



SPE 114034

Thermodynamic Modelling of Naphthenate Formation and Related pH Change Experiments

Murtala A. Mohammed and K.S. Sorbie, Heriot-Watt University, and A.G. Shepherd, Shell Global Solutions International B.V.

Copyright 2008, Society of Petroleum Engineers

This paper was prepared for presentation at the 2008 SPE International Oilfield Scale Conference held in Aberdeen, UK, 28–29 May 2008.

This paper was selected for presentation by an SPE program committee following review of information contained in an abstract submitted by the author(s). Contents of the paper have not been reviewed by the Society of Petroleum Engineers and are subject to correction by the author(s). The material does not necessarily reflect any position of the Society of Petroleum Engineers, its officers, or members. Electronic reproduction, distribution, or storage of any part of this paper without the written consent of the Society of Petroleum Engineers is prohibited. Permission to reproduce in print is restricted to an abstract of not more than 300 words; illustrations may not be copied. The abstract must contain conspicuous acknowledgment of SPE copyright.

Abstract

The prediction and prevention of both sodium and calcium naphthenate “scales” is an important issue in oil production. A broad description of how these scales form has been available for some time although most experimental findings are still of a qualitative nature. In this paper, we present an equilibrium thermodynamic model for predicting naphthenate partitioning and precipitation in an oil/brine immiscible system from some chosen initial conditions (i.e. naphthenate initial concentration in oil, brine pH and $[Ca^{2+}]$ etc). This model has, with some assumptions, been applied to both model and real naphthenate system.

This model describes *two* types of naphthenate experiment, viz. (i) full naphthenate precipitation, and (ii) simpler “pH change” experiments where no precipitation occurs. In order to predict naphthenate precipitation, the theory suggest that we need to know (a) the partition coefficient of the naphthenic acid, HA, between the oil and the water phases, K_{ow} ; (b) the pK_a of the naphthenic acid in water; and (c) the solubility product, K_{CaA_2} (or other similar solubility parameter), of the naphthenate deposit. In the simpler pH change experiments, we only require the first two of these parameters, i.e. K_{ow} and pK_a . Using the naphthenate model without precipitation, we studied the effect of varying parameters on the degree of pH change predicted at equilibrium in the oil/naphthenic acid/brine system. We also applied the model to examine the sensitivities of the various parameters on the final pH. The comparison between the model predictions and experiment at a higher brine pH value is overall satisfactory.

Background and Introduction

The development of acidic, sometimes biodegraded, crudes in different parts of the world may lead to naphthenate problems during oil production¹⁻¹¹. These naphthenate deposits have become an increasing flow assurance problem due to deposition and process disruption in production facilities^{1,6,8,9}.

A general view of the deposition mechanisms across the spectrum of naphthenate “scales”, from sodium rich emulsions to calcium naphthenate deposits, was recently put forward by Sorbie *et al.*¹¹. This work took the view that, in order to prevent naphthenate soap problems, we needed to develop a view of both the basic mechanism(s) through which they formed and a thermodynamic model to quantitatively describe their formation. An outline mechanism for the formation of naphthenate deposits was presented previously by Rousseau *et al.*⁹. Subsequent studies have used this conceptual mechanism to study deposition in both model and field naphthenate systems¹¹.

Naphthenic acids in hydrocarbons are defined as compounds containing carboxylic groups attached to saturated cyclic structures.^{7,10-17} There is a tendency for the naphthenic acid to partition between the oil and water phases during production. Once in the water phase, the weak acids will dissociate in accordance with normal equilibrium. However, with the exception of low molecular weight acids, naphthenic acids are relatively insoluble in water.¹⁰ The partition coefficient from the oil phase into the water phase (K_{ow}) therefore tends to increase as the molecular weight of the naphthenic acid decreases. For a single naphthenic acid, this mass transfer process is governed by the two main quantities the oil-water partitions coefficient, K_{ow} , and the acid dissociation constant, K_a . The study is aimed at using the model to use measured final brine pH (pH_f) in “pH change experiments” from which we can back calculate the quantities, K_{ow} and K_a . These “pH change experiments” are where we allow a naphthenate containing oil to contact a brine of given initial pH (pH_i) and $[Ca^{2+}]$ and then let the system equilibrate without the formation of naphthenate precipitates. Only this type of experiment is presented in this paper.

pH Change Experiments

As noted above, in this type of experiment we observe the effect of naphthenic acid mass transfer from the oil phase to the brine phase as they come into contact and equilibrate. No naphthenate precipitate or emulsion was observed since these experiments were performed at lower values of initial pH ($pH_i \leq 6$), even with the presence of buffers. However, a change in pH of the brine phase may be observed as a result of the mass transfer (of the naphthenic acids) between the phases. The final brine pH was measured after coming into contact with different concentrations of extracted naphthenic acid dissolved in toluene at initial brine pH values of 6, 5, 4 and 3. The result of this type of experiment depends only on K_{ow} and K_a .

Experimental Procedure: Extracted naphthenic acid from a naphthenate field deposit was dissolved in toluene at a concentration of 1g/100ml (1%w/v \approx 10,000ppm) of naphthenic acid extract in a volumetric flask and this is referred to as the stock solution. Sample naphthenic acid solutions in toluene were then prepared at concentrations ranging from 0.1 wt%, 0.25wt%, 0.5wt%, 0.75wt% and 1.0 wt%. Synthetic brine solution was prepared (composition: 25,000ppm Na^+ and 20,000ppm Ca^{++}) by dissolving 63.55 g NaCl and 109.32 g of $CaCl_2 \cdot 6H_2O$ in a litre of distilled water. The solution was allowed to stand for 24 hrs for proper dissolution and it was filtered through a 0.45 μ m filter prior to use. Brine samples were then conditioned to initial pH values 6, 5, 4 and 3. At such low brine pH values precipitation did not occur as metal soaps will not precipitate when the solution pH value is below 6 with buffered systems.²

The oil (+ naphthenic acid) and brine (at pH_i) phases were then contacted: 2 ml of adjusted pH brine phase were added to 2 ml of naphthenic acid samples in the toluene phase (10000, 7500, 5000, 2500 and 1000 ppm). Test tubes were shaken vigorously for 1 minute in fume cupboard and samples were left to partition. The oil phase was decanted and the final brine pH was measured.

Naphthenate Thermodynamic Modelling

The naphthenate precipitation model is illustrated in Figure 1A in Appendix A where a full derivation of the equations is given and the notation is explained. The model is defined by the initial (known) conditions, $[HA]_{oi}$, $[Ca^{2+}]_{wi}$, pH_i (i.e. $[H^+]_i$) and $[OH^-]_i$ and the final 7 unknowns are $[HA]_{of}$, $[HA]_{wf}$, $[Ca^{2+}]_{wf}$, pH_f , $[A^-]_{wf}$, $[OH^-]_f$, m_{sol} (the mass of solid “precipitate” CaA_2). The 4 parameters in the model are K_{ow} , K_a , K_w and K_{CaA_2} and only the first 3 apply if there is no precipitation (pH change only). The 7 final unknown quantities in the model can be found by numerically solving the 7 equations A1, A2, A3, A4, A6, A7=A8 and A9=A10 in Appendix A and which are summarised in Table 1.

In fact, when there is no naphthenate precipitation (just pH change), the 7 equations can be successively reduced by substitution down to 1 or 2 chosen solution variables. This can be done in various ways but we have chosen to solve for the 2 unknown variables, $[HA]_{wf}$ and $[H^+]_f$. This leads to the following 2 equations:

$$[HA]_{oi} = [HA]_{wf} \left[\frac{1}{K_{ow}} + \frac{V_w}{V_o} + \frac{K_a V_w}{[H^+]_f V_o} \right] \quad (1)$$

and

$$([H^+]_i - [OH^-]_i) = [H^+]_f - \frac{1}{[H^+]_f} (K_w + K_a [HA]_{wf}) \quad (2)$$

which gives us 2 equations in 2 unknowns which have been solved numerically by the Newton-Raphson method applied in a spreadsheet. Once $[HA]_{wf}$ and $[H^+]_f$ have been found, the remaining 5 unknowns can be found readily using the appropriate equations given in Appendix A.

Experimental and Modelling Results

pH Change experiment: In all of these “pH change” experiments, we observed a decrease in pH from an initial value of pH_i (6, 5, 4 and 3) to a final value pH_f below this initial value. This is as expected from the model equations presented above and it is due to the transfer of the naphthenic acids from the oil phase to the interface and/or to the bulk of the brine phase. The magnitude of the change in the brine pH after coming in contact with the oil phase to the final value pH_f depends on the values of the parameters K_{ow} and K_a and on the *known* initial input values (at $t=0$) of the brine pH and the initial naphthenic acid concentration in the oil phase. The higher the naphthenic acid concentration in the oil phase, then the more acid that will transfer to the brine phase thereby decreasing the brine pH to a lower value. It was also observed that at a very low initial brine pH value (say $pH_i = 3$) and high concentration of naphthenic acid in toluene (say 10.000 ppm), the final brine pH value (pH_f) change was less drastic than the change for high initial pH value (say $pH_i = 6$). At an initial brine pH of 3, the solution is already very acidic hence there will be little opportunity for any substantial mass transfer effect of naphthenic acid.

Plots of experimental final brine pH (pH_f) vs. initial % naphthenic acid concentration in toluene ($[HA]_{oi}$) are presented in Figures 1, 2, 3 and 4 for initial brine pH values 6, 5, 4 and 3, respectively. Note that each pH change experiment is performed in duplicate and the results of each repeat are shown in these figures. The reproducibility of these experiments is clearly very good. It can be observed from Figures 1 and 2 ($pH_i = 6$ and 5) that there is a sharp decrease in the pH_f value as the concentration of naphthenic in toluene increase to minimum values of $pH_f = 3.45$ and 3.25, respectively at 1 wt% $[HA]_{oi}$. At the lowest initial pH value ($pH_i = 3$) in Figure 4, a steady decrease was noticed to a $pH_f = 1.95$ at 1 wt% $[HA]_{oi}$. At lower brine pH, the HA is more in the more protonated form and hence remains in the oil phase, whereas at higher pH, more mass

transfer of naphthenic acid into the brine phase occurs. These “pH change” experimental results are summarised together for all experiments in Figure 5 and these results can now be modeled using the thermodynamic model described above.

Modelling results – Approach 1: The model equations for the pH change experiments were solved by estimating values of acid dissociation constant (K_a) and partition coefficient (K_{ow}), and then calculating the final brine pH (pH_f) at the various initial brine $pH_i = 6, 5, 4$ and 3 and initial naphthenic acid $[HA]_{oi}$ concentrations $[0.0033M (0.1 \text{ wt\%}), 0.0083 (0.25 \text{ wt\%}), 0.0166 (0.5 \text{ wt\%}), 0.025 (0.75 \text{ wt\%}) \text{ and } 0.0333 (1.0 \text{ wt\%})]$.

Virtually all dissociation constants of naphthenic acids (K_a) in the literature are found to be in the range of, $K_a = 1 \times 10^{-4}$ to 1×10^{-6} ($pK_a = 4 - 6$)¹⁶. In addition, it is well known that naphthenic acids are quite sparingly soluble in water and so the partition constant, K_{ow} (defined in Eq. A1) is expected to be low, of order $\sim 10^{-5} - 10^{-3}$.^{10,16}

By a process of trial and error using the model, the values $K_a = 7.0 \times 10^{-5}$ and $K_{ow} = 3.0 \times 10^{-2}$ were found to give the best overall fit to the experimental data. Table 3 gives the final pH (pH_f) values calculated for the initial pH values $6, 5, 4$ and 3 , and a plot of these calculated pH_f vs. initial naphthenic acid concentration $[HA]_{oi}$ is presented in Figure 6. Comparing the graphs of experimental data (Figure 5) with modelling data (Figure 6), the two plots show qualitatively similar trends with a progressive decrease of the final pH value from a higher value to a lower pH. For the higher initial pH values ($pH_i = 6$ and 5), moderate qualitative agreement is seen between the modeling results and experiment for these fixed values of K_a and K_{ow} although the *quantitative* agreement is poor. However, it is evident that using fixed values of K_a and K_{ow} cannot even give a good qualitative representation for the observed behaviour at lower initial pH values. For $pH_i = 3$, the experimental final $pH_f \sim 2$, whereas the model prediction is that the pH hardly changes at all. To determine why our model is not reproducing experimental observations correctly, an alternative modeling approach was taken as explained in the following section.

Modelling results – Approach 2: Another modelling approach was investigated which involved trying to match each individual experiment in Table 2 using an optimised solver. This solver was designed to find the best fit values of K_a and K_{ow} for each individual pH change experiment. However, when this procedure was carried out, we found that exact fits to the data were only possible by assuming that different sets of K_a and K_{ow} values applied for each of the initial brine pH values of $6, 5, 4$ and 3 . Table 4 shows the experimental data and generated data from the code together with corresponding pairs for K_a and K_{ow} for each initial brine pH. A plot of the calculated final brine pH (pH_f) versus initial % naphthenic acid $[HA]_{oi}$ using the data from Table 4 is also presented in Figure 7. A direct comparison with experiment is made for this approach in Figure 8 where it is observed that there is now a good quantitative and qualitative correlation between the experimental and the calculated data at higher pH values of 6 and 5 , and a moderate qualitative behaviour at lower pH values. The corresponding plots of best fit K_a and K_{ow} values vs. initial naphthenic acid concentration ($[HA]_{oi}$) for the individual experiments is shown in Figure 9. Clearly, there is no definite trend in these parameters with naphthenic acid concentration. This is not physically satisfactory and points to the fact that one of the assumptions of our simple model is not correct. This weak assumption *may* be the fact that a single naphthenic acid is assumed in the model whereas the pH change experiments involve deposits from a crude oil which we know (from Electrospray Mass Spectrometry and Atmospheric Pressure Chemical Ionisation Mass Spectrometry results) has many naphthenic acids (HA) components.^{11,16} This matter is currently being investigated.

Conclusions

In this study, we have proposed a simple thermodynamic model for naphthenic acid partitioning between oil and water and the subsequent formation of naphthenate deposits. We model this here by considering only a single “pseudo-naphthenic acid” species denoted as HA. This has been applied to experiments in which the naphthenate deposit does not actually appear – the so-called “pH change experiments”. For this particular case, the change in brine pH from $pH_i \rightarrow pH_f$ is governed only by the parameters of K_a (naphthenic acid dissociation constant) and K_{ow} (partition coefficient) and the initial conditions (pH_i and $[HA]_{oi}$).

The pH change experimental results showed a progressive change in brine pH value (i.e. from high to low) upon mixing of the oil phase (extracted naphthenic acid dissolved in toluene) with the brine phase. Applying our thermodynamic naphthenate model to the pH change experiments reveals that, at a higher brine pH (pH 5 to 6), the model data agrees qualitatively with the experimental data using a single fixed value of K_a and K_{ow} . However, using different sets of values of K_a and K_{ow} for each of the initial brine pH value (say $6, 5, 4$ and 3) shows very good quantitative behaviour between the model and experimental data although having to adjust both of these quantities to match each experiment is not physically justified. These latter results indicate that a more accurate or complete model for naphthenate formation is required and this is currently under development.

Acknowledgements

The authors would like to thank the sponsors of the Flow Assurance and Scale Team (FAST) at Heriot-Watt University: FAST III sponsors – Baker Hughes, BP, BWA Water additives, Champion Technologies, Chevron, Clariant Oil Services, ConocoPhillips, Halliburton, MI Swaco, Nalco, Petrobras, Petronas, REP, Rhodia, Saudi Aramco, Shell, Statoil-Hydro and Total. We also thank Dr Oscar Vasquez of FAST for writing the optimized solver code.

References

1. Goldszal, A., Hurtevent, C. and Rousseau, G.: "Scale and Naphthenate Inhibition in Deep-Offshore Fields", SPE 74661, presented at the SPE Oilfield Scale symposium, Aberdeen, UK, 2002.
2. Laredo, G. C., Lopez, C. R., Alvarez, R. E. and Cano, J. L.: "Naphthenic Acids, Total Acid Number and Sulfur Content Profile Characterization in Isthmus and Maya Crude Oils", *Fuel*, (2004) **83**, 1689-1695.
3. Havre, T. E., Sjoblom, J. and Vindstad, J. E.: "Oil/Water Partitioning and Interfacial Behavior of Naphthenic Acids", *Journal of Dispersion Science and Technology*, (2003) **24** (6), 789-801.
4. Shepherd, A. G., Thomson, G., Westacott, R., Neville, A. and Sorbie, K. S.: "A Mechanistic Study of Naphthenate Scale Formation", SPE 93407, presented at the SPE international Symposium on oilfield Chemistry, Houston, Texas, USA, 2005.
5. Ese, M. H. and Kilpatrick, P. K.: "stabilization of Water-in-Oil Emulsion by Naphthenic Acids and Their Salts: Model Compounds, Role of pH, and Soap: Acid Ratio", *Journal of Dispersion Science and Technology*, (2004) **25** (3), 253-261.
6. Vindstad, J. E., Bye, A. S., Grande, K. V., Hustad, B. M., Hustvedt, E. and Nergard, B.: "Fighting Naphthenate Deposition at the Statoil-operated Heidrun Field", SPE 80375, 5th SPE Oilfield Scale symposium, Aberdeen, UK (2003).
7. Dyer, S. J., Graham, G. M. and Arnott, C.: "Naphthenate Scale Formation-Examination of Molecular Controls in Idealised System," paper SPE 80395 presented at the 2003 SPE Oilfield Scale Sym., Aberdeen.
8. Gallup, D. L., Smith, P. C., Chipponeri, J., Abuyazid, A. and Mulyono, D.: "Formation and Mitigation of Metallic soap Sludge, Attaka, Indonesia Field", SPE 73960, SPE International Conference on Health Safety and Environment in Oil and Gas Exploration and Production, Kuala Lumpur, Malaysia (2002).
9. Rousseau, G., Zhou, H. and Hurtevent, C.: "Calcium Carbonate and Naphthenate Mixed Scale in Deep-Offshore Fields," paper SPE 68307 presented at the 2001 SPE Oilfield Scale Sym., Aberdeen
10. Havre, T. E.: "Formation of Calcium Naphthenate in Water/Oil System, Naphthenic Acid Chemistry and Emulsion stability", PhD Thesis, Department of Chemical Engineering, Norwegian University of Science and Technology, Trondheim, Norway (2002).
11. Sorbie, K.S., Shepherd, A.G., Turner, M., Smith, P.C. and Westacott, R.: "Naphthenate Formation in Oil Production: General Theories and Field Observations", *Proc. Royal Society of Chemistry, Chemistry in the Oil Industry IX*, Manchester, UK, 31 October – 2 November 2006.
12. Fan, T. P.: "Characterization of Naphthenic Acids in Petroleum by Fast Atom Bombardment Mass Spectrometry," *Energy & Fuels* (1991) **5**, 371-375.
13. Gaikar, V. G. and Maiti, D.: "Adsorptive Recovery of Naphthenic Acids Using Ion-Exchange Resins," *Reactive and Functional Polymers* (1996) **31**, 155-164.
14. Robbins, W. K.: "Challenges in the Characterization of Naphthenic Acids in Petroleum," *ACS Petrol. Chem. Div. pre-print* (1998) **43** (1), 137-140.
15. Shepherd, A.G., Thomson, G., Westacott, R., Sorbie, K.S., Turner, M., Smith, P.C.: "Analysis of Organic Field Deposits: New Types of Calcium Naphthenate Scale or the Effect of Chemical Treatment", SPE 100517, Proc. the 2006 SPE International Oilfield Scale Symposium held in Aberdeen, Scotland, U.K., 30 May–1 June 2006.
16. Mohammed, M. A., Sorbie, K.S. and Shepherd, A., forthcoming publication.

Appendix A: Naphthenate Modelling

The general model for naphthenic acid, denoted HA, partitioning between oil and water and its subsequent precipitation as calcium salt in the aqueous phase is presented here. The process is shown schematically in Figure 1A where the initial and final conditions are shown. Note that although the calcium naphthenate "precipitate" is shown in this figure as a deposit in the aqueous phase, it is generally at the interface between the oil and the water. The particular case of where no precipitate forms – which is relevant to the "pH change" type experiments presented in this paper – is discussed below. The usual principles of scale prediction are used to derive the set of constraint equations for the naphthenate formation as follows:

(i) set up the chemical system, which in this case involves partitioning of the naphthenic acid between the oil and water phases which is described by a water oil partition factor, K_{ow} ;

(ii) derive the equilibrium expressions for dissociation of the weak naphthenic acid, HA (described by K_a), the ionic product of water (K_w) and precipitation of the calcium naphthenate (assumed to be CaA_2 in this case);

(iii) from the initial conditions of naphthenic acid in the oil only where $[\text{HA}] = [\text{HA}]_{oi}$ and calcium in the water only, $[\text{Ca}^{2+}] = [\text{Ca}^{2+}]_{wi}$ set up the mass balance equations (one for "A" and one for Ca);

(iv) write the one charge balance equation for the aqueous phase.

As will be shown below, going through this procedure leads to seven equations in seven unknowns, which can be solved numerically given certain initial conditions. The main species are identified in the schematic of Figure A1 where the initial conditions are shown in Figure A1(a) and the final (equilibrium) situation is shown in Figure A1(b). The volumes of oil and water are V_o and V_w , respectively. Also note that the quantities M_{HA} , M_A , M_{Ca} and M_{CaA_2} are the molecular/atomic weights of the various species (where approximately $M_{HA} = M_A$ and $M_{CaA_2} = M_{Ca} + 2 M_A$. In Figure A1, "i" and "f" subscripts denote the initial and final (equilibrium) concentrations of the various species in the water (subscript "w") and oil (subscript "o") phases. Ions, such as H^+ , Ca^{2+} , A^- , do not require any subscripts "aq" or "o" since they only appear in the aqueous phase. The set of equations governing this system can be written as follows:

Equilibrium partitioning and solution equilibrium:

(i) The partitioning of the naphthenic acid between the water and the oil is described by a partition coefficient, K_{ow} , given by:

$$K_{ow} = \frac{[HA]_{aq,f}}{[HA]_{o,f}} \quad (A1)$$

we note that the HA may become less soluble as the salinity of the aqueous phase increases i.e. K_{ow} will be lower at higher ionic strengths. It is numerically convenient to define this quantity as the ratio of the lower solubility species over the higher solubility species; the naphthenic acid is much more soluble in the oil (toluene) phase.

(ii) The dissociation of the weak naphthenic acid and water are given by the usual expressions as follows:

$$K_a = \frac{[H^+]_f \cdot [A^-]_f}{[HA]_{aq,f}} \quad (A2)$$

where it is known that, typical pK_a values ($-\log_{10}K_a$) for these species are in the range 4 to 5, and the ionic product of water is:

$$K_w = [H^+]_f \cdot [OH^-]_f \quad (A3)$$

where K_w is or order, 1.0×10^{-14} .

(iii) the quantity of “precipitated” calcium naphthenate - assumed formula, CaA_2 - is viewed in this model as being given by a solubility product term, as follows:

$$K_{CaA_2} = [Ca^{2+}]_f \cdot [A^-]_f^2 \quad (A4)$$

but in principle *any* solubility expression (mathematical model of the deposit) may be included here.

Mass balance:

(iv) The initial mass of the "A" species, m_{Ai} , is as follows:

$$m_{Ai} = [HA]_{oi} \cdot M_{HA} \cdot V_o \quad (A5)$$

while, at equilibrium, the "A" appears in several components and the final mass is given by the expression:

$$m_{Af} = [HA]_{of} \cdot M_{HA} \cdot V_o + [HA]_{wf} \cdot M_{HA} \cdot V_w + [A^-]_f \cdot M_A \cdot V_w + m_{sol} \left(\frac{2M_A}{M_{CaA_2}} \right) \quad (A6)$$

where, by material balance, $m_{Ai} = m_{Af}$

(v) The initial mass of the Ca species, $m_{Ca,i}$, is as follows:

$$m_{Ca,i} = [Ca^{2+}]_{wi} \cdot M_{Ca} \cdot V_w \quad (A7)$$

while, at equilibrium, the Ca appears both in solution and also in the precipitated CaA_2 and the final mass is given

$$m_{Ca,f} = [Ca^{2+}]_f \cdot M_{Ca} \cdot V_w + m_{sol} \left(\frac{M_{Ca}}{M_{CaA_2}} \right) \quad (A8)$$

where, again by material balance, $m_{Ca,i} = m_{Ca,f}$

Charge balance:

(iv) Finally, we must constrain the final equilibrium concentrations by ensuring that there is charge balance. The initial total charge in the system, C_i - considering only the active ions - is as follows:

$$C_i = (2[Ca^{2+}]_{wi} + [H^+]_{wi} - [OH^-]_{wi}) \cdot V_w \quad (A9)$$

and this charge is set by the initial conditions by specifying $[Ca^{2+}]_{wi}$, $[H^+]_{wi}$. The final charge at equilibrium is given by:

$$C_f = (2[Ca^{2+}]_f + [H^+]_f - [OH^-]_f - [A^-]_f) \cdot V_w \quad (A10)$$

where, by charge conservation, $C_i = C_f$.

Model summary: the model is defined by the following initial conditions, final conditions and parameters (Figure 1A):

Initial known quantities \Rightarrow $[HA]_{oi}$, $[Ca^{2+}]_{wi}$, pH_i (i.e. $[H^+]_{wi}$) and $[OH^-]_{wi}$

Final 7 unknown quantities \Rightarrow $[HA]_{of}$, $[HA]_{wf}$, $[Ca^{2+}]_{wf}$, pH_f , $[A^-]_{wf}$, $[OH^-]_f$, m_{sol} (the mass of “precipitate” CaA_2)

Parameters \Rightarrow K_{ow} , K_a , K_w and K_{CaA_2} (first 3 if only pH change – no precipitate)

The 7 final unknown quantities in the model can be found by numerically solving the 7 equations above, A1, A2, A3, A4, A6, A7=A8 and A9=A10.

<p>4 equilibria</p> $K_{ow} = \frac{[HA]_{nf}}{[HA]_{of}} \quad \text{A1}$ $K_a = \frac{[H^+]_f \cdot [A^-]_f}{[HA]_{nf}} \quad \text{A2}$ $K_w = [H^+]_f \cdot [OH^-]_f \quad \text{A3}$ $K_{CaA_2} = [Ca^{2+}]_f \cdot [A^-]_f^2 \quad \text{A4}$	<p>2 mass balance</p> $[HA]_{oi} \cdot M_{HA} \cdot V_o = [HA]_{of} \cdot M_{HA} \cdot V_o + [HA]_{nf} \cdot M_{HA} \cdot V_o + [A^-]_f \cdot M_A \cdot V_o + m_{sol} \left(\frac{2M_A}{M_{CaA_2}} \right) \quad \text{A5=A6}$ $[Ca^{2+}]_{oi} \cdot M_{Ca} \cdot V_o = [Ca^{2+}]_f \cdot M_{Ca} \cdot V_o + m_{sol} \left(\frac{M_{Ca}}{M_{CaA_2}} \right) \quad \text{A7=A8}$ <p>1 charge balance</p> $2[Ca^{2+}]_{oi} + [H^+]_i - [OH^-]_i = 2[Ca^{2+}]_f + [H^+]_f - [OH^-]_f - [A^-]_f \quad \text{A9=A10}$
--	--

Table 1: The 7 governing equations of the naphthenate deposition model when there is naphthenate formation. The relevant Eq. numbers in Appendix A are shown.

Initial pH of brine, pH _i	Final of brine (measured), pH _f Initial [HA] _{oi} in toluene				
	0.1 wt% (0.0033 M)	0.25 wt% (0.0083 M)	0.5 wt% (0.0166 M)	0.75 wt% (0.025 M)	1.0 wt% (0.0333 M)
6	5.5 5.4	5.1 5.0	4.8 4.7	4.2 4.0	3.5 3.4
5	5.0 4.9	4.5 4.4	4.2 4.1	4.0 3.9	3.3 3.2
4	3.9 3.8	3.5 3.3	3.0 2.9	2.8 2.7	2.5 2.4
3	3.0 2.9	2.7 2.6	2.5 2.4	2.2 2.1	2.0 1.9

Table 2: Experimentally measured final brine pH (pH_f) for various initial brine pH values, pH_i = 6, 5, 4 and 3; experiments were performed in duplicate.

Initial HA conc. in toluene, $[HA]_{oi}$	$pH_i = 6$	$pH_i = 5$	$pH_i = 4$	$pH_i = 3$
	pH_f	pH_f	pH_f	pH_f
0.1 wt% (0.0033M)	4.08	4.06	3.84	2.99
0.25 wt% (0.0083M)	3.88	3.87	3.72	2.99
0.5 wt% (0.0166M)	3.73	3.72	3.62	2.98
0.75 wt% (0.025M)	3.65	3.64	3.55	2.98
1.0 wt% (0.0333M)	3.58	3.58	3.50	2.99

Table 3: Calculated values of the final brine pH at initial brine pH values 6, 5, 4 and 3 using the values of $K_a = 7.0 \times 10^{-5}$ and $K_{ow} = 3.0 \times 10^{-2}$.

Calculated					
Calc pH =					
6	5.448326	5.049786	4.749296	4.100036	3.45002
Calc pH =					
5	4.94995	4.449995	4.149965	3.950015	3.25013
Calc pH =					
4	3.854	3.467254	3.338684	3.259624	3.20317
Calc pH =					
3	2.986463	2.968053	2.941693	2.918893	2.89915
Experimental					
Exp pH = 6	5.456	5.056	4.756	4.16	3.45
Exp pH = 5	4.955	4.455	4.155	3.955	3.25
Exp pH = 4	3.854	3.44	2.954	2.754	2.45
Exp pH = 3	2.953	2.653	2.453	2.153	1.95
Ka					
pH/Conc.	0.0033	0.0083	0.0166	0.025	0.0333
pH = 6	0.000277	0.000852	1.00E-05	5.95E-05	0.000772
pH = 5	0.000416	1.99E-05	0.000426	0.000505	0.00097
pH = 4	0.000881	0.001	0.001	0.001	0.001
pH = 3	0.001	0.001	0.001	0.001	0.001
Kow					
pH/Conc	0.0033	0.0083	0.0166	0.025	0.0333
pH = 6	1.00E-05	1.00E-05	0.001808	0.004206	0.004905
pH = 5	1.00E-05	0.005505	0.000609	0.000909	0.0097
pH = 4	0.002008	0.01	0.01	0.01	0.01
pH = 3	0.01	0.01	0.01	0.01	0.01

Table 4: Calculated pH_f values from the code and the corresponding K_a and K_{ow} for each pH_i value.

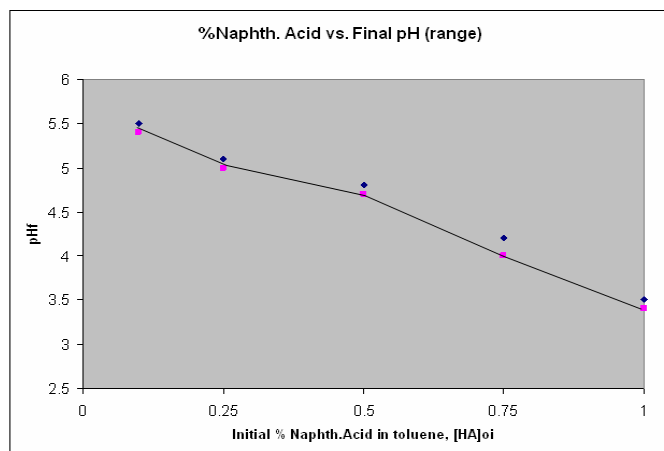


Figure 1: Plot of experimental pH_f values for a system vs. % naphthenic acid in toluene with $\text{pH}_i = 6$.

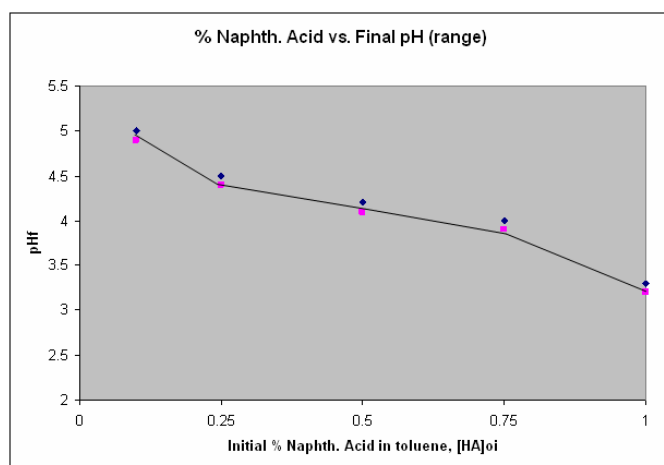


Figure 2: Plot of experimental pH_f values for a system vs. % naphthenic acid in toluene with $\text{pH}_i = 5$.

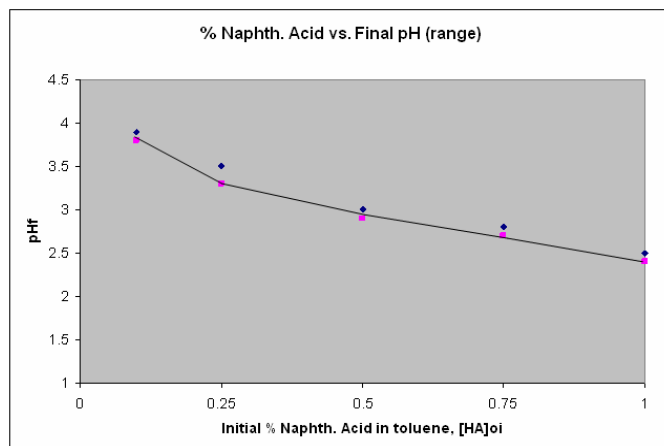


Figure 3: Plot of experimental pH_f values for a system vs. % naphthenic acid in toluene with $\text{pH}_i = 4$.

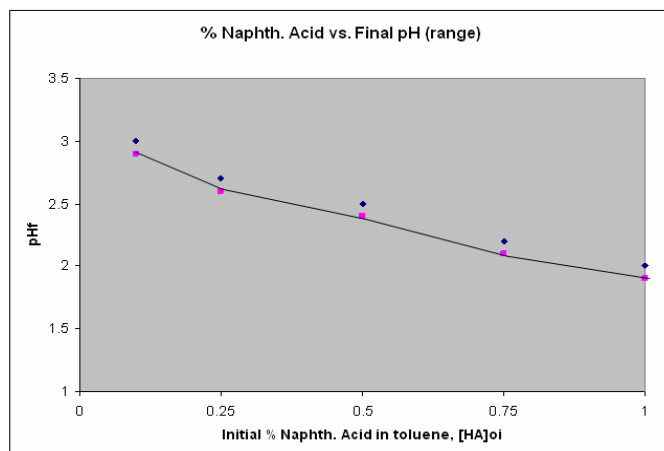


Figure 4: Plot of experimental pH_f values for a system vs. % naphthenic acid in toluene with $pH_i = 3$.

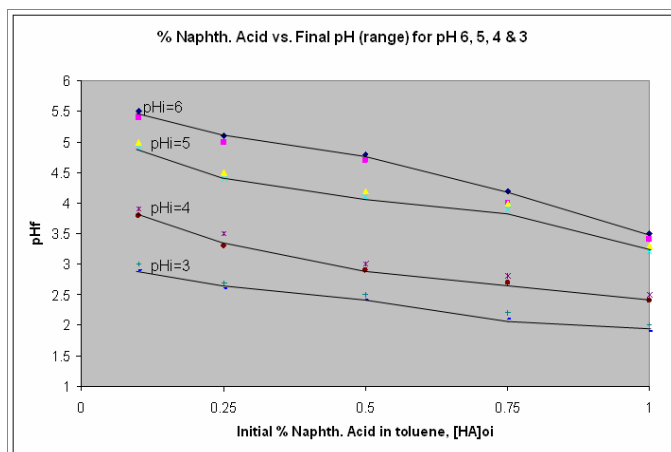


Figure 5: Summary of the plot of experimental pH_f values for the systems vs. % naphthenic acid in toluene with $pH_i = 6, 5, 4$ and 3 .

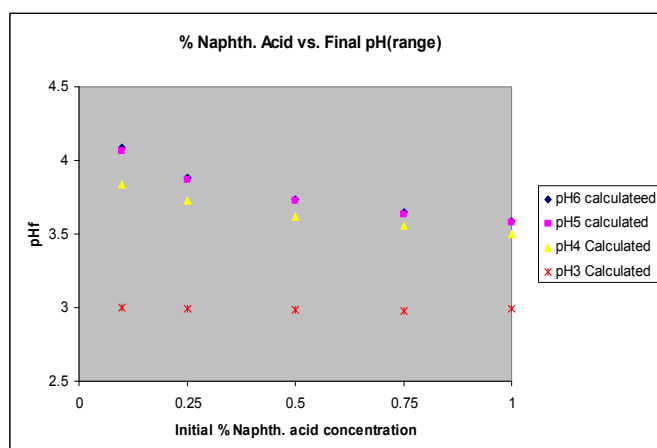


Figure 6: Plot of pH_f vs. initial % naphthenic acid for various values of initial pH_i for values of $K_a = 7.0 \times 10^{-5}$ and $K_{ow} = 3.0 \times 10^{-2}$.

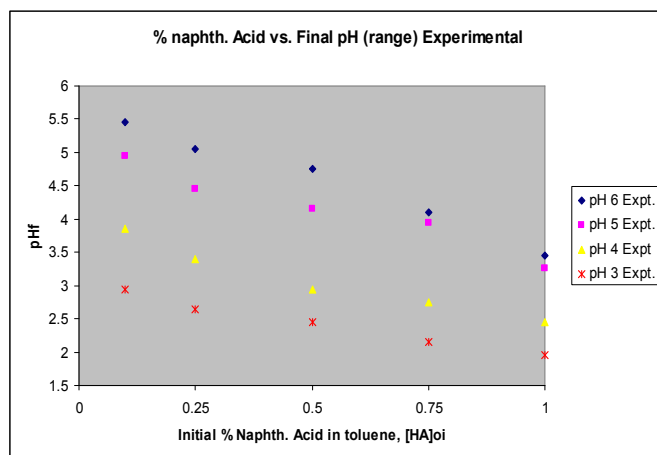


Figure 7: Plot of calculated pH_f vs. initial % naphthenic acid concentration for the case where different K_a and K_{ow} values were found by optimized fitting for each of the individual experiments.

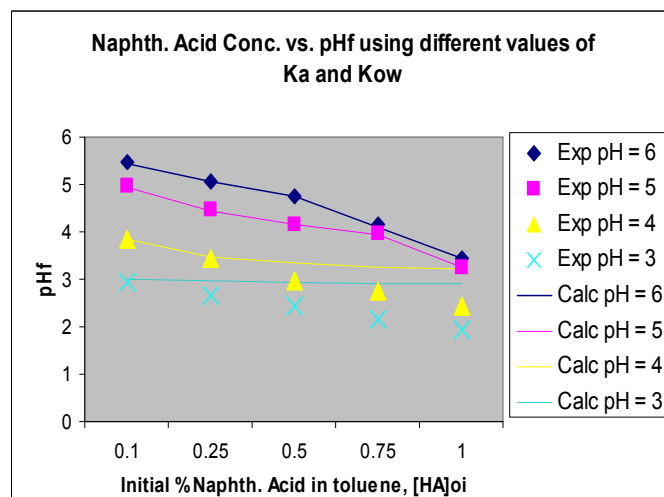


Figure 8: Comparison of the Experimental pH change data with the calculated pH_f vs. initial % naphthenic acid concentration for the case where different K_a and K_{ow} values were found by optimized fitting for each of the individual experiments.

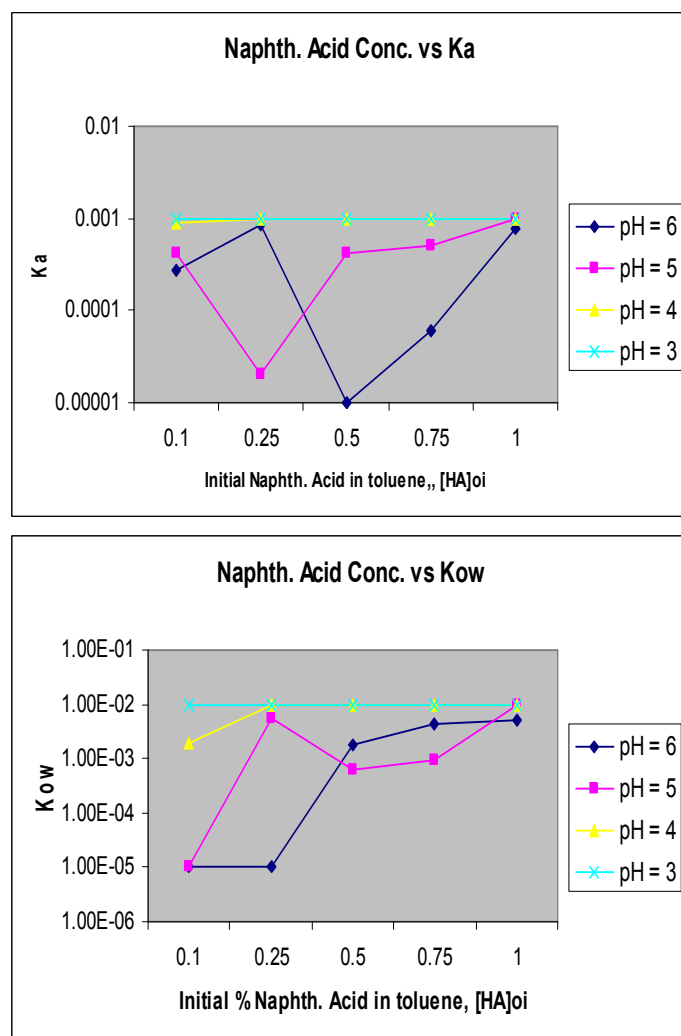


Figure 9: Plots of K_a vs. $[HA]_{oi}$ and K_{ow} vs. $[HA]_{oi}$ for the cases where K_a and K_{ow} are directly fitted for each pH change experiment; data in Table 4.

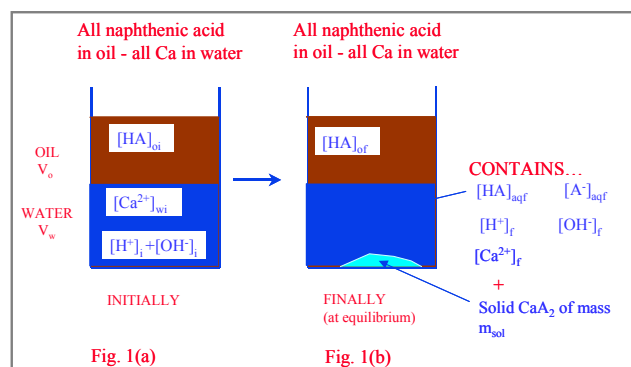


Figure A1: The schematic of a model naphthenate system, HA (a) at initial conditions with all the naphthenic acid in the oil and (b) at equilibrium where the HA has partitioned between the oil and aqueous phases and may have precipitated as a calcium salt (CaA_2 in this case). V_o and V_w are the volumes of oil and water, respectively (assumed that $V_o = V_w$ here). Note: the naphthenate precipitate actually forms at the interface, not in the bulk of the aqueous phase as shown here.