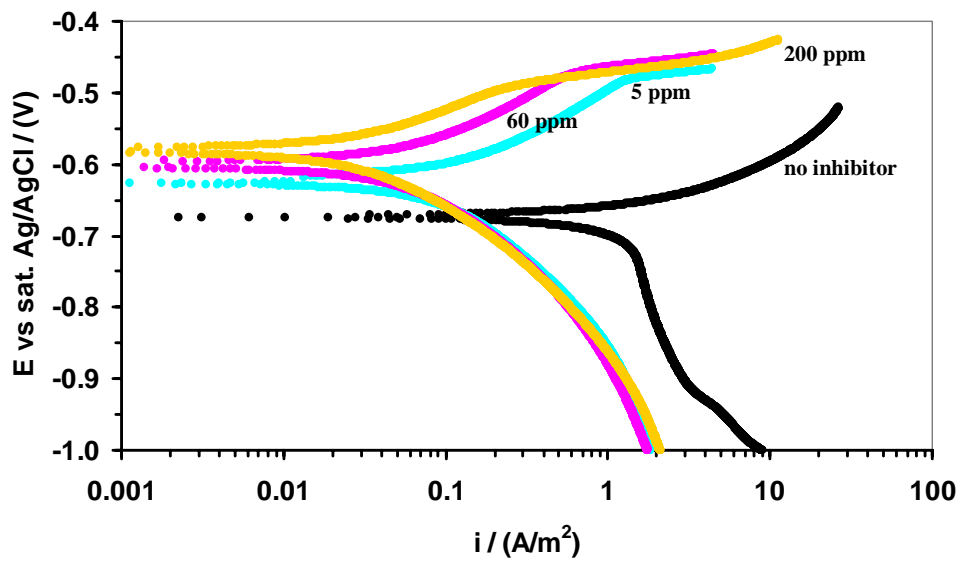


Figure 8 Potentiodynamic sweeps for “fatty amino” inhibitor.

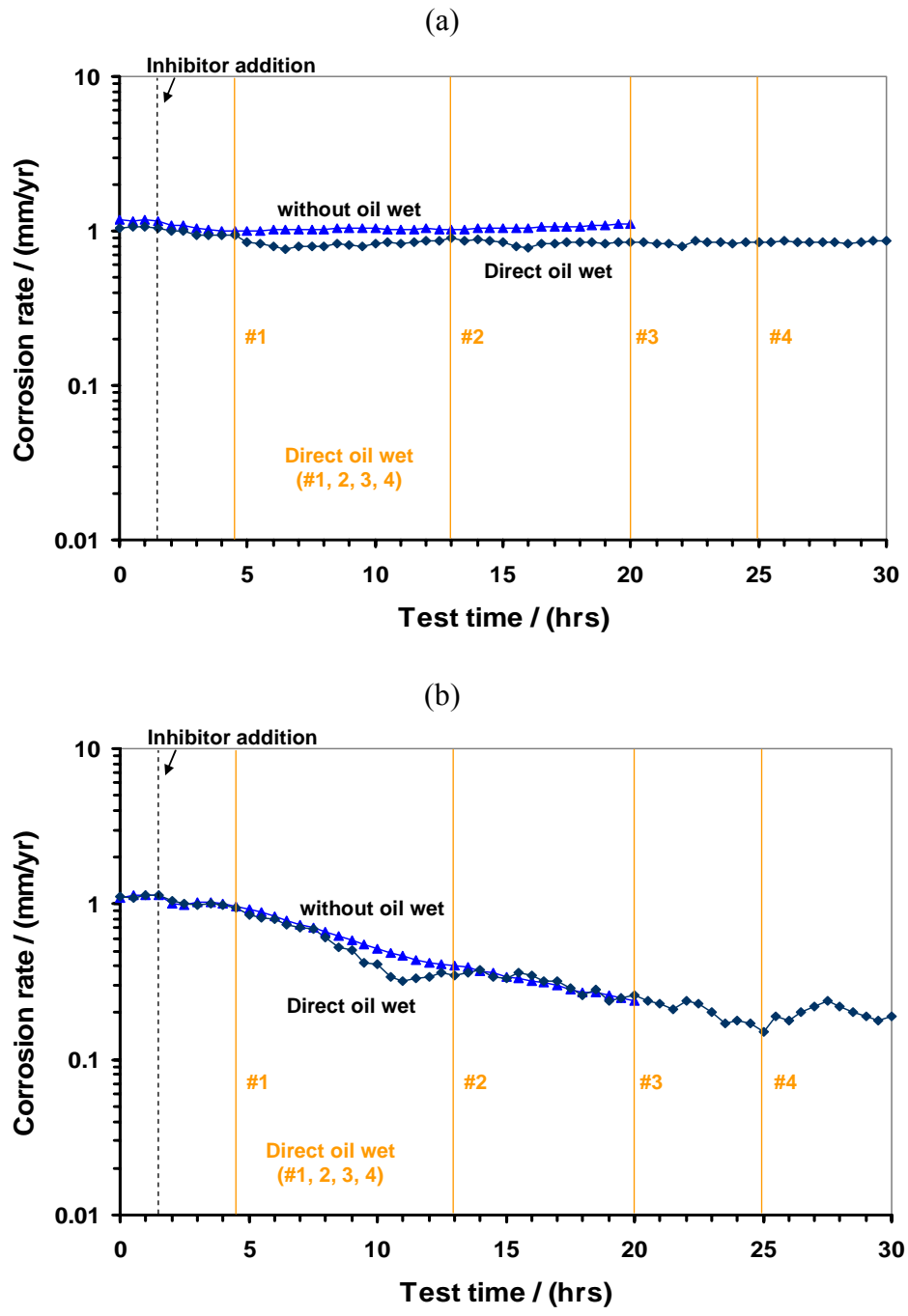


Figure 9 Direct oil wetting test results for “quaternary ammonium chloride” (a) 20 ppm and (b) 60 ppm. The inhibitor was added at 1.5 hours and the coupon was oil wet at 4.5, 13, 20 and 25 hours.

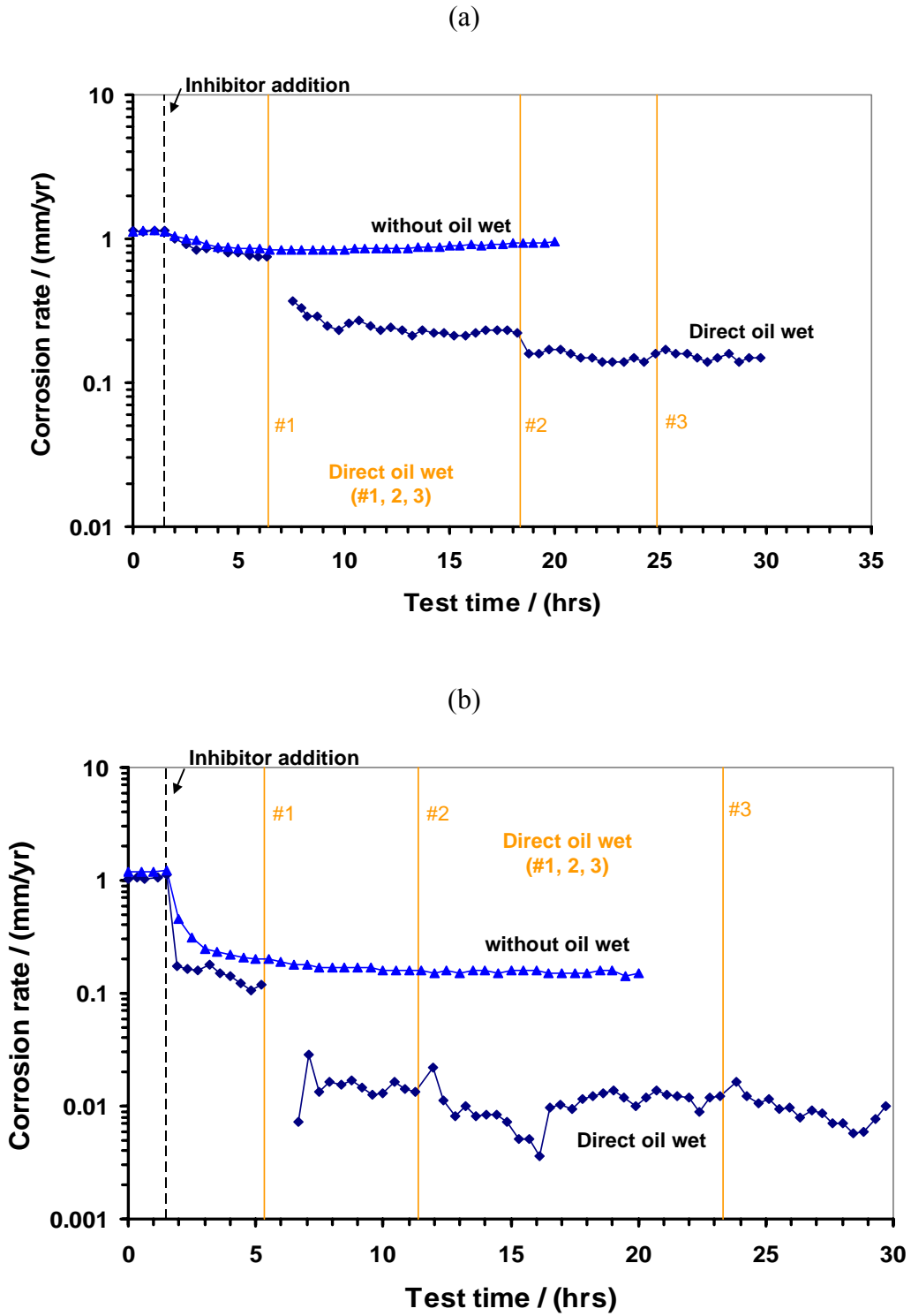


Figure 10 Direct oil wetting test results for “fatty amino” (a) 1 ppm and (b) 5 ppm. The inhibitor was added at 1.5 hours and the coupon was oil wet at 5.3, 11.2 and 23.2 hours.

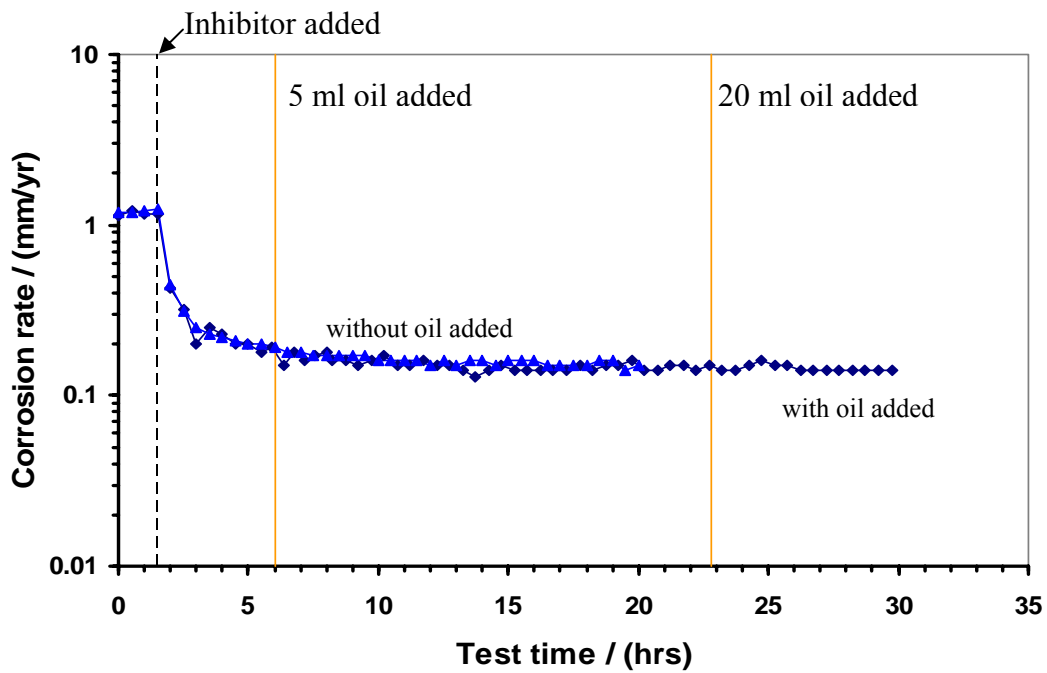


Figure 11 Partitioning test with 5 ppm “fatty amino” inhibitor.

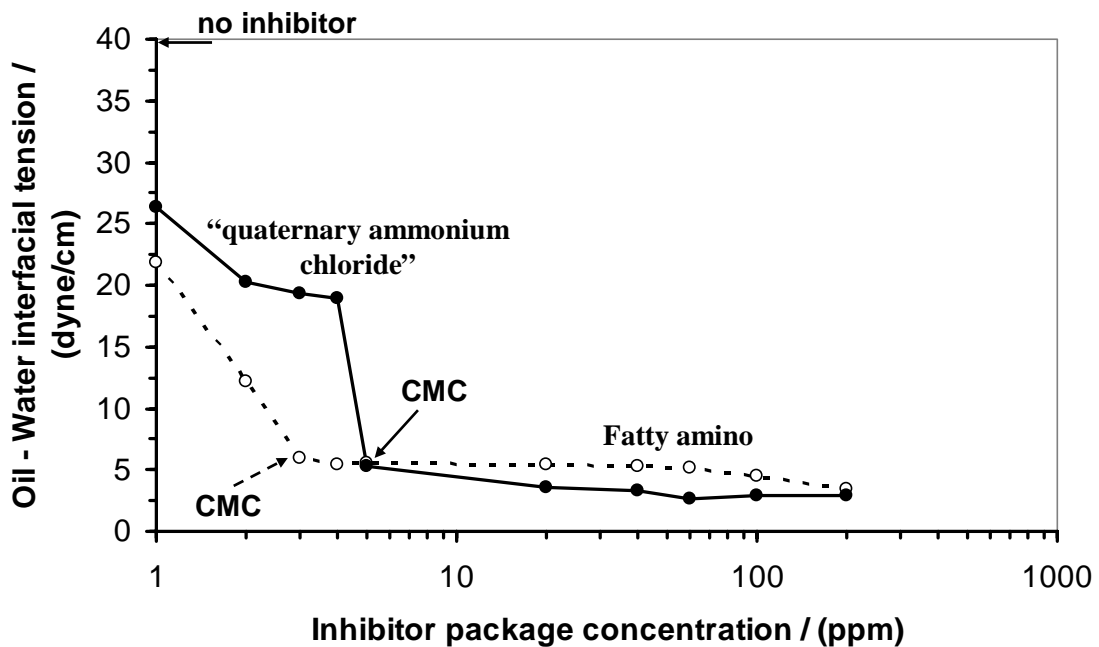


Figure 12 Model oil – brine interfacial tension vs. inhibitor concentration; Critical Micelle Concentration (CMC) points were determined for two inhibitor packages based on the test results.

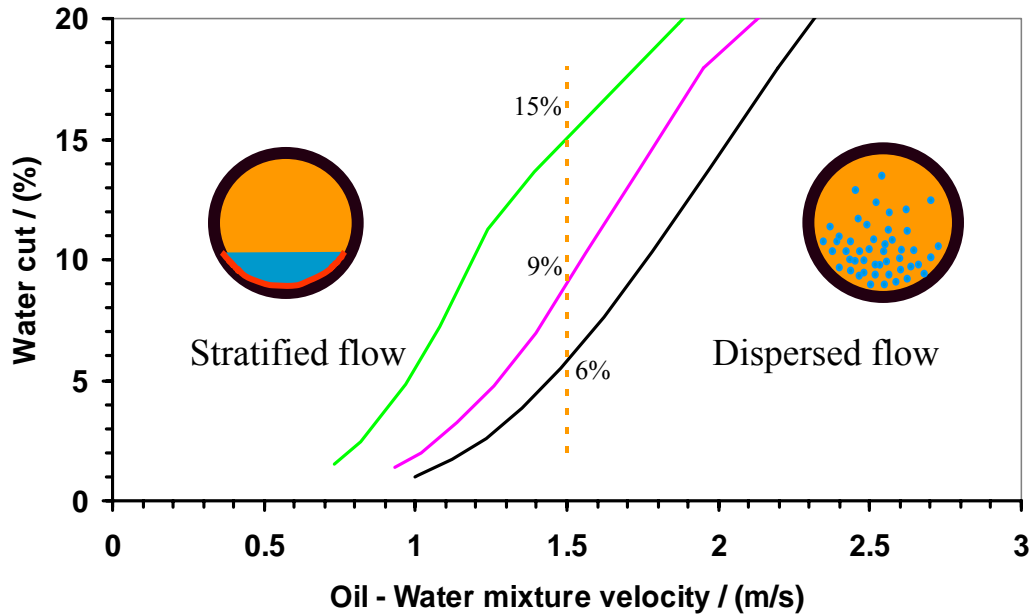


Figure 13 Flow regime prediction by current water wetting model for transition line between fully dispersed flow and stratified flow to clarify the effect of corrosion inhibitor on model oil – brine flow regimes; black line: no inhibitor; pink line: 1 ppm “fatty amino” inhibitor addition; green line: 3 ppm “fatty amino” inhibitor addition based on the total volume of fluid. At the given 1.5 m/s mixture velocity, 6% water cut is the transition point without inhibitor addition; 9% and 15% water cuts are the transition points for 1 and 3 ppm “fatty amino” inhibitor addition.

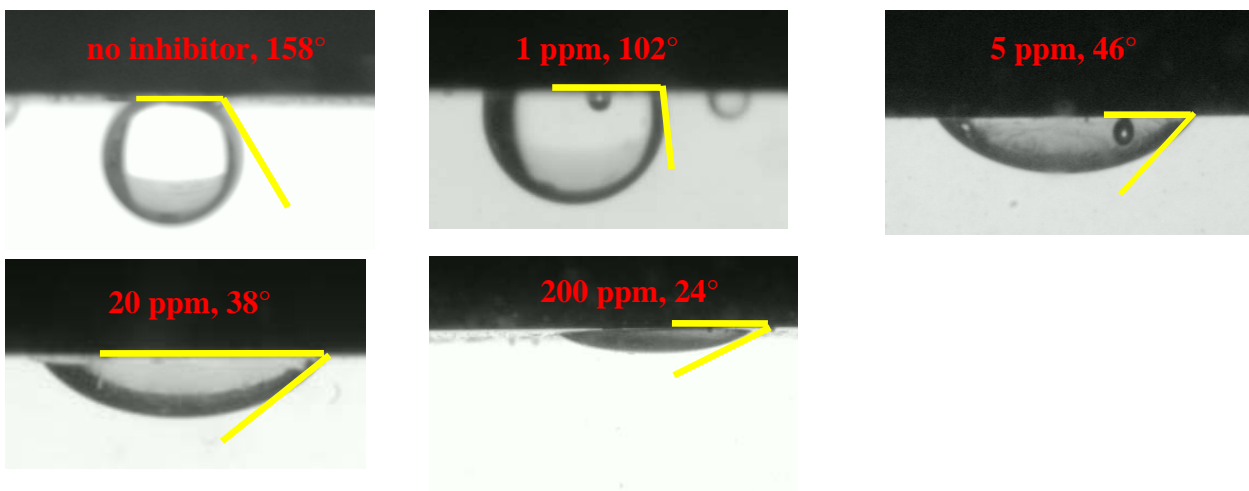


Figure 14 Images of oil-in-water contact angle measurements with 0, 1, 5, 20 and 200 ppm “fatty amino” inhibitor addition in the continuous brine phase.

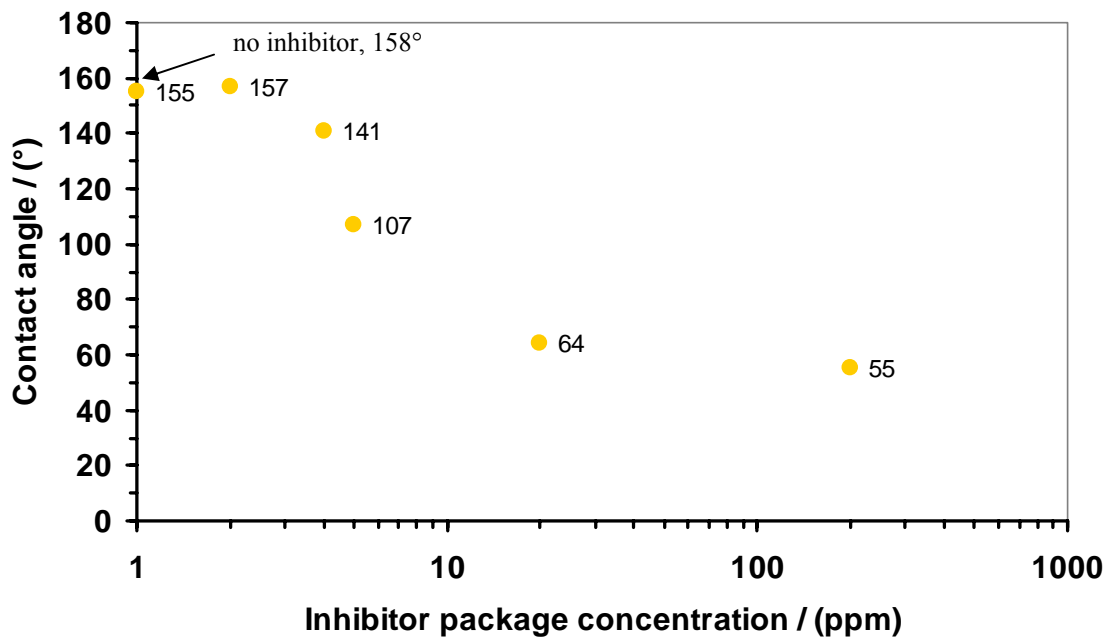


Figure 15 Contact angles of oil-in-water tests with “quaternary ammonium chloride” inhibitor.

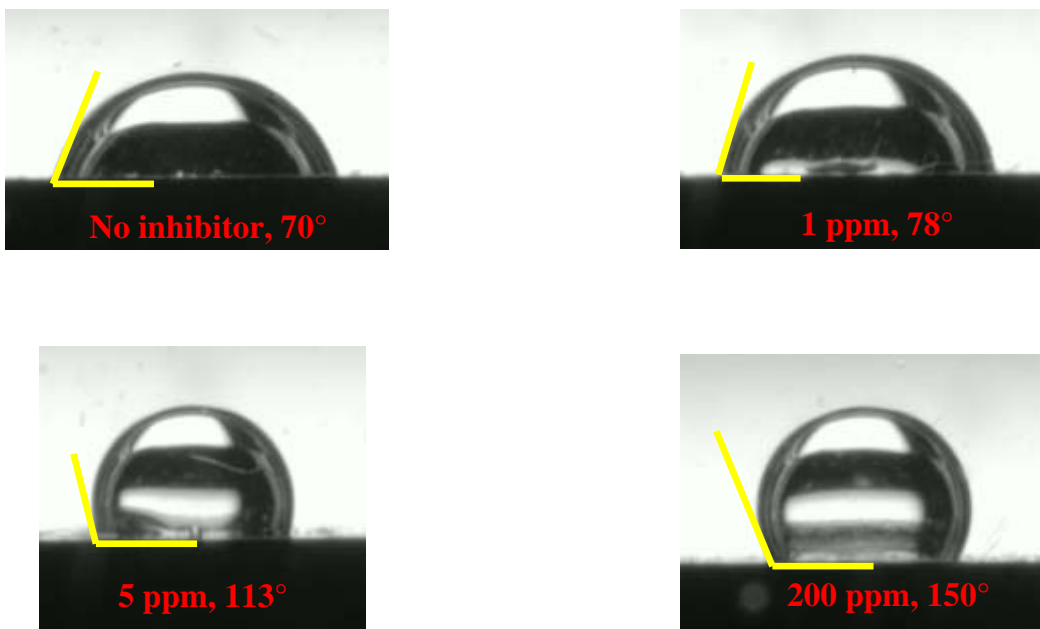


Figure 16 Images of water-in-oil contact angle measurements with 0, 1, 5 and 200 ppm “fatty amino” inhibitor addition in the continuous model oil phase.

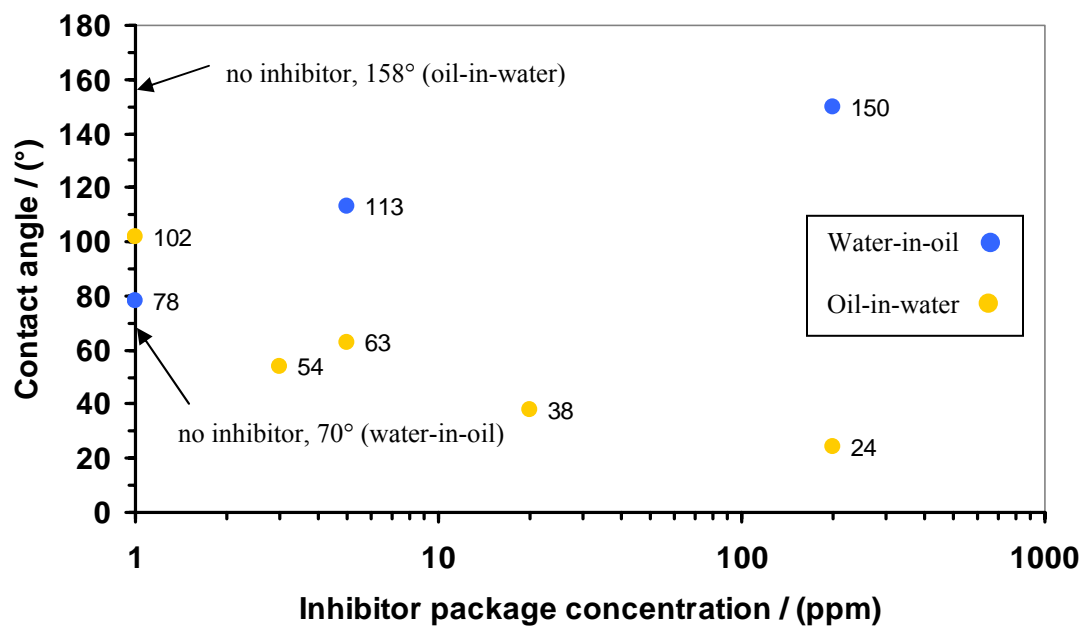


Figure 17 Contact angles of oil-in-water and water-in-oil tests with different concentrations of “fatty amino” inhibitor.