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Stabilization of Water-in-Oil Emulsions by Naphthenic Acids and Their Salts: Model Compounds, Role of pH, and Soap : Acid Ratio[#]

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ABSTRACT

Increasingly, crudes of high acidity are observed in production of petroleum reserves. Naphthenic acids, which are generally cyclic and branched aliphatic carboxylic acids, are interfacially active and adsorb at water–oil interfaces to form monolayers, liquid crystalline films, and other colloidal structures. A serious challenge in petroleum production is the resulting stabilization of water-in-oil emulsions, which can cause problems in topside and subside separators, and in refining processes. A variety of acids and their corresponding soaps have been thoroughly studied in order to investigate how these compounds interact in aqueous solutions at different pH, and how these association structures relate to emulsion formation and stability. The formation of aggregates and hence, the stabilizing properties of this class of material are strongly sensitive to the relative proportion of uncharged acid and charged soap anion. In this paper, we review our experimental results on naphthenic acid/naphthenate stabilized emulsions utilizing several model compounds, including heptylbenzoic acid (HB), *trans*-4-pentylcyclohexane-carboxylic acid (PCA), and 5-β-cholanic acid (CA).

Key Words: Napthenic acid; Heptylbenzoic acid; Water-in-oil emulsion; pH.

INTRODUCTION

Exploitation of oil fields containing acidic petroleum will inevitably give rise to many challenges through the line of production, such as

1. Acids together with their corresponding soaps are surface- and interfacially active, resulting in adsorption at the oil/water interface, and hence formation of stable colloidal

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[#] A special tribute to Dr. Jan Czarnecki on the occasion of his 65th birthday.

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structures.[1,2] These structures hinder separation process,[3] and complicate fluid transport.

2. Calcium or magnesium soaps of low water and oil solubility might form. Precipitation of Ca^{2+}- or Mg^{2+}-naphthenates in oil/water separators, de-salters, tubes and/or pipelines might cause severe operational problems.[4–8]
3. Acidic species in the petroleum are known to cause corrosion problems during refining and transport.[9–12] Acids might also interact with added corrosion inhibitors, and thus negatively impact inhibitor efficiency.
4. Compared to other crude oil components, low molecular weight acids have relatively high water solubility. Acidic wastewaters present severe environmental problems.[13]

Considering these and related problems, it is clear that a better understanding of the surface activity, adsorption properties, and emulsion-stabilizing capability of crude oil acids (naphthenic acids) is of crucial importance to our ongoing ability to address and cope with these issues.

Naphthenic acids are defined as carboxylic monoacids with the generic formula RCOOH, where R is any cycloaliphatic structure. However, in general the term "naphthenic acid" is used to describe all carboxylic acids present in crude oils, also including aromatic and acyclic acids. This class of material is, like most petroleum fractions, a complicated mixture of compounds. Characterization studies of these acids have been carried out by means of many different methods and analytical techniques.[1,2,14–20] Based upon these studies naphthenic acids can be described mainly as C_{10}–C_{50} compounds with 0–6 fused rings, most of which are saturated, where the carboxylic acid group is attached to a ring through a short side chain.[21] The fact that naphthenic acids with similar molecular weight and total acid number (TAN) might have remarkably different molecular structures[22] and ability to stabilize emulsions increases the complexity of mixtures of these materials.

Even though nearly all crude oils contain some naphthenic acids, some are more acidic than others; heavy crudes—i.e., crudes of high gravity and asphaltene content—usually contain more acid than paraffinic crudes.[23]

Naphthenic acids found in petroleum originate from in-reservoir biodegradation of hydrocarbons in fossil deposits.[24] Naphthenic acids act as biological markers, and are closely linked to the maturity and biodegradation level of the fields.[5]

While the literature on characterization of naphthenic acids remains sparse, paraffinic fatty acids have been thoroughly studied with regard to association and micellization in water, phase equilibrium, formation of lyotropic liquid crystals and microemulsions, monomolecular film properties, ternary phase equilibria, and related properties.[25–42]

Friberg[43–46] has documented a dramatic enhancement of emulsion stability when a lamellar liquid crystalline phase (LLC) is present in a three-phase system. The liquid crystalline phase adsorbs onto and coats the emulsion droplets, reducing the interface mobility and bending ability[47] and providing for a more gradual density variation across the oil–water interface. All of these effects serve to stabilize the emulsion droplets. This increased film rigidity hampers the coalescence of the emulsion droplets. Skurtveit et al.[29] has also shown the importance of stabilization of oil continuous emulsions due to presence of LLC. Urdahl and Sjoblom[48] emphasized the possibility of LLC-stabilization of crude oil and water emulsions.

Microemulsions are also widely known to have a profound effect on emulsion stability. Dramatic changes in emulsion stability have been reported by several groups;[49–51] the presence of microemulsions reduces emulsion stability. Friberg proposed a mechanism[46] that might explain these observations. In a system containing microemulsions, low interfacial tension and low bending resistance is found. Deformation of approaching droplets, due to their mutual van der Waals attractions, increases the coalescence rate and hence reduces the emulsion stability.

The above discussion indicates the link between phase equilibrium in water/oil/surfactant systems and emulsion stability. From this it is clear that mapping of the phase behavior together with the emulsion stability might provide valuable insight with respect to efficient methods for manipulation of emulsion stability. Horvath-Szabo, Czarnecki, and coworkers have studied the phase equilibria of sodium naphthenates in aqueous solutions[52] and "sodium naphthenates/toluene/water" systems.[50] Their elegant work demonstrates that liquid crystalline phases dominate a large composition range and are largely responsible for stabilization of emulsions. However, by adding heptane to this system Horvath-Szabo, Czarnecki, and coworkers illustrated that the LLC phase range was reduced while the microemulsion phase range was increased. As a result, the region where stable w/o-emulsions existed was reduced.[51] Horvath-Szabo and coworkers have also demonstrated the presence of sodium naphthenate liquid crystalline phases at oil/water interfaces.[47]

In this article, we have investigated the emulsions stabilized by different model compounds. 5-β-cholanic acid (CA), 4-heptylbenzoic acid (HB), or *trans*-4-pentylcyclohexane-carboxylic acid (PCA) have been used as model compounds because the structures of these chemicals are believed to resemble the naphthenic acids found in crude oils (Table 1). The inversion from water continuous to oil continuous emulsions with varying pH and concentration has been studied. Stability of oil-in-water emulsions was mapped by means of centrifugation experiments.

EXPERIMENTAL

Chemicals

All chemicals were used as supplied without any purification. CA (99%, Sigma), HB (97%, Aldrich), and PCA (99%, Aldrich) were used as model compounds. The chemical structures of these compounds are shown in Table 1. Toluene (99.8%, Fisher) and *n*-heptane (99.6%, Fisher) were used as the oil phase (a 50/50 mixture by volume). NaOH (98%, Fisher) was used to adjust the pH in the aqueous phase. NaCl (99.5%, Fluka) was added to the water phase in order to illustrate the effect of altering the ionic strength of the solution.

Methods

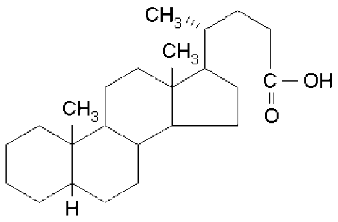
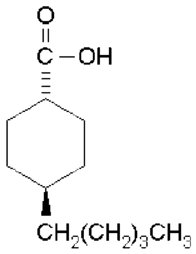
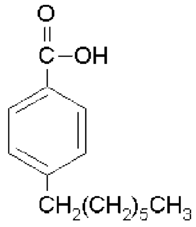
Emulsification

The emulsions were prepared by adding the model compounds to 1.3 g pH-adjusted water or brine (3.5 wt% NaCl in water). The pH of the aqueous phase was pre-adjusted with NaOH, and the pH was measured by means of a calibrated pH-meter. This blend was mixed with equal amounts of a toluene/heptane solution (50/50 by volume). The emulsification was carried out using a 750-W Virtis Cyclone I.Q. Homogenizer with a 6 mm rotor-stator mixing head. The oil/water-blend was mixed at 15,000 rpm for 3 min. Between each mixing step, the mixtures were allowed to equilibrate for 12–24 h.

Emulsion Characterization (w/o or o/w)

Immediately following the emulsification, the nature of the emulsion, whether it was oil- or water continuous, was determined by adding a droplet of the emulsion to pure oil phase or pure aqueous phase. The procedures discussed so far are illustrated in Fig. 1. Based on the

Table 1. Structure of CA, PCA, and HB.

Short	Full name	Structure
CA	5-*β*-Cholanic acid	
PCA	*trans*-4-Pentylcyclohexane-carboxylic acid	
HB	4-Heptylbenzoic acid	

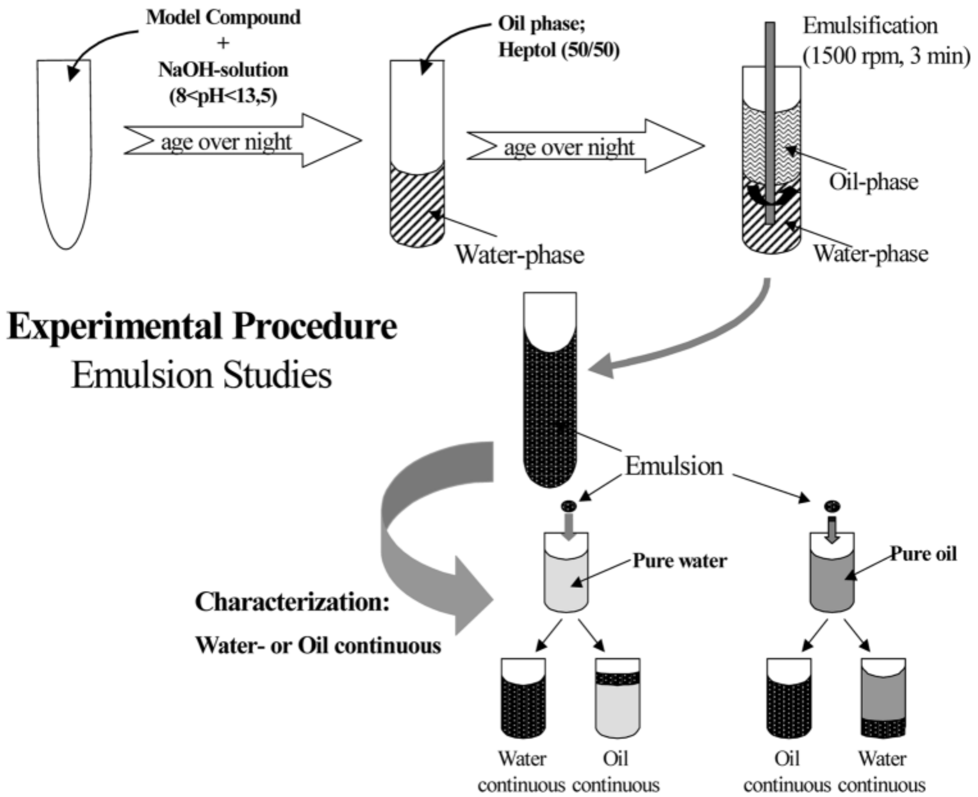


Figure 1. Schematic illustration of emulsion-making protocol and method for determining the continuous phase of the emulsion.

observed dissolution characteristics of these droplets and the resulting growth of the bulk phases or layering of the droplets, the continuous phase of the emulsion was easily identified.

Emulsion Stability

After homogenization, a known mass of the emulsion was transferred into 2.0 mL microcentrifuge tubes. Following a 30 min period of ageing, the emulsions were centrifuged for 30 min at 10,000 rpm in an Eppendorf MiniSpin plus centrifuge. Usually three layers were observed following centrifugation corresponding to creamed oil, emulsion, and coalesced water. Resolved water was recovered by means of a glass pipette, and transferred to a pre-weighed container. Emulsion stabilities were calculated from the volume of water resolved as shown in Eq. (1):

$$\begin{aligned}\%\ \text{Water recovered} \\ &= \frac{\text{Mass water resolved}}{\text{Mass of emulsion}} \times 100 \\ &\quad \times \text{fraction of water in emulsion}\end{aligned} \qquad (1)$$

Microscopy

A drop of the fluid of interest was placed on a glass slide followed by a cover slide. Images were captured with an Olympus BH-2 microscope and Olympus PM-10AD 35 mm camera system. Photographs were taken of several regions from each slide in order to capture the representative structure of each fluid.

RESULTS AND DISCUSSION

CA in pH Adjusted Water

Figure 2 identifies the emulsion type (w/o or o/w) and a qualitative gauge of stability of the emulsions formed by CA in water at varying CA-concentrations and pH; and hence varying acid/soap-ratios. The acid/soap-ratio is calculated based on the fact that a strong base will react completely with a weak acid. Hence, the total number of NaOH-molecules (n_{OH^-}-ions) added to the system is equal to the number of ionized CA-molecules ($n_{\text{CA-soap}}$). At high pH (pH = 13.2), the acid/soap-ratio is low, which implies that the negatively

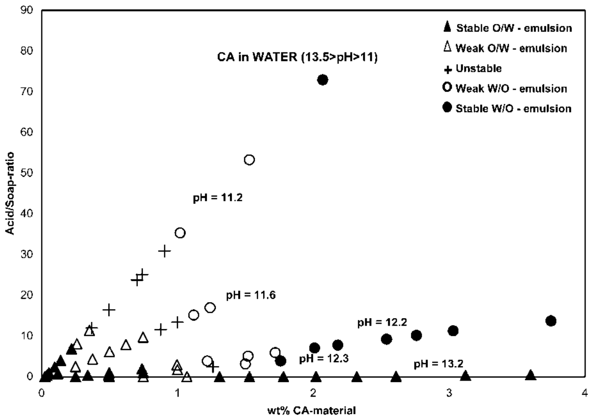


Figure 2. Emulsion type and relative stability of CA-stabilized emulsions comprise pH-adjusted water and heptol (see Methods section for more detail) as functions of CA concentration and acid/soap-ratio.

charged sodium soap is the compound that dominates the chemistry in the solution. Electrostatically stabilized water continuous emulsions are formed for all the investigated concentrations of CA at this highest pH. Even at ~13 wt% (data not shown), a concentration at which there are five times more acid than soap species in the solution, the total concentration of soap is high enough to form stable o/w-emulsions.

Reducing the pH produces an inversion in the type of emulsion; with increasing CA-concentration at intermediate pH values (10.5–12.5), a transition from water- to oil continuous emulsions is observed. Typically, as CA concentration is increased and the acid/soap-ratio correspondingly increases, water continuous emulsions are observed at the lowest concentrations. At higher CA concentrations, a region with no emulsion stability is typically found before the oil continuous emulsions are formed. Two completely different stabilizing mechanisms are dominating the system depending on whether acid or soap dominates the chemistry in the mixture. A soap-dominated system will, as mentioned above, give rise to electrostatically stabilized emulsions. However, in a system where the acid/soap-ratio is high, the CA molecules with a distribution of charge form ordered liquid crystalline structures which adsorb to the water droplets dispersed in the oil, and hence stabilize the emulsion.

CA is amphiphilic in character but has relatively short, bulky, and compact hydrophobic moities, and thus falls into the category of components that forms hydrotropes.[52–55] Beyond the minimal hydrotropic concentration (MHC), the molecules self-aggregate to yield open-layer structures, reminiscent of LLC, consisting of alternating hydrophobic clustering of the nonpolar regions adjacent to ionic or polar regions that are knitted together in a 2D network. Figure 3 shows micrographs of CA-material (intermediate acid/soap-ratio) in water under cross-polarized light. From these pictures, it is obvious that an ordered liquid crystalline structure is formed. The molecular packing parameter (MPP) might also be a good indication as to what kind of aggregates might be formed by CA at the conditions studied here. MPP gives a connection between the shape of the monomer and the type of aggregate structure it is likely to form:

$$\mathrm{MPP} = \frac{V_\mathrm{t}}{a_\mathrm{h} l_\mathrm{c,t}} \tag{2}$$

where V_t is the volume of the hydrocarbon tail of the surfactant/lipid in the core, a_h is the area of polar head group, and $l_\mathrm{c,t}$ is the effective length of the hydrocarbon chain in the liquid state.

MPP-values in the order of unity will favor formation of planar association structures, like LLC or hydrotropes, while molecules with lower MPP-values will tend to form spherical or cylindrical aggregates and MPP > 1 results in inverted micelle formation.

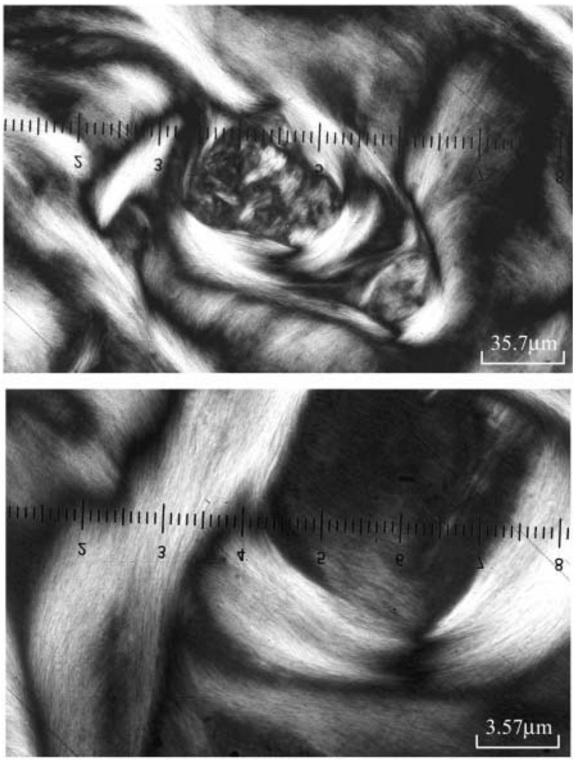


Figure 3. Optical polarizing micrographs of precipitate phase of CA in water at intermediate pH values (11–12.5). Layered birefringent textured appearance is typical of lamellar liquid crystals and hydrotropes.

Changing acid/soap-ratios from low to high will affect the area of polar head groups, and thus the MPP-value, in two ways:

1. The majority of the head groups are no longer charged, and hence the electrostatic repulsions between the polar parts of the molecules are weakened, which leads to a reduced effective area of each head group (a_h).
2. H-atoms present on the acidic head group enable formation of H-bonds, which will "knit" the polar groups closer together, and possibly further reduce a_h.

Taking the shape and volume of the model compound into consideration; the short hydrocarbon chain gives a relatively small value of $l_{c,t}$ while the rather large volume of the bulky hydrocarbon moiety results in large V_t. Consequently, MPP will be large (on the order of unity), especially for high acid counts, which allows for lamellar structures.

The presence of the intermediate region between water- and oil continuous emulsions, where no stable emulsions are formed, might be explained as a result of the transition in stabilizing mechanisms going. Under these conditions, neither the acid nor the soap concentration is sufficiently high to mask the competing mechanism.

CA in pH Adjusted Brine (3.5 wt% NaCl)

In order to verify the electrostatic stabilizing mechanism responsible for formation of o/w-emulsions at low acid/soap-ratios and to probe the impact of ionic strength, electrolyte was added to the aqueous phase. Figure 4 shows the type of emulsions formed with CA as stabilizing material in a 3.5 wt% NaCl solution at varying pH (acid/soap-ratio).

The presence of an electrolyte in the system prevents the formation of water continuous emulsions altogether. Under a threshold combination of CA-concentration and acid/soap-ratio, no emulsion stability is observed until protonated acid molecules dominate the chemistry in the system, and w/o-emulsions are formed. This confirms that the o/w-emulsions are indeed electrostatically stabilized. In addition to this absence of oil-in-water emulsions, it is also observed that oil continuous emulsions are formed at lower total CA-concentration when brine is used as the aqueous phase. The explanation for this can be found in the interactions between the different stabilizing mechanisms mentioned above. Under these conditions, the competing electrostatic mechanism has been eliminated, so the only possible mechanism is stabilization by ordered association structures covering the dispersed water droplets in the emulsion. Figure 5 shows a typical micrograph of a CA-stabilized w/o-emulsion. The stabilizing liquid crystalline films appear as white (shining) regions under cross-polarized light.

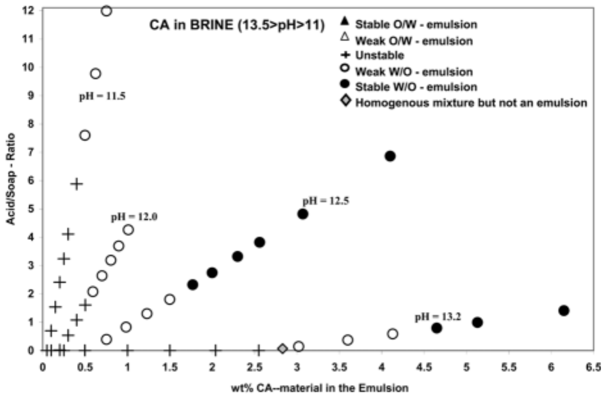


Figure 4. Emulsion type and relative stability of CA-stabilized emulsions comprise pH-adjusted water to which 3.5% (w/w) of NaCl has been added and heptol (see Methods section for more detail) as functions of CA concentration and acid/soap-ratio.

A curiosity is observed at relatively high CA-concentration (~2.8 wt%), with brine at pH = 13.2 as solvent and acid/soap-ratio just above zero; a homogenous phase is seen which is not an emulsion (through study of the mixed sample by means of microscopy). We believe this phase consists of swollen ordered association structures of CA-soap, where the oil phase is trapped inside the lamellar network.

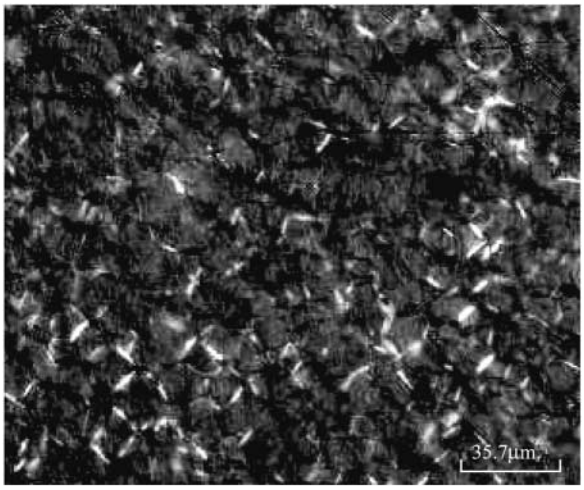


Figure 5. Optical polarizing micrograph of CA-stabilized oil-continuous emulsion.

Effect of pH on Threshold CA-Concentration for Formation of w/o-Emulsion

Figure 6 illustrates how pH in the aqueous phase influences the concentration of stabilizing material (CA) needed in order to produce a water-in-oil emulsion. A minimum in total CA-concentration is observed for the pH-region between ~11.2 and ~12.2. This implies an acid/soap-ratio between 35 and 4 with water as solvent and between 8 and 2 with brine as solvent. The reason this ratio needs to be higher without electrolyte present is because the electrostatic stabilization mechanism needs to be overcome in this environment. In other words, there exists an optimal combination of total CA-concentration and acid/soap-ratio. An acid/soap-ratio lower than the optimal implies more soap and hence more charged species in the system, which might hamper the formation of ordered lamellar structures. However, some soap present in the system might have a positive effect on the aggregate formed. The negative charge on the soap might interact with the protons on the acid groups and "knit" the head groups even closer together. Hence, under optimal conditions (A/S-ratio) the total CA-concentration needed to form stabilizing association structures is at its minimum.

Stability of CA-Stabilized Emulsions

In order to quantify the stability of these CA-stabilized oil-continuous emulsions, the centrifugal method of gauging stability was employed. A plot of resolved water after centrifugation at different pH and CA-concentration is shown in Fig. 7. According to these data a rather narrow set of conditions yield emulsions of high stability; at an initial water pH of ~12, stable water-in-oil-emulsions are formed at CA-concentrations around 1.6 wt% and above an acid/soap of 5. Emulsions formed when adding CA to aqueous solution of pH lower than ~12 are relatively weak. These conditions correspond to acid/soap-ratios considerably higher than what seems to be the optimal acid/soap-mixture with approximately five times more acid than soap.

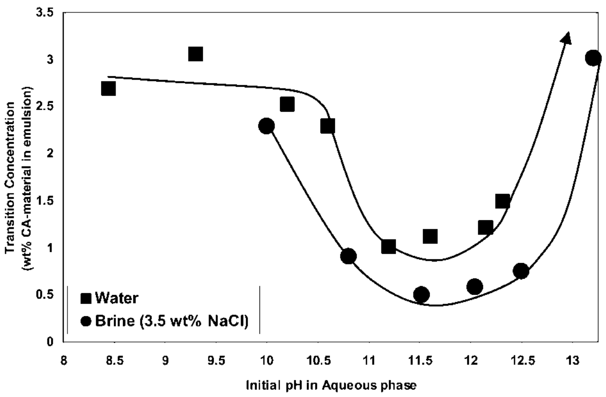


Figure 6. Emulsion phase map showing pH at which transition occurs from water-continuous to oil-continous emulsions and then back to water-continuous in CA-stabilized emulsions. Transition region is shown as a function of CA concentration and for both pH-adjusted water and pH-adjusted brine to which 3.5% NaCl (w/w) has been added.

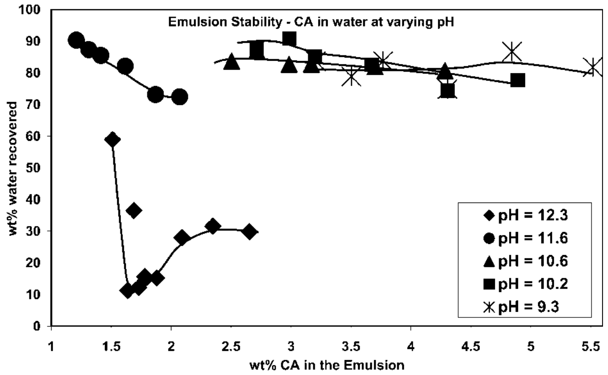


Figure 7. Centrifugal emulsion stability of CA-stabilized emulsions comprise pH-adjusted water and heptol (see Methods section for more details).

When pH-adjusted brine is used as aqueous phase (Fig. 8), the pH-range where very stable w/o-emulsions are formed is broadened to the following conditions:

- pH = 12.5 at CA-concentration ≥1.6 wt% (acid/soap ≥ 2)
- pH = 12 at CA-concentration ≥1 wt% (acid/soap ≥ 5)

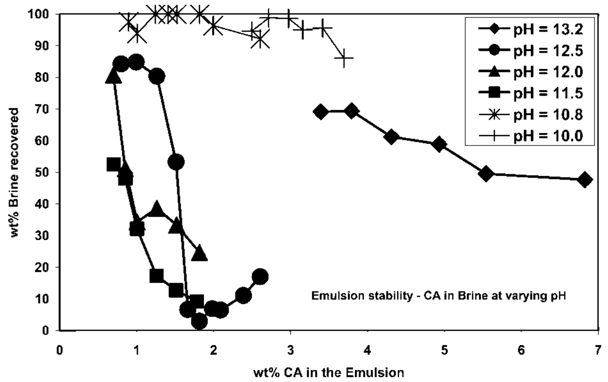


Figure 8. Centrifugal emulsion stability of CA-stabilized emulsions comprise pH-adjusted brine with 3.5% added NaCl (w/w) and heptol (see Methods section for more details).

- pH = 11.5 at CA-concentration ≥1 wt% (acid/soap ≥ 20)

This broadening of the stability region in which oil-continuous emulsions are observed when electrolyte is added to the system is a consequence of the masking of the competing electrostatic stabilizing mechanism. Stable emulsions are observed for acid/soap-ratios as low as 2 because the charge on the soap is being neutralized by the electrolyte. Hence, LLC might form even though a relatively high concentration of charged soap is present in the system.

Emulsion Type and Stability Formed with HB or PCA as Stabilizing Compound

Similar studies as those reported for CA were carried out with HB and PCA (Table 1) as model compounds. These smaller less "bulky" molecules do not stabilize w/o-emulsions over such a wide range of concentrations and pH (acid-to-soap-ratios) as CA.

HB does not form w/o-emulsions at all when pH-adjusted water is used as aqueous phase. On the other hand, electrostatically stabilized water continuous emulsions are formed at high pH where the acid/soap-ratio is relatively low.

PCA resembles HB in its ability to stabilize w/o-emulsions, however this compound will give rise to weak w/o-emulsions in a very narrow range of concentrations and pH (acid-to-soap-ratios); pH ~ 12.3 and conc. ~15 wt% (acid/soap ~90). The "window" where emulsion transition is observed illustrates that PCA might form stabilizing structures at some very definite conditions (mixture of acid and soap).

No emulsions are formed by either HB or PCA if the pH of the water is below 12. At these conditions acid dominates the chemistry in the system and these acids will not stabilize emulsions by themselves.

Upon introduction of 3.5 wt% NaCl to the aqueous phase, no o/w-emulsions are formed. The added electrolyte eliminates the electrostatic stabilizing mechanism found in the stable water continuous emulsions. However, a small region with w/o-emulsions is observed when HB or PCA are used as stabilizing material; pH ~12/conc. ~2 wt% (acid/soap ~10). Hence, at these conditions there exists an optimal mixture of acid and soap resulting in formation of stabilizing structures.

Centrifugal stability studies of all of the observed w/o-emulsions showed us that none of the HB- or PCA-stabilized emulsions were stable upon centrifugation. This suggests that the molecular structure needed to form oil continuous structures of reasonably high stability falls within a specific class of bulky fused ring naphthenic acid molecules. Further work is being performed to elucidate this hypothesis.

CONCLUSIONS

In this study a thorough investigation of several naphthenic acid model compounds ability to form stable oil continuous emulsions was carried out. Two completely different stabilizing mechanisms were seen depending on which form (acid or soap) of the model compound that dominated the system. Electrostatically stabilized water continuous emulsions are formed when de-protonated (charged) naphthenates dominate the system. Intermediate to high acid/soap-ratios will, on the other hand, give formation of LLC, which adsorb to dispersed water droplets in a water-in-oil emulsion. It has been demonstrated that naphthenic acid/naphthenates alone at optimal conditions are well suited as stabilizers for w/o-emulsions.

ACKNOWLEDGMENTS

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REFERENCES

1. Acevedo, S.; Escobar, G.; Ranaudo, M.A.; Khazen, J.; Borges, B.; Pereira, J.C.; Mendez, B. Energ. Fuel **1999**, *13*, 333–335.
2. Hsu, C.S.; Dechert, G.J.; Robbins, W.K.; Fukuda, E.K. Energ. Fuel **2000**, *14*, 217–223.
3. Pathak, A.K.; Kumar, T. Proceedings of PETROTECH-95, Technology Trends in Oil Industry, New Delhi, 1995; 217–224.
4. Goldszal, A.; Hurtevent, C.; Rousseau, G. SPE Oilfield Scale Symposium, Aberdeen, UK, 2002; SPE74661, 1–11.
5. Rousseau, G.; Zhou, H.; Hurtevent, C. SPE Oilfield Scale Symposium, Aberdeen, UK, 2001; SPE68307, 1–8.
6. Gallup, D.L.; Smith, P.C.; Chipponeri, J.; Abuyazid, A.; Mulyono, D. SPE International Conference on Health, Safety and Environment in Oil and Gas Exploration and Production, Kuala Lumpur, Malaysia, 2002; SPE73960, 1–16.

7. Poggesi, G.; Hurtevent, C.; Buchart, D. SPE Oilfield Scale Symposium, Aberdeen, UK, 2002; SPE74649, 1–6.
8. Vinstad, J.E.; Bye, A.S.; Grande, K.V.; Hustad, B.M.; Hustvedt, E.; Nergaard, B. 5th SPE Oilfield Scale Symposium, Aberdeen, UK, 2003.
9. Slavcheva, E.; Shone, B.; Turnbull, A. Br. Corros. J. **1999**, *34*, 125–131.
10. Babaiankibala, E. Oil Gas J. **1994**, *92*, 31–35.
11. Babaiankibala, E.; Craig, H.L.; Rusk, G.L.; Blanchard, K.V.; Rose, T.J.; Uehlein, B.L.; Quinter, R.C.; Summers, M.A. Mater. Perform. **1993**, *32*, 50–55.
12. Piehl, R.L. Mater. Perform. **1988**, *27*, 37–43.
13. Rogers, V.V.; Wickstrom, M.; Liber, K.; MacKinnon, M.D. Toxicol. Sci. **2002**, *66*, 347–355.
14. Fan, T.P. Energ. Fuel **1991**, *5*, 371–375.
15. Koike, L.; Reboucas, L.M.C.; Reis, F.D.M.; Marsaioli, A.J.; Richnow, H.H.; Michaelis, W. Org. Geochem. **1992**, *18*, 851–860.
16. Tomczyk, N.A.; Winans, R.E.; Shinn, J.H.; Robinson, R.C. Energ. Fuel **2001**, *15*, 1498–1504.
17. Qian, K.N.; Robbins, W.K.; Hughey, C.A.; Cooper, H.J.; Rodgers, R.P.; Marshall, A.G. Energ. Fuel **2001**, *15*, 1505–1511.
18. Headley, J.V.; Peru, K.M.; McMartin, D.W.; Winkler, M. J. AOAC Int. **2002**, *85*, 182–187.
19. Rogers, V.V.; Liber, K.; MacKinnon, M.D. Chemosphere **2002**, *48*, 519–527.
20. Jones, D.M.; Watson, J.S.; Meredith, W.; Chen, M.; Bennett, B. Anal. Chem. **2001**, *73*, 703–707.
21. Robbins, W.K. Abstr. Pap. Am. Chem. Soc. **1998**, *215*, 019-PETR.
22. Brient, J.A. Abstr. Pap. Am. Chem. Soc. **1998**, *215*, 018-PETR.
23. Brient, J.A.; Wessner, P.J.; Doyle, M.N. *Encyclopedia of Chemical Technology*; Kirk-Othmer, Ed.; John Wiley & Sons: New York, 1995; 1017–1029.
24. Meredith, W.; Kelland, S.J.; Jones, D.M. Org. Geochem. **2000**, *31*, 1059–1073.
25. Friman, R.; Stenius, P. Acta Chem. Scand. A. **1978**, *32*, 289–296.
26. Stenius, P. Acta Chem. Scand. **1973**, *27*, 3435–3451.
27. Stenius, P. Acta Chem. Scand. **1973**, *27*, 3452–3466.
28. Stenius, P.; Zilliacu, Ch. Acta Chem. Scand. **1971**, *25*, 2232.
29. Skurtveit, R.; Sjoblom, J.; Hoiland, H. J. Colloid Interf. Sci. **1989**, *133*, 395–403.
30. Sjoblom, J.; Lindberg, R.; Friberg, S.E. Adv. Colloid Interf. Sci. **1996**, *65*, 125–287.
31. Gillberg, G.; Lehtinen, H.; Friberg, S. J. Colloid Interf. Sci. **1970**, *33*, 40.
32. Friberg, S.; Mandell, L.; Ekwall, P. Kolloid Z. Z. Polym. **1969**, *233*, 955.
33. Lindman, B.; Wennerstrom, H. Top Curr. Chem. **1980**, *87*, 1–83.
34. Ekwall, P.; Danielsson, I.; Stenius, P. MTP Int. Rev. Sci. Phys. Chem. Ser (London: Butterworths) **1972**, *1*, 97–145.
35. Ekwall, P. *Advanced Liquid Crystalls*; Brown, G.H., Ed.; Academic Press: New York, 1975; 1–142.
36. Ekwall, P.; Mandell, L.; Fontell, K. Mol. Cryst. Liq. Cryst. **1969**, *8*, 157.
37. Wennerstrom, H.; Lindman, B. Phys. Rep.-Rev. Sec. Phys. Lett. **1979**, *52*, 1–86.
38. Kilpatrick, P.K.; Bogard, M.A. Langmuir **1988**, *4*, 790–796.
39. Blackburn, J.C.; Kilpatrick, P.K. J. Colloid Interf. Sci. **1992**, *149*, 450–471.
40. Blackburn, J.C.; Kilpatrick, P.K. Langmuir **1992**, *8*, 1679–1687.
41. Kilpatrick, P.K.; Blackburn, J.C.; Walter, T.A. Langmuir **1992**, *8*, 2192–2199.
42. Blackburn, J.C.; Kilpatrick, P.K. J. Colloid Interf. Sci. **1993**, *157*, 88–99.
43. Friberg, S.; Mandell, L.; Larsson, M. J. Colloid Interf. Sci. **1969**, *29*, 155.
44. Friberg, S. J. Colloid Interf. Sci. **1971**, *37*, 291.
45. Friberg, S.; Jansson, P.O.; Cederberg, E. J. Colloid Interf. Sci. **1976**, *55*, 614–623.
46. Friberg, S.E.; Solans, C. Langmuir **1986**, *2*, 121–126.
47. Horvath-Szabo, G.; Czarnecki, J.; Masliyah, J.H. J. Colloid Interf. Sci. **2002**, *253*, 427–434.
48. Urdahl, O.; Sjoblom, J. J. Disper. Sci. Technol. **1995**, *16*, 557–574.
49. Graciaa, A.; Barakat, Y.; Schechter, R.S.; Wade, W.H.; Yiv, S. J. Colloid Interf. Sci. **1982**, *89*, 217–225.
50. Horvath-Szabo, G.; Masliyah, J.H.; Czarnecki, J. J. Colloid Interf. Sci. **2001**, *242*, 247–254.
51. Horvath-Szabo, G.; Masliyah, J.H.; Czarnecki, J. J. Colloid Interf. Sci. **2003**, *257*, 299–309.
52. Horvath-Szabo, G.; Czarnecki, J.; Masliyah, J. J. Colloid Interf. Sci. **2001**, *236*, 233–241.
53. Balasubramanian, D.; Friberg, S.E. *Surface and Colloid Science*; Matijevic, E., Ed.; Plenum Press: New York, 1993; Vol. 15, 197–220.
54. Balasubramanian, D.; Srinivas, V.; Gaikar, V.G.; Sharma, M.M. J. Phys. Chem. **1989**, *93*, 3865.
55. Horvath-Szabo, G.; Yin, Q.; Friberg, S.E. J. Colloid Interf. Sci. **2001**, *236*, 52.

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