

# Thermodynamic Modeling of Naphthenate Formation and Related pH Change Experiments

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

## Summary

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, an equilibrium thermodynamic model is presented 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,  $[Ca^{2+}]$ , etc.). This model has, with some assumptions, been applied to both model and real naphthenate system.

This model describes two types of naphthenate experiment: 1) full naphthenate precipitation, and 2) simpler “pH change” experiments in which no precipitation occurs. To predict naphthenate precipitation, the theory suggests knowing: 1) the partition coefficient of the naphthenic acid, HA, between the oil and the water phases,  $K_{ow}$ ; 2) the  $pK_a$  of the naphthenic acid in water; and 3) the solubility product,  $K_{CaA_2}$  (or other similar solubility parameter), of the naphthenate deposit. In the simpler pH change experiments, only the first two of these parameters (i.e.,  $K_{ow}$  and  $pK_a$ ) are required. Using the naphthenate model without precipitation, the effect of varying parameters on the degree of pH change predicted at equilibrium in the oil/naphthenic acid/brine system was studied. Also, the model was used to examine the sensitivities of the various parameters on the final pH was also applied. 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 production (Goldszal et al. 2002; Laredo et al. 2004; Havre et al. 2003; Shepherd et al. 2005; Ese and Kirkpatrick 2004; Vinstad et al. 2003; Dyer et al. 2003; Gallup et al. 2002; Rousseau et al. 2001; Havre 2002; Sorbie et al. 2005). These naphthenate deposits have become an increasing flow assurance problem because of deposition and process disruption in production facilities (Goldszal et al. 2002; Vinstad et al. 2003; Gallup et al. 2002; Rousseau et al. 2001).

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. (2005). This work took the view that, to prevent naphthenate soap problems, a view of both the basic mechanism(s) through which they formed and a thermodynamic model to quantitatively describe their formation needed to be developed. An outline mechanism for the formation of naphthenate deposits was presented previously by Rousseau et al. (2001). Subsequent studies have used this conceptual mechanism to study deposition in both model and field naphthenate systems (Sorbie et al. 2005).

Naphthenic acids in hydrocarbons are defined as compounds containing carboxylic groups attached to saturated cyclic structures (Dyer et al. 2003; Havre 2002; Sorbie et al. 2005; Fan 1991; Gaiker and Maite 1996; Robbins 1998; Shepherd et al. 2006; Mohammed et al., forthcoming). 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 dissociate in accordance with normal equilibrium. However, with the exception of low-molecular weight acids, naphthenic acids are relatively insoluble in water (Havre 2002). 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<sub>f</sub>) in “pH change experiments” from which the quantities,  $K_{ow}$  and  $K_a$  can be calculated. These pH change experiments are how a naphthenate containing oil to contact a brine of given initial pH (pH<sub>i</sub>) and  $[Ca^{2+}]$  is allowed and lets the system equilibrate without the formation of naphthenate precipitates. Only this type of experiment is presented in this paper.

## pH Change Experiments

As previously noted, in this type of experiment, the effect of naphthenic acid mass transfer from the oil phase to the brine phase is observed when coming into contact and equilibrate. No naphthenate precipitate or emulsion was observed, because these experiments were performed at lower values of initial pH (pH<sub>i</sub> ≤ 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 1 g/100 ml (1% w/v ≡ 10,000 ppm) 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%, 0.25 wt%, 0.5 wt%, 0.75 wt%, and 1.0 wt%. Synthetic brine solution was prepared (composition: 25,000 ppm Na<sup>+</sup> and 20,000 ppm Ca<sup>++</sup>) by dissolving 63.55 g NaCl and 109.32 g of CaCl<sub>2</sub>·6H<sub>2</sub>O in a liter of distilled water. The solution was allowed to stand for 24 hours for proper dissolution, and it was filtered through a 0.45 μm filter before 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 do not precipitate when the solution pH value is below 6 with buffered systems (Laredo et al. 2004).

The oil (+ naphthenic acid) and brine (at pH<sub>i</sub>) phases were then contacted: 2 ml of adjusted pH brine phase were added to 2 ml of naphthenic acid samples in the toluene phase (10,000, 7,500, 5,000, 2,500, and 1,000 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.

**TABLE 1—THE SEVEN GOVERNING EQUATIONS OF THE NAPHTHENATE DEPOSITION MODEL WHEN THERE IS NAPHTHENATE FORMATION\***

<u>Four Equilibria</u>	
A1	$K_{ow} = \frac{[HA]_{wf}}{[HA]_{of}}$
A2	$K_a = \frac{[H^+]_f [A^-]_f}{[HA]_{wf}}$
A3	$K_w = [H^+]_f [OH^-]_f$
A4	$K_{CaA_2} = [Ca^{2+}]_f [A^-]_f^2$
<u>Two Mass Balance</u>	
A5=A6	$[HA]_{oi} M_{HA} V_o = [HA]_{of} M_{HA} V_o + [HA]_{wf} M_{HA} V_w + [A^-]_f M_A V_w + m_{sol} \left( \frac{2M_A}{M_{CaA_2}} \right)$
A7=A8	$[Ca^{2+}]_{wi} M_{Ca} V_w = [Ca^{2+}]_f M_{Ca} V_w + m_{sol} \left( \frac{M_{Ca}}{M_{CaA_2}} \right)$
<u>One Charge Balance</u>	
A9=A10	$(2 [Ca^{2+}]_{wi} + [H^+]_i - [OH^-]_i) = (2 [Ca^{2+}]_f + [H^+]_f - [OH^-]_f - [A^-]_f)$

\* the relevant equation numbers in Appendix A are shown

## Naphthenate Thermodynamic Modelling

The naphthenate precipitation model is illustrated in Fig. 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 seven unknowns are  $[HA]_{of}$ ,  $[HA]_{wf}$ ,  $[Ca^{2+}]_{wf}$ ,  $pH_f$ ,  $[A^-]_{wf}$ ,  $[OH^-]_f$ , and  $m_{sol}$  (the mass of solid “precipitate”  $CaA_2$ ). The four parameters in the model are  $K_{ow}$ ,  $K_a$ ,  $K_w$ , and  $K_{CaA_2}$ , and only the first three apply if there is no precipitation (pH change only). The seven final unknown quantities in the model can be found by numerically solving the seven equations A1, A2, A3, A4, A6, A7 = A8 and A9 = A10 in Appendix A and are summarized in **Table 1**.

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

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

and

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

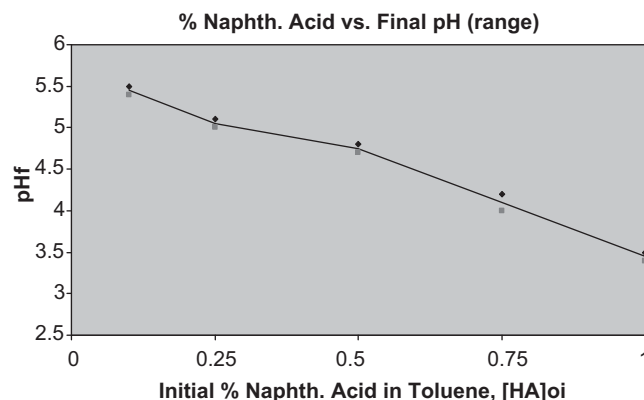
that gives us two equations in two unknowns that have been solved numerically by the Newton-Raphson method applied in a spreadsheet. Once  $[HA]_{wf}$  and  $[H^+]_f$  have been found, the remaining five unknowns can be found readily using the appropriate equations given in Appendix A.

## Experimental and Modeling Results

**pH Change Experiment.** In all these pH change experiments, 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 was observed. This decrease

is as expected from the model equations previously presented and is caused by 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  $K_a$ , as well as 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 transfers 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 (i.e.,  $pH_i = 3$ ) and high concentration of naphthenic acid in toluene (i.e., 10,000 ppm), the final brine pH value ( $pH_f$ ) change was less drastic than the change for high initial pH value (i.e.,  $pH_i = 6$ ). At an initial brine pH of 3, the solution is already very acidic therefore 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 **Figs. 1 through 4** for initial brine pH values 6, 5, 4, and 3, respectively.



**Fig. 1—Plot of experimental  $pH_f$  values for a system vs. % naphthenic acid in toluene with  $pH_i = 6$ .**

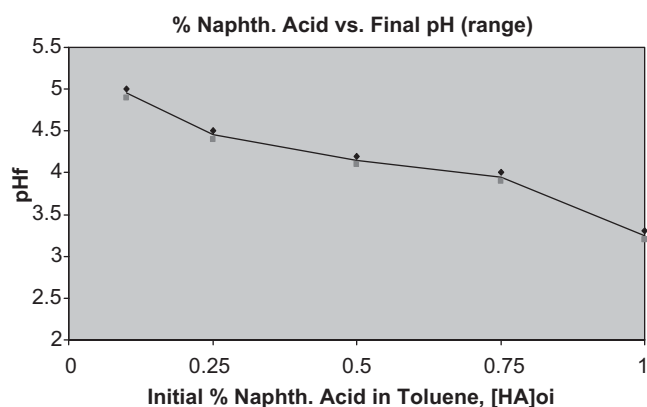


Fig. 2—Plot of experimental pH<sub>f</sub> values for a system vs. % naphthenic acid in toluene with pH<sub>i</sub> = 5.

Note: Each pH change experiment is performed in duplicate, and the results of each experiment repeat are shown in these figures. The reproducibility of these experiments is clearly very good. It can be observed from Figs. 1 and 2 (pH<sub>i</sub> = 6 and 5) that there is a sharp decrease in the pH<sub>f</sub> value as the concentration of naphthenic acid in toluene increases to minimum values of pH<sub>f</sub> = 3.45 and 3.25, respectively, at 1 wt% [HA]<sub>oi</sub>. At the lowest initial pH value (pH<sub>i</sub> = 3) in Fig. 4, a steady decrease was noticed to a pH<sub>f</sub> = 1.95 at 1 wt% [HA]<sub>oi</sub>. At lower brine pH, the HA is more in the protonated form and therefore remains in the oil phase, whereas at a higher pH, more mass transfer of naphthenic acid into the brine phase occurs. These pH change experimental results are summarized together for all experiments in Fig. 5, and these results can now be modeled using the thermodynamic model previously described.

**Modeling 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<sub>f</sub>) at the various initial brine pH<sub>i</sub> = 6, 5, 4, and 3, and initial naphthenic acid [HA]<sub>oi</sub> concentrations [0.0033 M (0.1 wt%), 0.0083 (0.25 wt%), 0.0166 (0.5 wt%), 0.025 (0.75 wt%), and 0.0333 (1.0 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  $1 \times 10^{-6}$  (pK<sub>a</sub> = 4 to 6) (Mohammed et al., forthcoming). In addition, it is well known that naphthenic acids are quite sparingly soluble in water and therefore the partition constant,  $K_{ow}$  (defined in Eq. A-1), is expected to be low, on the order of  $\sim 10^{-5}$  –  $10^{-3}$  (Havre 2002; Mohammed et al., forthcoming).

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 2 gives the final pH (pH<sub>f</sub>) values

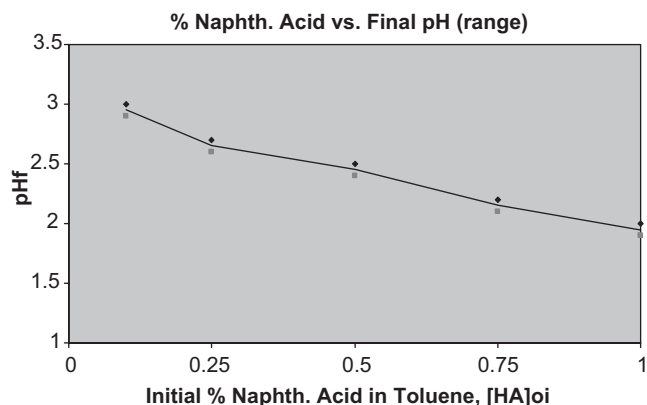


Fig. 4—Plot of experimental pH<sub>f</sub> values for a system vs. % naphthenic acid in toluene with pH<sub>i</sub> = 3.

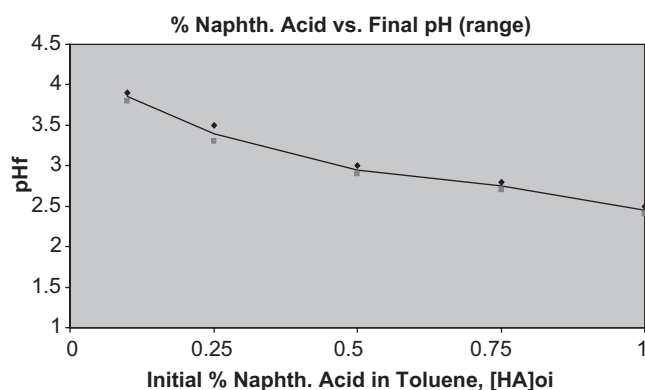


Fig. 3—Plot of experimental pH<sub>f</sub> values for a system vs. % naphthenic acid in toluene with pH<sub>i</sub> = 4.

calculated for the initial pH values 6, 5, 4, and 3, and a plot of these calculated pH<sub>f</sub> vs. initial naphthenic acid concentration [HA]<sub>oi</sub> is presented in Fig. 6. Comparing the graphs of experimental data (Fig. 5) with modeling data (Fig. 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<sub>i</sub> = 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 give a good qualitative representation for the observed behavior at lower initial pH values. For pH<sub>i</sub> = 3, the experimental final pH<sub>f</sub> ~2, whereas, the model prediction is that the pH hardly changes at all. To determine why the model is not reproducing experimental observations correctly, an alternative modeling approach was taken, as explained in the following section.

**Modeling Results—Approach 2.** Another modeling approach was investigated that involved trying to match each individual experiment in Table 3 using an optimized 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 conducted, it was 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<sub>f</sub>) vs. initial % naphthenic acid [HA]<sub>oi</sub> using the data from Table 4 is also presented in Fig. 7. A direct comparison with experiment is made for this approach in Fig. 8 in which it is observed that there is now a good

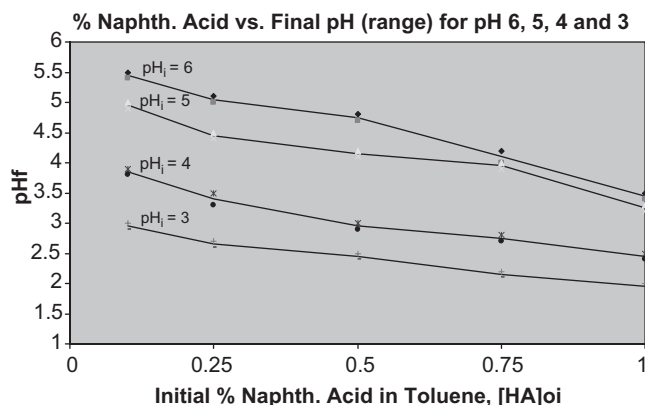
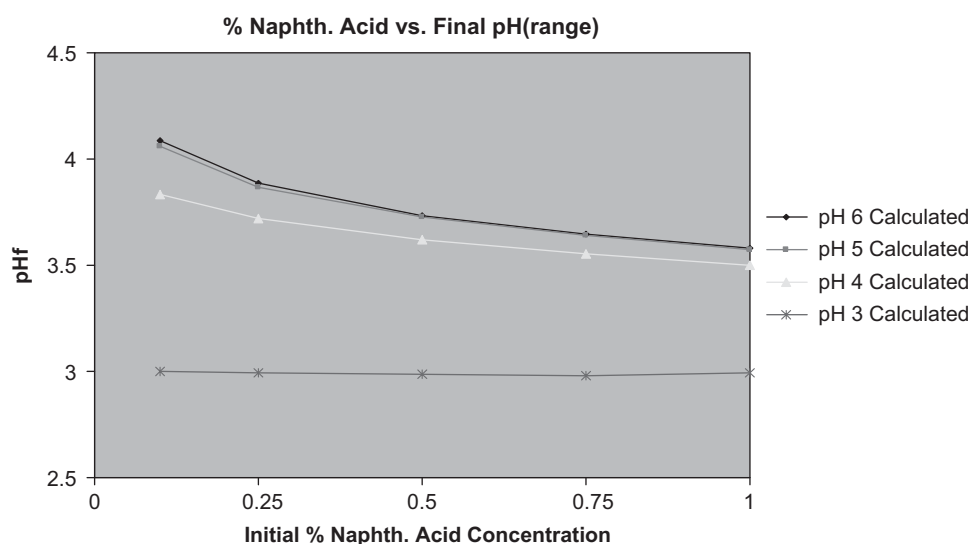


Fig. 5—Summary of the plot of experimental pH<sub>f</sub> values for the systems vs. % naphthenic acid in toluene with pH<sub>i</sub> = 6, 5, 4, and 3.

**TABLE 2—EXPERIMENTALLY MEASURED FINAL BRINE PH (pH<sub>f</sub>) FOR VARIOUS INITIAL BRINE pH VALUES\***

Initial pH of Brine (pH <sub>i</sub> )	Final of Brine (measured) pH <sub>f</sub> Initial [HA] <sub>oi</sub> in Toluene				
	0.1 wt% (0.0033M)	0.25 wt% (0.0083M)	0.5 wt% (0.0166M)	0.75 wt% (0.025M)	1.0 wt% (0.0333M)
6	5.5	5.1	4.8	4.2	3.5
	5.4	5.0	4.7	4.0	3.4
5	5.0	4.5	4.2	4.0	3.3
	4.9	4.4	4.1	3.9	3.2
4	3.9	3.5	3.0	2.8	2.5
	3.8	3.3	2.9	2.7	2.4
3	3.0	2.7	2.5	2.2	2.0
	2.9	2.6	2.4	2.1	1.9

\* pH<sub>i</sub> = 6, 5, 4 and 3; experiments were performed in duplicate



**Fig. 6—Plot of pH<sub>f</sub> vs. initial % naphthenic acid for various values of initial pH (pH<sub>i</sub>) for values of  $K_a = 7.0 \times 10^{-5}$  and  $K_{ow} = 3.0 \times 10^{-2}$ .**

**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  $K_{ow} = 3.0 \times 10^{-2}$**

Initial HA Conc. in Toluene, [HA] <sub>oi</sub>	pH <sub>i</sub> = 6	pH <sub>i</sub> = 5	pH <sub>i</sub> = 4	pH <sub>i</sub> = 3
	(pH <sub>f</sub> )	(pH <sub>f</sub> )	(pH <sub>f</sub> )	(pH <sub>f</sub> )
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

quantitative and qualitative correlation between the experimental and the calculated data at higher pH values of 6 and 5, and a moderate qualitative behavior at lower pH values. The corresponding plots of best fit  $K_a$  and  $K_{ow}$  values vs. initial naphthenic acid concentration ([HA]<sub>oi</sub>) for the individual experiments is shown in **Fig. 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, known (from Electrospray Mass Spectrometry and Atmospheric Pressure Chemical Ionisation Mass Spectrometry results) to have many naphthenic acids (HA) components (Sorbie et al. 2005;

Mohammed et al., forthcoming). 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 by considering only a single “pseudonaphthenic acid” species denoted as HA, which 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<sub>i</sub> → pH<sub>f</sub> is governed only by the parameters of  $K_a$  (naphthenic acid dissociation constant) and  $K_{ow}$  (partition coefficient) and the initial conditions (pH<sub>i</sub> and [HA]<sub>oi</sub>).

TABLE 4—CALCULATED pH <sub>i</sub> VALUES FROM THE CODE AND THE CORRESPONDING $K_a$ AND $K_{ow}$ FOR EACH pH <sub>i</sub> VALUE					
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
$K_a$					
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
$K_{ow}$					
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

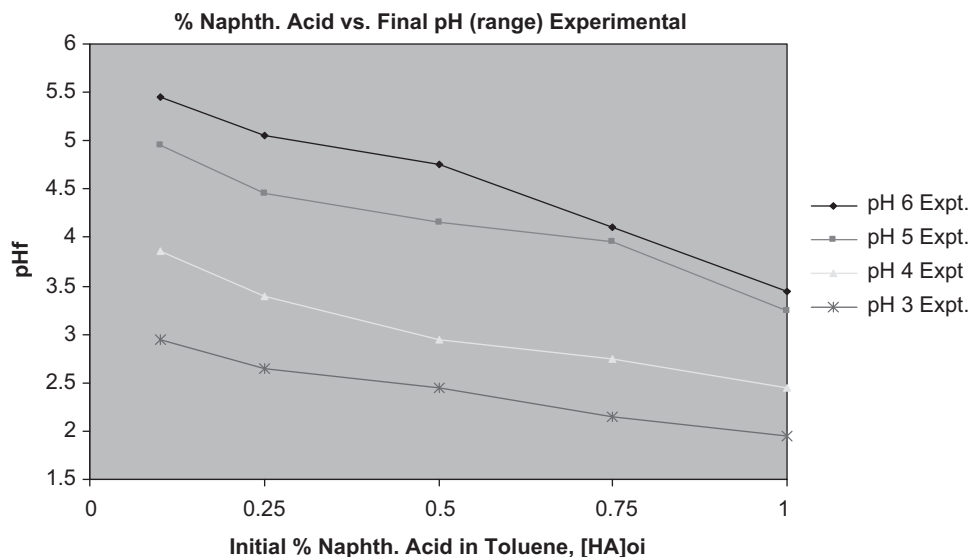


Fig. 7—Plot of calculated pH<sub>i</sub> vs. initial % naphthenic acid concentration for the case where different  $K_a$  and  $K_{ow}$  values were found by optimized fitting for each of the individual experiments.

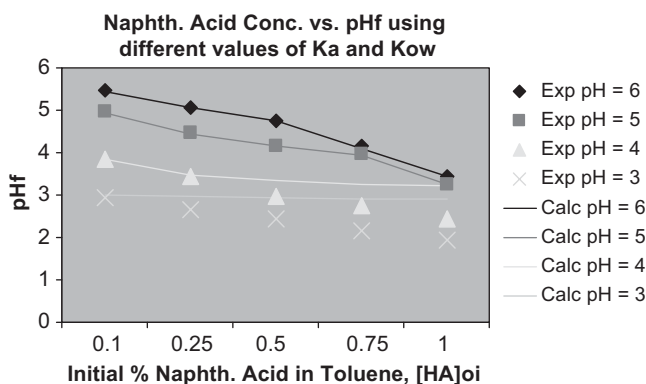
The pH change experimental results showed a progressive change in brine pH value (i.e., from high to low) when mixing of the oil phase (extracted naphthenic acid dissolved in toluene) with the brine phase. Applying our thermodynamic naphthenate model to the pH change experiments reveals that, at a higher 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 behavior 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.

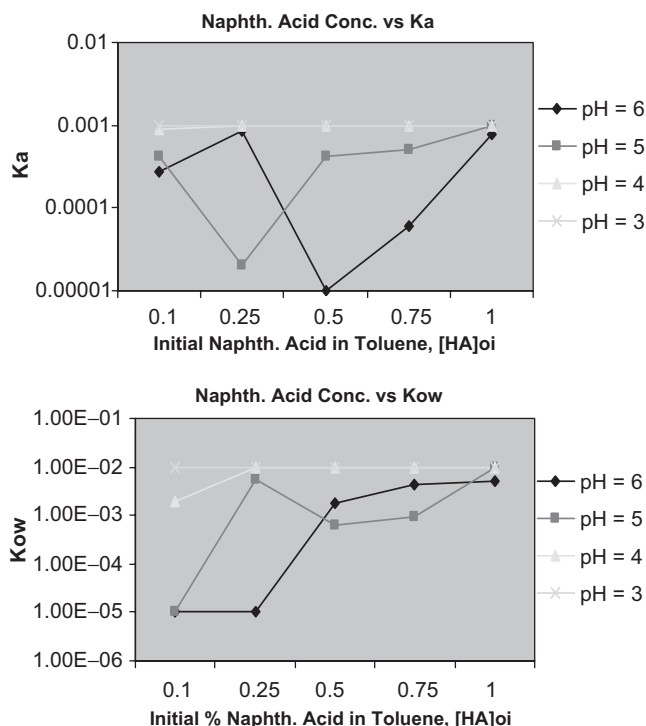
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**Fig. 8—Comparison of the experimental pH change data with the calculated pH, vs. initial % naphthenic acid concentration for the case where different  $K_a$  and  $K_{ow}$  values were found by optimized fitting for each of the individual experiments.**



**Fig. 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.**

## References

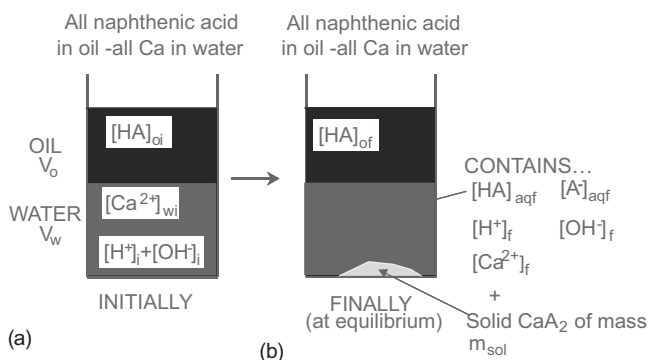
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## Appendix A—Naphthenate Modeling

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 **Fig. A-1** in which the initial and final conditions are shown. Note: 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” experiments presented in this paper is subsequently discussed. The usual principles of scale prediction are used to derive the set of constraint equations for the naphthenate formation as follows:

- 1) Set up the chemical system, which in this case involves partitioning of the naphthenic acid between the oil and water phases described by a water oil partition factor,  $K_{ow}$ .
- 2) 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).
- 3) From the initial conditions of naphthenic acid in the oil only where  $[HA] = [HA]_{oi}$  and calcium in the water only,  $[Ca^{2+}] = [Ca^{2+}]_{wi}$  set up the mass balance equations (one for “A” and one for Ca).
- 4) Write the one charge balance equation for the aqueous phase.



**Fig. A-1—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<sub>2</sub> 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.

As subsequently shown, 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 Fig. A-1 in which the initial conditions are shown in Fig. A-1a, and the final (equilibrium) situation is shown in Fig. A-1b. 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  $M_{CaA_2} = M_{Ca} + 2M_A$ ). In Fig. A-1, “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  $H^+$ ,  $Ca^{2+}$ , and  $A^-$ , do not require any subscripts “aq” or “o,” because they only appear in the aqueous phase. The set of equations governing this system can be written as follows:

#### Equilibrium Partitioning and Solution Equilibrium.

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

$$K_{ow} = \frac{[HA]_{aq,f}}{[HA]_{o,f}} \quad \text{..... (A-1)}$$

It is noted that the HA may become less soluble as the salinity of the aqueous phase increases (i.e.,  $K_{ow}$  is 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.

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

$$K_a = \frac{[H^+]_f \cdot [A^-]_f}{[HA]_{aq,f}} \quad \text{..... (A-2)}$$

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 as follows:

$$K_w = [H^+]_f \cdot [OH^-]_f \quad \text{..... (A-3)}$$

where  $K_w$  is on the order of  $1.0 \times 10^{-14}$ .

3) 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:

$$K_{CaA_2} = [Ca^{2+}]_f \cdot [A^-]_f^2 \quad \text{..... (A-4)}$$

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

#### Mass Balance

1) The initial mass of the “A” species,  $m_{Ai}$ , is as follows:

$$m_{Ai} = [HA]_{oi} \cdot M_{HA} \cdot V_o \quad \text{..... (A-5)}$$

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

$$m_{Af} = [HA]_{of} \cdot M_{HA} \cdot V_o + [HA]_{wf} \cdot M_{HA} \cdot V_w + [A^-]_f \cdot M_A \cdot V_w + m_{sol} \left( \frac{2M_A}{M_{CaA_2}} \right) \quad \text{..... (A-6)}$$

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

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

$$m_{Ca,i} = [Ca^{2+}]_{wi} \cdot M_{Ca} \cdot V_w \quad \text{..... (A-7)}$$

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

$$m_{Ca,f} = [Ca^{2+}]_f \cdot M_{Ca} \cdot V_w + m_{sol} \left( \frac{M_{Ca}}{M_{CaA_2}} \right) \quad \text{..... (A-8)}$$

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

**Charge Balance.** 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:

$$C_i = (2[Ca^{2+}]_{wi} + [H^+]_i - [OH^-]_i) \cdot V_w \quad \text{..... (A-9)}$$

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

$$C_f = (2[Ca^{2+}]_f + [H^+]_f - [OH^-]_f - [A^-]_f) \cdot V_w \quad \text{..... (A-10)}$$

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

**Model Summary.** The model is defined by the following initial conditions, final conditions and parameters (Fig. A-1).

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

**Final Seven Unknown Quantities.**  $\Rightarrow [HA]_{of}$ ,  $[HA]_{wf}$ ,  $[Ca^{2+}]_{wf}$ ,  $pH_f$ ,  $[A^-]_{wf}$ ,  $[OH^-]_f$ , and  $m_{sol}$  (the mass of “precipitate”  $CaA_2$ ).

**Parameters.**  $\Rightarrow K_{ow}$ ,  $K_a$ ,  $K_w$ , and  $K_{CaA_2}$  (first three, if only pH change—no precipitate).

The seven final unknown quantities in the model can be found by numerically solving the previous seven equations: A-1, A-2, A-3, A-4, A-6, A-7 = A-8, and A-9 = A-10.

**Murtala Ahmed Mohammed** holds BSc and MSc degrees, and is currently a PhD student in petroleum engineering at Heriot-Watt University working on Naphthenate problems in oil production. He is a member of SPE. **Ken S. Sorbie** holds BSc and D.Pil degrees and is a professor of petroleum engineering at Heriot-Watt University. **Andrew G. Shepherd** holds a PhD degree in petroleum engineering and is an SPE member.