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Study of the partitioning behaviour of a quaternary ammonium salt between oil and water phases

Abstract. Partitioning of corrosion inhibitors between oil/ water phases is one of main factors governing the inhibitor performance. It is important for the inhibitor to be dissolved in water phase at a particular concentration in order to provide protection from corrosion. Partitioning behaviour of a quaternary ammonium salt that is widely used as a corrosion inhibitor was studied by carrying out partitioning tests and determining the concentration of the inhibitors by conventional colorimentry method. The tests were performed using various water cuts, hydrocarbon phases, and concentrations in order to find out the effects of these factors. Comparison of partitioning behaviour of the inhibitors in low and high water cut mixtures resulted in some loss of the inhibitor from bulk water phase as water cut decreased. Partitioning of quaternary ammonium compound seems to be dependent on the nature of the hydrocarbon phase. Also, general suggestions about silanisation procedure of glassware were made.

Key words: corrosion inhibitors, partitioning, oil, water cut.

Introduction

Metallic corrosion in its broad meaning can be described as a destructive process of metal caused by its interaction with the environment. The majority of corrosive processes in the Oil and Gas industry incorporate electrochemical reactions. Inhibitors are compounds that are added in a small amount to the system to slow down a chemical reaction. Corrosion inhibitors are used in the Oil and Gas industry as a part of corrosion mitigation program. These chemicals affect the destructive process by retarding the rate of either electrochemical reaction. In practice, the chemicals are used as formulations and complex mixtures rather than a single component. It is done because synergism and cooperation, that enhance protective properties, exist between different inhibitors. Although numerous chemicals that act as inhibitors are known, few of them are utilized in practice. This happens because of environmental legislations, cost, and availability [1].

Oil field inhibitors are usually utilised in a small concentration (<0.1%). Corrosion inhibitor formulations may include up to six individual surface active ingredients, and may contain up to 30% w/w of them. The inhibitors are usually dissolved in a carrier solvent which may be water, hydrocarbon, or alcohol. The solvent makes the inhibitors easier to inject into the system since it reduces their viscosity. Corrosion inhibitors used for petroleum production can be soluble, dispersible, or insoluble in either the oil or water phases. However, the classification is not strict due to the fact that the inhibitors in most cases partition between hydrocarbon and aqueous phases. The examples of preferentially water soluble inhibitors are quaternary amines, amine salts, and salted imidazolines. These chemicals are susceptible to desorption and may lose solubility in high temperatures and in highly mineralised brines respectively [2]. The protective film formed by water soluble inhibitors is not as tenacious as formed by oil soluble inhibitors; therefore, they must be continuously supplied to maintain system protection. Inhibitors that are preferentially oil soluble are primary amines, phosphate esters, fatty acids, and imidazolines [3].

Partitioning behaviour of the corrosion inhibitor is one of the key factors along with efficiency, solubility, optimum concentration, and film stability. Partitioning test is an irreplaceable and highly recognised standard procedure for inhibitor selection, which aims to find out the adequate inhibitor dosage required for injection in total fluids. Ideally, real field fluids from production sites should be used for the tests [4]. However, clean untreated fluids are not always available. Therefore, sometimes synthetic fluids are prepared in the testing laboratories. Corrosion takes place mainly at the surface, which has a contact with water. Thus, corrosion inhibitors should present in the aqueous phase in order to provide protection. Logically, the practical purpose of any partitioning test is to reach adequate amount of an inhibitor in aqueous phase. Partitioning coefficient is not a fixed value. For instance, the inhibitor distribution depends on water cut, i.e. the ratio of the aqueous phase to the total fluid volume. That is why partitioning test also should include fluids with different water cuts. It is important because in the oil production water cut is not constant and tends to change as time passes. If results from partitioning studies are available, the injection rate of the corrosion inhibitors can be adjusted to the current water cut [5].

The literature review shows that there is a need for an extensive study of partitioning of oil field corrosion inhibitors between oil and water phases under various conditions, for example, different concentrations of the chemicals and water cuts. The aim of the project is to study the partitioning behaviour of an individual corrosion inhibitor like quaternary ammonium salt.

Materials and methods

Standard solutions. Stock standard solutions of benzyldimethylcocoalkylammonium chloride (10,000 ppm-parts per million) were prepared by weighing and dissolution in 1% NaCl solution or in Forties brine. An analytical balance with accuracy up to ±0.0001 g was used for weighing. Working solutions were prepared by dilution of the stock standard solutions in blank aqueous phase for colorimetry.

Silanisation of glassware. Quaternary ammonium compounds are surfactants that have tendency to be adsorbed on glassware surface. To prevent this all glassware was silanised before each partitioning experiments. Before silanisation the glassware was rinsed with acetone and placed in a drying oven for 30 minutes. Clean dry glassware was submerged in the silanisation solution and kept there for 2-3 minutes. The procedure was repeated with acetone. Silanised glassware was placed in the oven for 30 minutes to dry.

Partitioning test. Both 1% NaCl dissolved in deionised (DI) water and Forties brine were used as a water phase for partitioning experiments. Composition of Forties brine was taken from published literature sources [6]. Required amounts of salts were weighed using an analytical balance accurate to ±0.0001 g and dissolved in DI water. Undissolved solid particles were removed by simple filtration. 1% NaCl solution and synthetic Forties brine were saturated with carbon dioxide gas until they reached pH 4 and 5.5 respectively. LAWS (low aromatic white spirit), Tiffany crude oil, kerosene, and toluene were used as the hydrocarbon phase for the experiments with the corrosion inhibitors. The total volume of water and hydrocarbon phases was 100 mL and kept constant for all partitioning tests. Required amount of the stock solution of the inhibitor (10,000 ppm) was pipetted into the mixture and shaken with the Flask shaker SF1 (Stuart Scientific, Essex, UK) for 30 minutes in a maximum mode of 800 oscillations per minute. After shaking, the mixture was kept for equilibration for 3 hours. Water and hydrocarbon phases were separated using separation funnels. The concentration of the inhibitor in the water phase was measured by colorimetry. Blank sample, i.e. mixture of hydrocarbon and water phases without any addition of corrosion inhibitors, was shaken simultaneously for each partitioning experiment. Three different water/hydrocarbon ratios were applied for the experiments: 1:3 (25 mL:75 mL), 1:1 (50 mL:50mL), and 3:1 (75 mL: 25 mL).

Colorimetry (Molecular absorbance). Concentration of quaternary ammonium chloride was measured using molecular absorbance spectroscopy. Hach Lange DR 2800 was supplied by HACH LANGE Company, Berlin, Germany.

Fluorescence spectroscopy. For Tiffany crude oil excitation (200-500 nm) and emission (300-500 nm) ranges were used. For LAWS, kerosene, and toluene full excitation (200-800 nm) and emission (200-900 nm) ranges were used in order to find out the region of maximum absorption and emission spectra. Fluorescence analysis was performed with LS55 Luminescence spectrometer supplied by Perkin Elmer (Massachusetts, USA).

Results and discussion

Partitioning behaviour of quaternary ammonium compound was studied using different hydrocarbon phases and different water cuts. After each partitioning test the residual concentration of quat (quaternary ammonium compound) in aqueous phase was measured and percentage of the amount that partitioned into aqueous phase was calculated. Table 1 represents results from partitioning tests using 1% NaCl solution (pH=4) as the water phase and LAWS as the hydrocarbon phase. Total concentration of quaternary ammonium compound in the mixture was kept constant for all three water cuts. Total volume of the mixture was also the same (100 mL) for all three experiments. The measurements were done with three replicates. Precision of obtained sets of the results was estimated with different chemometrics factors. The calculated RSD (relative standard deviation) values showed satisfactory results in terms of repeatability (>5%).

Table 1 – Partitioning of quaternary ammonium salt between aqueous (1% NaCl, pH=4) and LAWS phase

Water: LAWS	Quat (total), ppm	Quat (aqueous phase), ppm	% in aqueous phase
1:3	5.00	19.00	95
1:1	5.00	9.90	99
3:1	5.00	6.66	100

The results in Table 1 show that concentration of quat in aqueous phase after partitioning decreased as water content in the mixture was significantly reduced. Also, the data show that in the mixture of high water content (3:1) 100% of added quat partitioned into the aqueous phase. However, at low water content (1:3) the residual concentration of quat in aqueous phase was 95% of the total added amount of the inhibitor. The 5% decrease is greater than the experimental error. This was concluded by processing obtained data with Analysis of variance (ANOVA).

The next partitioning experiment with quat was performed using synthetic Forties brine (pH=5.5) with dissolved carbon dioxide and untreated Tiffany crude oil. Total concentration in the mixture was maintained as in the previous experiment (5 ppm). However, the measured concentration of quat in the water phase after the partitioning test was lower than limit of quantification (LOQ=6.2 ppm) but higher than limit of detection (LOD=1.8 ppm). The measured value is not justified to be quoted but with certain degree of confidence it can be reported that some amount of the inhibitor was present in the brine. The amount of added inhibitor was gradually raised to 100 ppm to obtain a concentration in the brine higher than LOQ. The results are shown in Table 2. All partitioning experiments were done with three replicates in order to avoid random errors. Precision and repeatability was assessed with basic statistical analysis and concluded to be adequate (RSD<5%).

Water cut (1:1) was kept constant for all partitioning tests. For the first three concentrations (5, 15, and 40 ppm) percentage of the inhibitor that partitioned into the brine cannot be given as a single value due to the fact that measured concentrations were lower than LOQ.

Table 2 – Partitioning of quaternary ammonium salt between Forties brine (pH=5.5) and Tiffany crude oil phases

Brine: Oil	Quat (total), ppm	Quat (aqueous phase), ppm	% in aqueous phase
1:1	5.0	<6.2	<62
	15.0	<6.2	<20
	40.0	<6.2	<8
	60.0	9.6	8
	100.0	12.0	6

The results in Table 2 show that significant proportion of quat was lost from the aqueous solution whereas in the previous experiment with LAWS and 1% NaCl solution the same inhibitor distributed itself almost fully (95-100%) in aqueous phase. This implies that quat significantly changed its partitioning behaviour when different aqueous and hydrocarbon phases were applied. The reason for quat to partition less into the brine in the latter experiment could be because of high salinity level of Forties brine (58,000 ppm Cl^-) or due to chemical differences between LAWS and Tiffany crude oil. Therefore, the initial experiment (Table 1) was repeated but with Forties brine as the aqueous phase. Table 3 represents results of the experiment. All tests were carried out with three replicates that showed good precision, reproducibility, and absence of random error (RSD<5%).

Table 3 – Partitioning of quaternary ammonium salt between Forties brine (pH=5.5) and LAWS phases

Brine: LAWS	Quat (total), ppm	Quat (aqueous phase), ppm	% in aqueous phase
1:3	5.00	19.20	96
1:1	5.00	9.90	99
3:1	5.00	6.66	100

Statistical analysis with ANOVA showed that decrease in percentage of the inhibitor that partitioned into the brine (4%) is higher than variation within replicates. Hence, decrease in water content caused quat to lose some part of the inhibitor from aqueous phase. The results from Table 3 shows that majority of the inhibitor partitioned into Forties brine. Also, quat lost 4% of the total added amount from the aqueous phase in the low water cut mixture (1:3). A similar partitioning pattern was observed in the previous experiment with the mixture of LAWS and 1% NaCl solution (Table 1).

This result imply that partitioning behaviour of the inhibitor was not affected by the high salinity of Forties brine. Probably, the significant loss of quat in the mixture of crude oil and Forties brine (Table 2) occurred because of the effect of crude oil. Therefore, it was decided to perform a series of partitioning tests with the following hydrocarbon phases: LAWS, kerosene, toluene, and Tiffany crude oil to determine effect of various hydrocarbon phases. For the best comparison, total concentration of quat (100 ppm) and water: hydrocarbon ratio (1:1) was kept constant for all tests. The total concentration was chosen as 100 ppm to ensure that the residual concentration would not be lower than LOQ. The results are summarised in Table 4. All partitioning tests were done with three replicates. The measurements showed good precision and repeatability.

Table 4 – Partitioning of Quat between Forties brine (pH=5.5) and selected hydrocarbon phases

Hydrocarbon phase	Quat (total), ppm	Quat (residual), ppm	% in aqueous phase
LAWS	100	200	100
Kerosene		190	95
Toluene		22	11
Tiffany crude		12	6

The results show that in the case of LAWS and kerosene, the quat partitioned mostly into aqueous phase (100% and 95%, respectively). Only 11% and 6% partitioned into the brine in the experiments where toluene and crude oil were used as hydrocarbon phases. Toluene is aromatic solvent whereas low aromatic white spirit, as the name implies, has low content (usually less than 5%) of aromatic hydrocarbons [7]. Kerosene is a distillate product of crude oil that usually does not contain aromatics and unsaturated hydrocarbons to give satisfactory properties as burning oil [8]. There is no available information about the exact composition of Tiffany oil but usually crude oil contains up to 30% of aromatic hydrocarbons. Therefore, one of the possible reasons for quaternary ammonium compound to lose a significant part of it from aqueous phase could be due to high content of aromatics in the hydrocarbon phase. The affinity of the dissolved inhibitor toward arenes could result in migration of quat from aqueous bulk solution to the liquid-liquid interface or even to bulk hydrocarbon phase. The fact that highest percentage of the quaternary compound was lost not in the pure aromatic hydrocarbon phase, i.e. toluene, but in crude oil phase could be attributed to the fact that oils usually contain various polycyclic arenes. This could affect the distribution of quat in the favour of hydrocarbon phase.

Fluorescence analysis of toluene, kerosene, LAWS, and Tiffany crude oil was carried out in order to compare their fluorescence patterns. Figures 1-4 illustrate 3D view of emission and excitation wavelengths of each hydrocarbon sample.

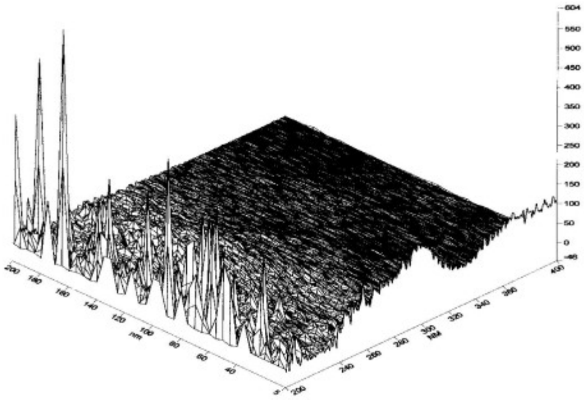

Figure 1 – 3D view of emission and excitation wavelength (LAWS)

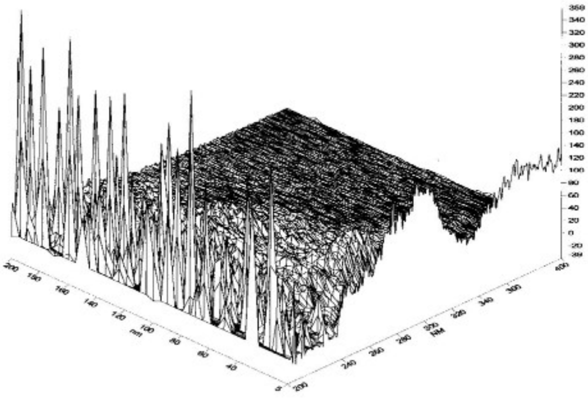

Figure 2 – 3D view of emission and excitation wavelength (Kerosene)

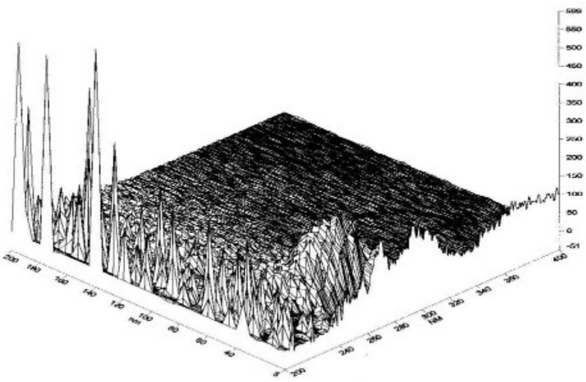

Figure 3 – 3D view of emission and excitation wavelength (Toluene)

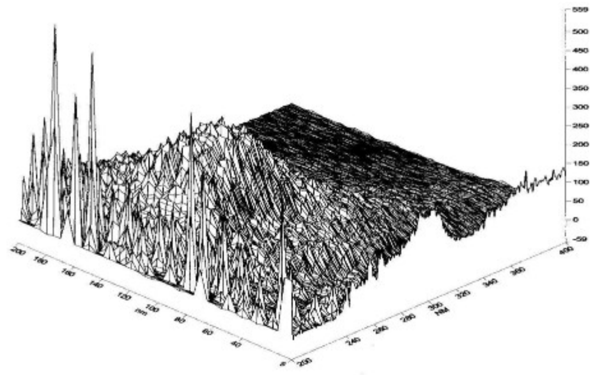

Figure 4 – 3D view of emission and excitation wavelength (Tiffany crude oil)

Fluorescence of crude oils and their fractions is attributed to presence of aromatic hydrocarbons: both mono-ring and poly-aromatic compounds. 3D excitation-emission view is a result of multiple wavelength scan, which involves measuring fluorescence intensities at individual emission wavelengths. The obtained spectra are frequently used to characterise crude oils and petroleum products that contain aromatic species [9]. Fluorescence intensities are directly proportional to the concentration and number of benzene rings; polyaromatic hydrocarbons give more intense spectra than single-ring compounds. Visual comparison of the 3D spectra of 4 different samples (Figures 1-4) reinforced theoretical information about low aromatic content of LAWS and kerosene: the 3D surfaces are quiet flat. However, surface projection of kerosene spectra has slightly more intense regions than in the case of LAWS. Probably, kerosene contains more aromatics than LAWS and as a result 5% of quat partitioned into kerosene phase. Fluorescence pattern of Tiffany crude oil and toluene differ with more intense and complicated 3D view pictures.

However, it is not possible to state that loss of quaternary ammonium salt was due to its partitioning into hydrocarbon phase. Quats having asymmetric structure of surfactants could stabilise emulsions and adsorb on the water-hydrocarbon interface.

Quaternary ammonium salts are considered to be preferentially water soluble corrosion inhibitors. As it was observed from the results of the quat partitioning between aqueous phases and LAWS (Tables 1 and 3), the inhibitor was distributed mostly (95-100%) into aqueous phase. Quats have both polar and non-polar parts, i.e. ionic "head" and hydrocarbon "tail", in the strong ionic character seems to be predominant factor that governed partitioning in described systems. If the inhibitor tends to distribute itself largely into aqueous phase, hydrophilicity of the polar group exceeds hydrophobicity of the non-polar group [10]. When the inhibitor solution was added to the mixture of 75 mL LAWS and 25 mL water (1% NaCl and Forties brine), 4-5% of quat could not reach the aqueous phase and stayed in LAWS. The reason of the tendency of quats to partition more into water phase as the water content is increased in the mixture could be poor dispersibility of quat in hydrocarbon phase.

Another possible reason for the 5% loss of quat from the aqueous phase is the fact that the inhibitors as surface active agents tend to adsorb on the water-hydrocarbon interface and lower the interfacial tension. Surfactant molecules adsorb onto the interface orientating themselves with polar "head" into water phase and with non-polar "tail" into hydrocarbon phase. When concentration of a surfactant is increased in a media and reaches the point that is called critical micelle concentration (CMC), aggregations of surfactant molecules start to form in the system [11]. This happens when oil-hydrocarbon interface becomes saturated with surfactant molecules. In 1:3 (water: LAWS) mixture concentration of quat in the water phase was increased even though total applied amount of the inhibitor was not changed. Thus, increase in concentration could lead to saturated solution of the quat in water phase with adsorption of some of the molecules on the liquid-liquid interface. This could be checked by measuring and comparing interfacial tension in the applied water cuts.

The significant loss of quat from aqueous phase during the partitioning tests between Tiffany crude oil and Forties brine (Table 2) was observed. One of the possible reasons for this phenomenon could be the fact that quaternary ammonium salt is a strong surfactant, which has a tendency to stabilise oil and water microemulsions. When most part of the surfactant is concentrated in the non-polar hydrocarbon phase, water-in-oil microemulsions are formed (Winsor II systems) [12].

Microemulsions are thermodynamically stable systems that are optically clear due to the very small sizes of suspended microdroplets (5-100 nm) which do not scatter visible light. Figure 4-6 illustrates the structure of water-in-oil microemulsion.

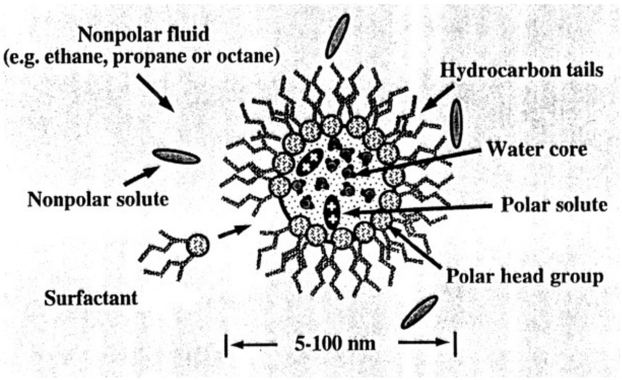

Figure 5 – Structure of water-in-oil microemulsions [13]

The surfactant molecules are adsorbed on the liquid-liquid interfaces and form a micelle-type structure by attaching to the water microdroplets with polar head group and projecting tail groups into the non-polar medium. As a result, some part of the dissolved surfactant can be lost from the bulk solution. Microemulsions are formed when the concentration of a surfactant exceeds Critical Microemulsion Concentration. When it occurs, the surfactant starts to form aggregates around microemulsion droplets to reduce the interfacial tension. Formation of emulsions can be critical for corrosion inhibition due to excessive "parasitic" consumption of the inhibitors to liquid-liquid interface and subsequent increase of corrosion risk [14].

More microdroplets form as the surfactant concentration increases in the system. Thus, more inhibitor molecules form aggregates at the interface and less monomeric forms reside in the bullk solution. Concentration of an added inhibitor directly affect the consumption of the inhibitor from the aqueous bulk solution [15]. To conclude, higher concentration of quat gave a larger interfacial area between oil and brine.

Conclusion

Partitioning behaviour of a quaternary ammonium salt was investigated with application of different water cuts. General tendency for the quat inhibitors is that they tend to lose some part during the partitioning in low water cut regions. This could happen as result of obtaining saturated surfactant solutions and formation of micelles that adsorb on the oil-water interface.

Investigation of partitioning pattern of quaternary ammonium compound revealed that the inhibitor partitioned almost fully into aqueous phase when LAWS and kerosene was used as the hydrocarbon phases. However, in the cases of Tiffany crude oil and toluene, significant part was lost from aqueous phase. The loss could be explained by the effect of high content of aromatics in the hydrocarbon phase or tendency to form of microemulsions with particular phases. Therefore, partitioning tests should take into consideration application of specially prepared model oil that has similar content as crude oil.

To conclude, partitioning of film-forming corrosion inhibitors cannot be expressed with a single value due to the fact that distribution of these compounds between oil and brine depends on factors like water cut, concentration, chemical composition of hydrocarbon phase, and presence of other chemicals.

The results obtained from the experimental part showed that there is a need for the extensive study of partitioning behaviour of corrosion inhibitors. As it is observed from results of the experiments with quaternary ammonium compound, the partitioning of the inhibitor depends not only on factors like water cut but also on the composition of the hydrocarbon phase. In order to check the assumption that cocobenzyl quaternary ammonium salt partitions more into the hydrocarbon phase if it has a high content of aromatics, different oils with known hydrocarbon composition must be applied for the tests. The effect of a type of aromatics, such as mono-ring and polycyclic arenes, on the partitioning is needed to be studied. Also, the new method for quantification of corrosion inhibitors with low LOD and LOQ should be developed to study the effect of concentrations on the partitioning.

Another way of studying partitioning behaviour of the inhibitors could be done by measuring surface tension at liquid-liquid interfaces. It would be possible to study micelle and microemulsion formation and its effect to partitioning behaviour of the inhibitors. These studies could help to identify factors that influence "parasitic" consumptions of the inhibitors due to adsorption on the liquid-liquid interfaces.

References

1 Energy Institute (2018) Guidance for corrosion management in oil and gas production and pro-

cessing. London: Energy Institute. pp.10-15. ISBN 9781787250642.

2 Javaherdashti R., Nwaoha C., Tan H. (2013) Corrosion and materials in the Oil and Gas industries. Boca Raton, Florida, USA: CRC Press. 21 p. ISBN: 9781466556249.

3 Palmer J.W., Hedges W., Dawson J.L. (2004) A working party report on the use of corrosion inhibitors in oil and gas production. London: Institute of Materials, Minerals and Mining, pp. 35-40. ISBN 9781907747885.

4 Achour M., Johlman C.L., Blumer D.J. (2008) Understanding the corrosion inhibitor partitioning in oil and gas pipelines. Proceedings of the Abu Dhabi International Petroleum Exhibition and Conference. Abu Dhabi, UAE. 95 p.

5 Kiran S.K., Nace V.M, Silvestri M.A. (2014) The HLD study of surfactant partitioning for oilfiled corrosion inhibitors. J. Surfac. Deterg., vol. 17, no. 1, pp. 1193-1201. https://doi.org/10.1007/s11743-014-1631-0.

6 Turnbull A. (2009) A multi-electrode approach to evaluating inhibition of underdeposit corrosion in CO_2 environments. Proceedings of International Corrosion Conference. Atlanta, USA. p. 50.

7 World health organization (1996) Environmental health criteria 187. White Spirit. Geneva, Switzerland.

8 Speight J.G. (2007) Chemistry and technology of petroleum. Boca Raton: CRC Press/Taylor & Francis, pp. 114-116. ISBN 0849390672.

9 Ryder A.G. (2005) Analysis of crude petrolerum oils using fluorescence spectroscopy. Boston, MA: Springer. 32 p. ISBN 978-0-387-23628-5.

10 Horsup D.I. (2007) “I Put It In, But Where Does It Go?”- The Fate Of Corrosion Inhibitors In Multiphase Systems. Proceedings of International Corrosion Conference. Nashville, Tennessee, USA. pp. 149-150.

11 Li C. (2009) Effect of corrosion inhibitor on water wetting and carbon dioxide corrosion in oil-water two-phase flow. Dr of Philosophy thesis, Ohio University. p. 55.

12 Wang Z. (2008) A downstream process with microemulsion extraction for microbial transformation in cloud point system. Biochemical Eng. J., vol. 41, no. 1, pp. 24-29. https://doi.org/10.1016/j.bej.2008.03.002.

13 McHardy, J. Sawan S.P. (1998) Supercritical Fluid Cleaning – Fundamentals, Technology, and Applications. Westwood, N.J.: Noyes Publications, 68 p. ISBN 9780815514169.

14 Gulbrandsen E., Kvarekval J. (2004) Effect of Oil-in-Water Emulsions on the Performance of CO_2 Corrosion Inhibitors. Proceedings of International Corrosion Conference. New Orleans, La, USA. pp. 236-238.

15 Knag M., Sjoblom J., Gulbrandsen E. (2006) Partitioning of a model corrosion inhibitor in emulsions. J. Disper. Sci. Technol., vol. 27, no. 1, pp. 65-75.