Articles

Simple Method to Determine the Partition Coefficient of Naphthenic Acid in Oil/Water

Anders Bitsch-Larsen[†] **and Simon Ivar Andersen***[,‡]

Engineering Research Centre IVC-SEP, Department of Chemical Engineering, Technical University of Denmark,
DK-2800 Kgs. Lyngby, Denmark

The partition coefficient for technical grade naphthenic acid in water/*n*-decane at 295 K has been determined ($K_{wo} = 2.1 \cdot 10^{-4}$) using a simple experimental technique with large extraction volumes (0.09 m^3 of water). Furthermore, nonequilibrium values at different pH values are presented. Analysis of the acid content in the oil phase was conducted by FT-IR and colormetric titration and found to be equivalent.

Introduction

Crude oils are made up of a complex mixture of different compounds. A group of these are named naphthenic acids. These are predominantly monovalent carboxylic acids with one or more alicyclic rings. They are present in crude oils in concentrations ranging from (0.3 to 3) % wt. The molecular structure is given by $C_nH_{2n+Z}O_2$ where Z is −2 for monocyclic acids, −4 for bicyclic acids, etc.[1] Naphthenic acids were first described in the literature in 1874 where they were identified in Romanian crude oil.[2] Since then, the adverse effects of naphthenic acids in operation of refineries due to corrosion and their roles as a surfactant and thus emulsion stabilizer have been well established.[3−5] Napthtenic acids furthermore cause environmental problems which have been documented over the years. This provides a challenge for the utilization of the vast Athabasca tar sand in Northern Alberta, where the content is high. For the time being, this problem is addressed by using large tailing ponds to avoid release to the environment.[6,7]

It is therefore of interest to determine the structure of naphthenic acids and how it partitions between oil and water. A recent review pertains to the different analysis techniques being used to determine structure of naphthenic acids[7] and will thus not be discussed further. The partition coefficients, K_{wo}, as defined by equation (1)

$$K_{wo} = \frac{[HA]_w}{[HA]_o} \qquad (1)$$

where $[HA]_w$ and $[HA]_o$ are the concentrations of acid in the water and oil phase, respectively, are uncommon in the literature with values from Havre et al. seemingly being the only reported values. These range from $3 \cdot 10^{-5}$ to $3 \cdot 10^{-2}$ depending on the structure between water and *n*-heptane/toluene (50:50 by volume). This value was determined by equilibrating water and oil with a known naphthenic acid content and extracting the acid with dichloromethane. Thereafter, the acid was derivatized with *N*,*O*-bis(trimethylsilyl) trifluoro acetamide and trimethylchlorosilane (99:1) prior to analysis by GC/MS where it was assumed that homologues series have the same ion sensitivities.[8] The present work describes an untraditional, albeit extremely simple and direct, method to obtain reliable values for K_{wo} between water and *n*-decane. Although the procedure may seem tedious, we believe that the approach involves a minimum of assumptions, and hence much more reliable results can be obtained.

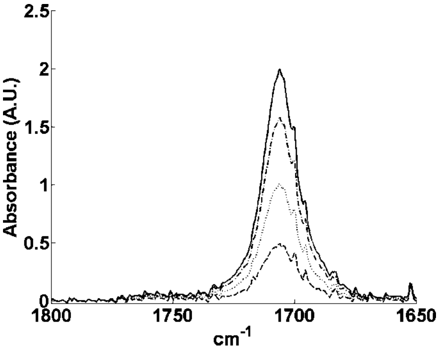

Figure 1. Variation of absorbance using FT-IR with different levels of naphthenic acid in *n*-decane. − (Solid line), 9.5 % wt; − • (dash-dotted line), 7.5 % wt; ••• (dotted line), 4.9 % wt; - - -, (dashed line) 2.1 % wt.

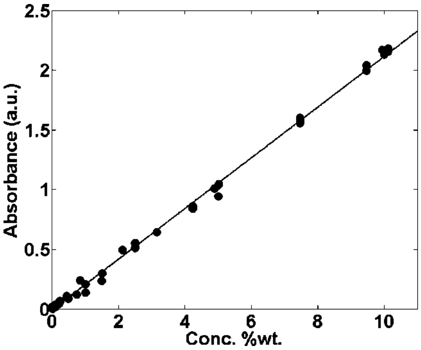

Figure 2. Calibration curve for FT-IR determination of naphthenic acid concentration in *n*-decane. ●, Data points; −, model.

---

* Corresponding author. E-mail: sia@topsoe.dk.

[†] Current address: Chemical Engineering and Materials Science Department, University of Minnesota, MN.

[‡] Current address: Haldor Topsøe A/S, R&D, Dk-2800 Kgs. Lyngby, Denmark.

10.1021/je800287f CCC: $40.75

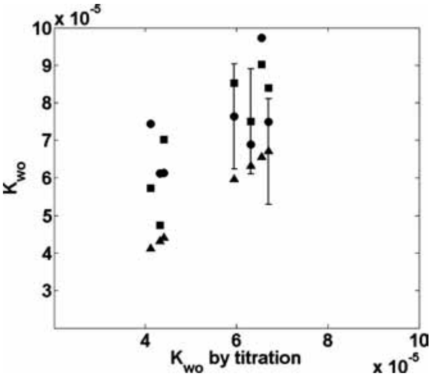

Figure 3. Comparison of techniques for determination of K_{wo} in naphthenic acid/*n*-decane after 20 h at 295 K. Error bars indicate 95 % confidence interval. ●, Ratio of peaks; ■, calibration curve; ▲, titration.

Table 1. Partition Coefficient of Naphthenic Acid in Water/*n*-Decane at 295 K vs Time

t/h	$K_{wo} \cdot 10^4$
6	0.4
12	0.6
20	0.8
24	1.0
48	1.1
96	1.1
180	2.1
256	2.2

Experimental Section

The experimental apparatus is based on a large (0.12 m^3) glass tank. The large volume is needed due to the small value of K_{wo}, which requires a significant amount of extraction volume to obtain reliable changes in the concentrations. Three different experimental methods were used to determine the concentration of naphthenic acid in the oil phase.

Infrared Spectroscopy (FTIR). FTIR spectra were obtained using a Perkin-Elmer 1000 Paragon using 256 scans with a resolution of 0.5 cm from 1800 cm^{-1} to 1650 cm^{-1}. All spectra were baseline corrected using the value at 1800 cm^{-1}. The spectra were recorded for the *n*-decane phase. IR was applied in two ways: the first relied on calibration using the peak at 1706 cm^{-1} corresponding to the carboxylic acid and application of Beers Law; the second method used relied on the ratio of the peaks at 1706 cm^{-1} before and after the experiment. Figure 1 shows typical FT-IR spectra for different concentrations of *n*-decane clearly showing significant variation with concentrations, while Figure 2 shows the excellent agreement with Beer's law in the form of proportionality between absorbance and concentration.

Colorimetric Titration. The concentration of naphthenic acid in the *n*-decane phase was determined following ASTM D974 which uses *i*-propanol as solvent. The standard was modified by the replacement of the indicator *p*-naptholbenzene by phenolphthalein. The exact concentration of KOH was measured by titration using a standard HCl solution (Titrisol, Merck).

Karl Fischer (KF) Titration. To determine the water content and its possible contribution to the IR spectra, KF titration using a KF 756 Coulometer from Metronohm was used. The measurements were carried out with a precision of ± 10 ppm. The calibration of the equipment was checked by Hydranal-Water Standard 1.00 from Riedel-de Haën. The water content was always below 150 ppm and thus insignificant for the precision of the obtained IR spectra.

Procedures. The experiments were carried out in a 0.120 m^3 tank which was cleaned thoroughly with dish washer soap before each experiment. Traces of calcium were removed by filling the tank with a weak solution of nitric acid, whereafter the tank was flushed with distilled water. The tank was then filled with 0.090 m^3 of deionized water. Then, 36 mL of organic phase with a known naphthenic acid concentration was carefully added to the surface. The amount of organic phase added was known by both weight and volume. Two different concentrations (5 % wt and 10 % wt) were used with identical results. The tank was sealed and left to equilibrate. After a given time, the tank was partially emptied, leaving the decane phase and a small amount of water. The majority of the water was taken out in containers and weighed to determine the exact mass. The remaining two phases transferred and separated in a smaller separator funnel. The acid content in the oil phase was determined by either IR or titration as described above. The amount of acid at the interface is negligible compared to the overall amount of acid used in these experiments.

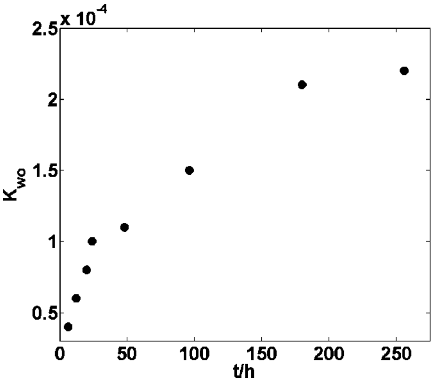

Figure 4. K_{wo} for naphthenic acid in the water/*n*-decane system as a function of time.

Table 2. K_{wo} for Naphthenic Acid in the Water/*n*-Decane System at 295 K after 48 h

pH	K_{wo}	buffer
3.0	$9.3 \cdot 10^{-5}$	citric acid/NaOH
5.3	$1.7 \cdot 10^{-4}$	citric acid/NaOH
7.0	$1.1 \cdot 10^{-4}$	none
9.0	$4.8 \cdot 10^{-3}$	NH_4Cl/NH_3
10.5	$1.1 \cdot 10^{-2}$	H_2O_2/NaOH

In the experiments with a pH value different from 7, a buffer solution was added during the filling of the tank.

Uncertainty. The uncertainty of the measured partition coefficients has been determined using analysis of variance with a 95 % confidence interval. This analysis showed the uncertainty to be no larger than $1 \cdot 10^{-5}$ M or 5 % of the reported values for values obtained after 24 h and for most measurements smaller. For values obtained in less than 24 h, the uncertainty increases to 15 % due to mixing when the sample is introduced. The reproducibility of the experiments was found to be within 3 %. The experiments were conducted at room temperature which is estimated to be (295 ± 2) K. The amount of water used in the experiment was recorded within 0.1 kg (ca. 0.1 %).

Materials. The materials used were *n*-decane (> 95 % purity, Fluka), Flukas technical grade naphthenic acid, KOH (> 85 %, Merck), *i*-propanol (> 99.7 %, Merck), citric acid anhydrodrous (> 99.7 %, Merck), ammonium chloride (> 96 %, Merck), and sodium hydroxide (1 M, Merck Titrisol). All chemicals were used without further purification. The average molecular weight for the naphthenic acid was determined by titration to be (235 ± 2) $g \cdot mol^{-1}$ assuming one carboxyl group per molecule.

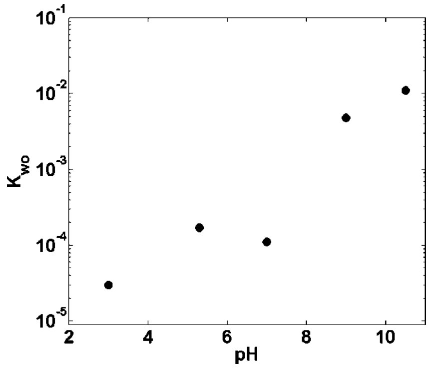

Figure 5. K_{wo} for naphthenic acid in the water/*n*-decane system as a function of pH after 48 h.

Results and Discussion

A statistical comparison of the three analytical methods showed that equal variance and mean could be assumed on a 95 % confidence level as shown in Figure 3 where results obtained by FT-IR are plotted versus the results from titration for each experiment.

The analysis of the data shows that the methods are equivalent to within the established experimental uncertainty. Due to the very good correlation obtained using the infrared absorbance calibration curve, it was decided to use this for further analysis. This was chosen because of the simplicity compared to titration. Following this, all further data are determined using the infrared method based on a calibration curve.

The progression of K_{wo} as a function of time is presented in Figure 4 and Table 1. The equilibrium value is in the same range as the only other reported value.[8] Equilibrium is obtained after approximately 200 h. This slow equilibrium time is caused by transport limitations. However, stirring was not applied to avoid emulsion formation which could affect the determination of an exact partition coefficient.

Table 2 and Figure 5 show the variation of K_{wo} with pH. Due to time constraints, it was decided only to use 48 h per experiment. Hence, the values are not equilibrium values and are presented only to establish trends. In accordance with Havre et al.,[8] the partition coefficient increases as the pH increases and shows a similar jump in K_{wo} with increasing pH. One may speculate, keeping in mind the relative short contact time, that equilibrium is actually obtained for the high pH values as the driving force in the transport is increased significantly. This is confirmed by visual observation of slight interface emulsion formation upon immediate contact between the two phases at high pH. The same has been observed in our laboratories during investigations of effects of pH on interfacial tension between crude oil and water (SIA, unpublished).

Conclusion

A simple method to determine small partition coefficients between oil and water has successfully been applied to the system water/*n*-decane/naphthenic acid. The method relies on low solubility of the oil phase in water which allows for quantitative separation after attainment of equilibrium. The K_{wo} for Fluka's naphthenic acid was determined to be $(2.1 \pm 0.1)\cdot 10^{-4}$. To the best of our knowledge, this is the first direct determination of a partition coefficient for this system. It has been done with a minimum of assumptions affecting the result.

Literature Cited

(1) Brient, J. A.; Wessner, P. J.; Doyle, M. N. *Naphthenic acids in Kirk-Othmer Encyclopedia of Chemical Technology*, 4th ed.; Wiley: New York, 1995.

(2) Maass, W. F.; Buchspiess-Paulentz, E.; Stinsky, F. *Naphthensäuren und naphthenate*; Verlag für chemische industire H. Ziolkowksy KG: Augsburg, 1961.

(3) Sjöblom, J.; Aske, N.; Auflem, I. H.; Brandal, J.; Harve, T. E.; Sither, J.; Westwik, A.; Johnsen, E. E.; Kallevik, H. Our current understanding of water in crude oil emulsions. Recent characterization techniques and high pressure performance. *Adv. Colloid Interface Sci.* **2003**, *100–102*, 399–473.

(4) Jayaraman, A.; Saxena, R. Corrosion and its control in petroleum refineries - a review. *Corros. Prev. Control* **1995**, *42* (6), 123–131.

(5) Turnbull, A.; Slavcheva, E.; Shone, B. Corrosion engineering - factors controlling naphthenic acid corrosion. *Corros., J. Sci. Eng.* **1998**, *54* (11), 922–930.

(6) Clemente, J. S.; Mackinnon, M. D.; Fedorak, P. M. Aerobic biodegradation of two commercial naphthenic acids preparations. *Environ. Sci. Technol.* **2004**, *38* (4), 1009–1016.

(7) Clemente, J. S.; Fedorak, P. M. A review of the occurrence, analyses, toxicity, and biodegradation of naphthenic acids. *Chemosphere.* **2006**, *60*, 585–600.

(8) Havre, T.; Sjöblom, J.; Vindstad, J. Oil/Water-Partitioning and Interfacial Behavior of Naphthenic Acids. *J. Dispersion Sci. Technol.* **2003**, *24* (6), 789–802.

Received for review October 3, 2007. Accepted July 7, 2008.

JE800287F