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Dynamics of bitumen fractions by thin-layer chromatography/flame ionization detection

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Abstract

Thin-layer chromatography/flame ionization detection (TLC/FID) allows for the fractionation of bitumen into four fractions, namely, the saturates, the aromatics, the resins A and the resins B (SARAB). The technique is rapid and economical, but it lack reproducibility. The effect of chromarod aging on reproducibility was investigated along with that of the time between bitumen dissolution and its analysis (time lapse effects). It is found that chromarod aging causes a 2-5% variation in SARAB content, and that time lapse causes a 50-75 % variation in the aromatics and resins A content. The effect of time lapse stems from the aging of bitumen in solution. A mechanism for this aging is provided. It is demonstrated to be a physical rather than a chemical transformation of bitumen that reveals itself as a conversion of aromatics into resins. The physical nature of aging is shown by the absence of oxidation and aromatization in solution and by the successful modeling of aging after a reversible process. The conversion of aromatics into resins is explained by the grouping of alkyl-aromatics into micelles. The latter mimic resins during chromatography and cause an apparent increase in resins concentration.

Keywords: bitumen, asphalt, model, microstructure, TLC/FID, chromatography, analysis, aging

Introduction

Bitumen is a residue of petroleum distillation that contains heavy hydrocarbons, typically in the range C_{24}-C_{150}. With the number of possible isomers exceeding 10^{15}, the complexity of the mixture precludes any precise molecular identification. As a result, physico-chemical characterization of bitumen often involves its fractionation into chemical families by a combination of solvent precipitation and liquid chromatography (LC). Rostler[1] and later Goodrich et al.[2] have reviewed the methods in details. Table 1 provides an overview. The products of fractionation are defined in terms of the procedure. Often the heavy fraction is called the asphaltenes.

In recent years, the use of thin-layer chromatography coupled to flame-ionization detection (TLC/FID) has gained much in popularity,[4] the impetus to the method being the availability of a commercial system, the Iatroscan. For bitumen analysis, the method offers better resolution and speed than LC. It requires milligram-size samples, little solvent, and no de-asphaltenation before analysis. The typical "iatrogramme" shows four signals (Figure 1a). The signals are often said to arise from saturates, aromatics, resins and asphaltenes (SARAs),[6-8] but this nomenclature is confusing because these asphaltenes are not obtained by precipitation (Table 1). To avoid confusion, the nomenclature of Ray et al.[3] should be preferred. Form left to right, the iatrogramme peaks should thus be identified as saturates, aromatics, resins A, and resins B. For convenience, we will refer to the group of fractions obtained from TLC/FID as the SARAB (<u>s</u>aturates, <u>a</u>romatics, <u>r</u>esins <u>A</u> and <u>B</u>). An earlier study showed that asphaltenes precipitated by n-heptane are made of resins A and B.[6]

Despite the advantages of the TLC/FID method, is has yet to constitute a standard test procedure for bitumen analysis. The lack of reproducibility and the non-linear FID-mass response[9] have been the main barrier to standardization. Bharati et al.[7] have suggested calibration standards to account for the non-linear FID-mass response, whereas Wan et al.[10] have shown the effect of sample size, spotting technique and relative humidity on reproducibility. In this paper, we show the effect of two parameters on TLC/FID results: the age of the chromarod and the time between bitumen dissolution and its analysis (time lapse effects). It is shown that older chromarods give higher polar contents (resins A and B) than new chromarods, and that the time lapse has a large effect on the results. Time lapse studies provide information on the microstructure of bitumen in solution.

Experimental Section

Materials. Two bitumens were used in this investigation. Bitumen A, supplied by Petro-Canada, had a penetration of 85/100 as per ASTM D5. Bitumen B, supplied by Ashwarren, had a penetration of 300/400. The solvents, HPLC grade from Sigma-Aldrich, were used as-received.

Solutions. Typically, 25.00 mg of bitumen was weighed in a glass vial, into which 2500 μL of trichloroethylene (TCE) were added with a micro-pipette. Benzene, toluene, carbon tetrachloride, carbon disulfide, tetrahydrofuran, and pyridine can also be used to dissolve bitumen, but TCE was chosen because of its relavive hydrophobicity and safety. Teflon-lined caps were used on the vials to minimize solvent evaporation. Bitumen was left to dissolve 1 h, with occasional shaking of the solution, before being applied to chromarods. In the time lapse study, however, the solutions were sampled at a regular interval from 1 h to 28 days.

Sample application and chromarods. Bitumen solutions were applied to ten S-III silica chromarods that had been blanked in the Iatroscan by the slow scanning of the chromarods over the hydrogen flame. To reduce the risk of chromarod contamination, less than 30 min was allowed to lapse between chromarod cleaning and solution deposition. About 1 μL of bitumen solution was applied to each chromarod in the following manner: A 2 μL syringe was cleaned by repeated rinsing in trichloroethylene followed by triple rinsing in the asphalt solution prior to deposition. Chromarods were spotted in two groups of five chromarods. Each group was spotted in parallel with 2 μL of solution, each chromarod receiving 0.4 μL. This was repeated with further 2.0 μL and 1.0 μL load applications, for a total of 1 μL/chromarod. The sample vial was closed and shaken between each application. The solution was deposited onto the chromarods to create a 1–2 mm wide band on the chromarod circumference. After spotting, the set of ten chromarods was placed into a glass storage tank and transferred to an oven at 55 ± 5°C for 5–7 min to evaporate the remaining solvent.

In the analysis of bitumen B, two sets of ten chromarods were used in parallel to study the effect of chromarod aging. The first set of chromarods was new when the study began, whereas the second set of chromarods had already been subjected to about sixty runs over the hydrogen flame of the Iatroscan.

Environment. A relative humidity (RH) and dust controlled environment was maintained during elutions and TLC/FID runs by using a two-chamber box with removable front panel and clear top. One chamber housed the Iatroscan (model MK-5) while the other was used to condition the chromarods prior to the fractionation of bitumen. Temperature was 23 ± 2°C, and RH was maintained at 50 ± 5% by keeping a large beaker of a saturated solution of sodium nitrite in the working chamber. The dust level within the box was controlled by minimizing outside air flow and by cleaning the box with a damp, dust-free, cloth.

Elutions and Iatroscan runs. Elution of bitumen along chromarods was done in TLC tanks (Aldrich # Z20,416-1) that contained about 125 ml of heptane, toluene, or tetrahydrofuran. The tanks were lined on the back wall with Whatman #4 filter paper, which elute solvent, and minimize solvent vapour gradient between the top and bottom of the chromarods. Heptane and toluene eluents were replaced daily, but the hygroscopic tetrahydrofuran was replaced before each elution.

Bitumen deposited on the chromarods was fractionated by successive elution in heptane (45 min), toluene (20 min), and tetrahydrofuran (5 min). After each elution, the chromarods were dried in an oven for 5 min at 55 ± 5°C. In the Iatroscan, the chromarods were scanned at 30 sec/chromarod, with the respective hydrogen and airflow rate at 160 and 2000 mL/min.

Results

Reproducibility. A typical iatrogramme for bitumen is shown in Figure 1a. An exact correspondence between area and weight percent was assumed although this is not strictly true[9]. To provide some basis for comparison, the reproducibility in obtaining the iatrogramme for bitumen A and B was assessed. Bitumen was fractionated after 1h in solution and the fractionation was repeated the next day with a fresh solution (Table 2). For both bitumens, the contents of saturates and resins B were similar, and the standard deviation (σ) was less than 1. Consequently, no statistical difference was found based on the z-test at a 0.05 level of confidence. In contrast, the variation in the content of aromatics and resins A was significantly larger for both bitumens. The relatively small sample set for bitumen A (five chromarods) led to a large σ, and as a result, no statistical difference between the repeats was obtained. A somewhat larger sample set of 7–8 chromarods for bitumen B lead to a tighter σ, from which a statistical difference was obtained between the repeats. The decrease in the number of usable chromarods from 10 to 5–8 was due to the overlap of bitumen signals with spikes that prevented the use of the iatrogramme in the calculation of bitumen composition (Figure 1b).

Time lapse. The time between the dissolution of bitumen and its analysis affects the results of size exclusion chromatography.[11] A similar phenomenon could affect TLC/FID results and help explain the difficulty in obtaining consistent results on a day-to-day basis. Accordingly, bitumen A was analyzed after it had been in solution for 1 h up to 8 days (Figure 2). In this time, the concentration of saturates and resins B remained fairly stable, but that of the aromatics and resins A varied greatly. The concentration of aromatics decreased over time whereas that of the resins A increased. The change in aromatics and resins A was such that the former appeared to partly convert into the latter.

In a second series of experiments, bitumen B was left up to 24 days in solution (Figure 3). The trend was the same as for bitumen A, but it is easier to see that the rate of conversion of aromatics into resins A was most rapid in the first 5 days in solution, after which time conversion was considerably slower. Equilibrium was reached in ~15 days.

Chromarod aging. The lifetime of a chromarod is about 100 scans[4]. This says little about the effect of chromarod aging on the fractionation of bitumen. Results obtained on bitumen B on chromarods at about half their lifetimes show that this effect can be significant (Figure 4). The old chromarods consistently gave a greater content in resins A and resins B than the new chromarods. The reverse was true for saturates and aromatics.

Discussion

Reproducibility. The results in Table 2 indicate that reproducibility for TLC/FID of bitumen is generally characterized by a large σ (e.g. bitumen A) and a small, but significant statistical difference in aromatics and resins A (e.g. bitumen B). As would be expected, the standard deviation is affected by the number of valid iatrogrammes that can be obtained in any given scan of ten chromarods. It is common to exclude results from some iatrogrammes because of the presence of spikes. These spikes are thought to arise from the presence of paper micro-fibrils on the chromarods. The fibrils come from the paper that lines the elution vessels. After they have contaminated the eluent, they move up the chromarod during elution. It is only after several changes of solvent in the TLC tank that this problem is reduced, but it is never fully controlled so that results from ten chromarods are consistently acceptable. The use of 5–8 chromarods, however, can be sufficient to obtain results for which $\sigma < 2$. The results for bitumen B are an example. They also indicate that the content of aromatics and resins A can vary by 5–8%. The time lapse studies suggest that the time dependant concentration of these fractions is responsible for the variation.

Time lapse. Figures 2 and 3 show that bitumen partly transforms itself upon standing in solution and that the change in SARAB can reach ±75% of the initial value, depending on the fraction. Recalling that the n-heptane precipitate, often defined as asphaltenes, show on the iatrogramme as resins A and B,[6] the transformation is reminiscent of that shown by bitumen upon oxidative aging, with the difference that in solution only one type of transformation occurs, that of aromatics to resins A (Figure 5). This result indicates that bitumen can transform itself, in a process similar to aging, without exposure to an oxidative environment. This process is recognized as solvent hardening in the extraction of bitumen from concrete cores.[12]

The transformation of bitumen in a non-oxidative environment suggests that bitumen aging may be as much a physical phenomenon as it is a suite of chemical transformations, i.e., ring closure, elimination, aromatization, oxidation. The conversion of aromatics into resins may proceed rapidly in solution because of the reduced viscosity of the solution, and it is not excluded that it also exists in solid bitumen where it would proceed over longer times. Hence, the conversion explains the day to day variability in TLC/FID of bitumen and it might be related to steric hardening in the solid state, i.e., self assembly of polar molecules.[13]

Chromarod aging. Results for TLC/FID of bitumen obtained on new and old chromarods are statistically different. The aging of the chromarods cause an apparent increase in the most polar fractions of bitumen (Figure 4). Such a change, similar to that expected when going from normal phase chromatography with high packing polarity to reverse phase chromatography with low packing polarity,[14] indicates that the polarity of the chromarods decreases over time. It is likely therefore that upon successive heat scans, SiOH groups on the chromarod surface are converted to SiOSi groups after the loss of H_2O. Upon chromarod aging, non-polar compounds interact with SiOSi groups, and adsorb more strongly than before onto the chromatographic support. Thus their adsorption behaviour resembles that of polar groups, which interact with the SiOH groups. The results is the apparent increase in polar content (resins A and B), and an apparent decrease in non-polar content (saturates and aromatics). From Figure 4, it is estimated that chromarod aging causes a variation of ~2% in saturates and resins B, and

~5% in aromatics and resins A. It is also estimated that on any single day the combination of chromarod aging and time lapse effects, cause an 8–10% variation in the results obtained by TLC/FID.

Bitumen aging in solution. Recent studies suggest that bitumen is a continuous network of mutually soluble and polydisperse molecules.[15, 16] Notwithstanding, the exact nature of the interactions between the various bitumen fractions remains undetermined. The same can be said for bitumen molecules in solution. Figures 3 and 4 do provide some answers, however. The time lapse study suggests a conversion of aromatics into resins A, whereas the study on chromarod aging reveals that some conversion is only apparent. By extension, it cannot be excluded that the total conversion of aromatics to resins A is only apparent. In other words, the conversion of aromatics into resins A may be the result of a simple physical transformation of a molecular structure and not the result of an increase in aromaticity or oxidation that would follow an actual conversion of aromatics into resins. This is demonstrated by infrared spectra of bitumen solutions acquired concurrently with the iatrogrammes. The spectra revealed no increase in carbonyl absorption due to oxidation or an increase in bitumen aromaticity.

The existence of a simple physical transformation is further demonstrated by the modeling of the apparent conversion or aromatics into resins A after a reversible reaction. Consider Figure 6 for example, which illustrates the transformation of a molecule from state A to state A*. The transformation can be expressed as:

$$[A] \underset{k'}{\overset{k}{\rightleftharpoons}} [A^*] \qquad \text{(eq. 1)}$$

The forward reaction proceeds at a rate defined by v(t)= k [A] and the reverse reaction at a rate $v(t)=k'[A^*]$, k and k' being the forward and reverse reaction constants. At equilibrium, an equilibrium constant can be written as $K_{eq}=k/k'=[A^*]_{eq}/[A]_{eq}$ and the total rate of change of the concentration of A as $d[A]/dt= -k[A]+k'[A^*]$. For the equilibrium transformation defined by eq. 1, the concentration of A at any time is found with eq. 2,[17] which can be plotted as a straight line.

$$\ln ([A] - [A]_{eq}) = \ln ([A]_o - [A]_{eq}) - (k+k')t \qquad \text{(eq. 2)}$$

From Figure 7, it is readily seen that the conversion of aromatics into resins A can be modeled after equation 2. For bitumen B, $K_{eq} = k/k'=14/37=0.38$ (Figure 6). From this value and that of the slope in Figure 7, the forward and reverse constants k and k' are calculated to be 4.7×10^{-7} and 1.2×10^{-6} s^{-1}, respectively. In bitumen A, equilibrium was not attained in eight days. Consequently, the reaction constants were not calculated. It would be of interest, however, to compare the rates for various bitumens and determine the intrinsic factors that affect these rates.

The values for k and k' are of the same order of magnitude as those for the entry and exit of a molecule to and from a micelle.[18] From the equation

$$\Delta G° = -RT \ln K_{eq}$$

$\Delta G°$ is calculated to be 2.4 kJ/mol, which corresponds well with a $\Delta G°$ of 2.5 kJ/mol for the Gibbs energy of transfer of a molecule from a solvent to a micelle.[18] Accordingly, the apparent conversion of aromatics to resins A appears to be a simple rearrangement of aromatics into micelles. A value of K_{eq} lower than 1 also shows that the equilibrium shown by equation 1 is shifted to the left. Hence, not all aromatics lend themselves to the formation of micelles.

The time dependant formation of micelles is consistent with the time lapse effects, the apparent conversion of some aromatics into resins A, and the absence of any chemical reaction. Consider that when bitumen molecules are suspended in a solvent, some alkyl-aromatic molecules can aggregate with the aromatic rings facing outward from the micelle center and leave a saturated hydrocarbon tail in the center of the micelle (Figure 8). It can be anticipated that only the aromatics with a single unbranched hydrocarbon chain would form micelles, the others, as suggested by K_{eq} would not participate in their formation. In adsorption chromatography, this micelle would show a polar surface that can mimic a large and polar molecule. As a result, some alkyl-aromatics can elute with the resins A rather than with the aromatics. This provides for an apparent increase in the concentration of resins A, without an increase in aromaticity or oxidation. Such a time dependant aggregation naturally lead to some increase in molecular size over time, which is consistent with results from size exclusion chromatography obtained over 21 days.[11]

Conclusions

Bitumen can be fractionated by a number of chromatographic methods, each providing its own nomenclature, and as a result, fractions from TLC-FID can be confused with those obtained by liquid chromatography. To prevent such confusion, it is suggested that TLC/FID fractions be referred to as saturates, aromatics, resins A and resins B (SARAB).

Two parameters that affect the reproducibility of TLC/FID were studied: the age of the chromarod and the time between bitumen dissolution and its fractionation (time lapse effects). Chromarod aging, identified as a conversion of SiOH groups into SiOSi groups, was found to cause a 2–5 % variation in the result. As the chromarods age, they cause an apparent increase in the most polar fractions of bitumen and a decrease in the less polar fractions. Time lapse affects the results much more severely. When bitumen is dissolved, it is found to age, which results in a 50–75 % variation in aromatics and resins A.

During routine analysis, reproducibility can be within 10 % for all four bitumen fractions if temperature, humidity, and time lapse is controlled. If time lapse is not controlled, however, it is suggested that bitumen be characterized by three fractions: saturates; the combination of aromatics and resins A; and resins B, rather than with the usual four fractions. This will alleviate the variation in aromatics and resins A related to bitumen aging in solution.

A mechanism for the aging of bitumen in solution is also provided. This aging reveals itself as a conversion of aromatics into resins, but this conversion is only apparent. The absence of oxidation and aromatization in solution shows the physical, rather than chemical, nature of aging. The physical nature of aging is further substantiated by modelling the change in solution after a reversible transformation with respective forward and reverse reaction rate constants of 4.7×10^{-7} and $1.2 \times 10^{-6}\ s^{-1}$. The apparent conversion of aromatics into resins is explained by the flocculation of alkyl-aromatics. The flocs mimic resins during chromatography and cause an apparent increase in its content.

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Table 1. Methods to Fractionate Bitumen and Fossil Fuels.

principle	products	precipitant	comment
solvent extraction	parafinnics, cyclics, asphaltics.	n-butanol	ref. 1, 2
acid precipitation	paraffins, nitrogen bases, acidaffins #1, acidaffins#2, asphaltenes.	n-pentane	ref. 1, 2
adsorption on alumina,	saturates, naphtene aromatics, polar aromatics, asphaltenes.	n-heptane	ASTM D 4124
adsorption on clay-gel,	saturates, aromatics, polars, asphaltenes.	n-pentane	ASTM D 2007
size-exclusion chromatography	hydrocarbons of different sizes		ref. 2
gas chromatography	volatile hydrocarbons		ref. 2
high pressure liquid chromatography	molecules of different polarities		ref. 2
thin-layer chromatography (Iatroscan)	saturates, aromatics, resins A, resins B.		ref. 4, 7
ion exchange chromatography	neutrals, bases, acids,		ref. 5
flash chromatography	saturates, aromatics, resins A, resins B.	n-heptane	ref. 6

Table 2. Percent SARAB Composition of Bitumen*

fraction	bitumen A		bitumen B	
	repeat 1	repeat 2	repeat 1	repeat 2
saturates	10.1 (0.4)†	10.1 (0.7)	12.2 (0.6)	11.4 (0.4)
aromatics	51.7 (3.0)	54.7 (2.0)	50.7 (0.9)	53.8 (1.1)
resins A	21.9 (2.1)	20.1 (1.5)	28.4 (0.8)	26.1 (0.8)
resins B	16.4 (0.9)	15.2 (0.9)	8.7 (0.3)	8.7 (0.4)
no. of rods	5/10	5/10	7/10	8/10

*Obtained on new chromarods after 1h in solution. †The standard deviation (σ) is in parenthesis.

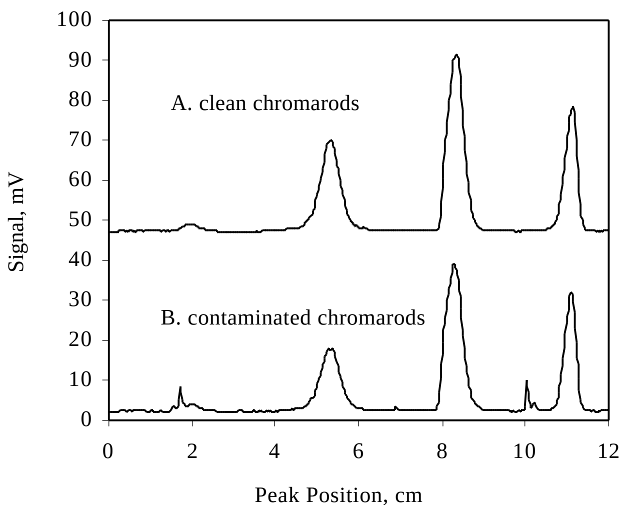

Figure 1. Typical iatrogrammes for bitumen. A) The saturates, eluted by n-heptane, show at 2 cm; the aromatics, eluted by toluene show at ~5 cm; the resins A, eluted by tetrahydrofuran, show at ~8cm; and the uneluted resins B show at 11 cm. B) An iatrogramme can be rendered useless by the overlap of a dust spike and a SARAB signal, as shown at 2 cm in the bottom iatrogramme.

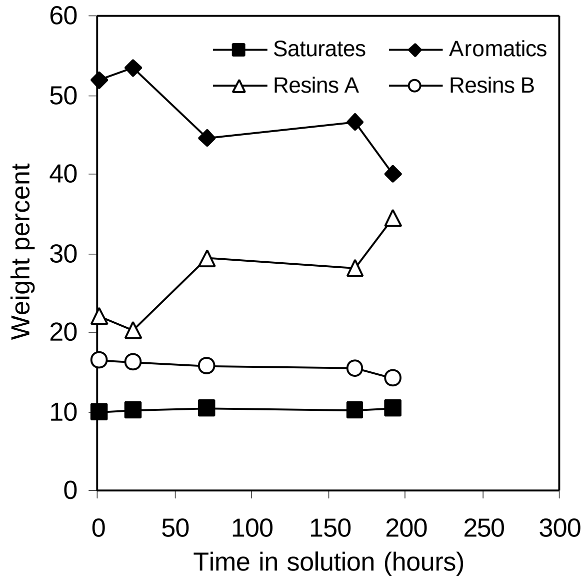

Figure 2. Evolution in the composition of bitumen A dissolved in trichloroethylene as obtained on new chromarods.

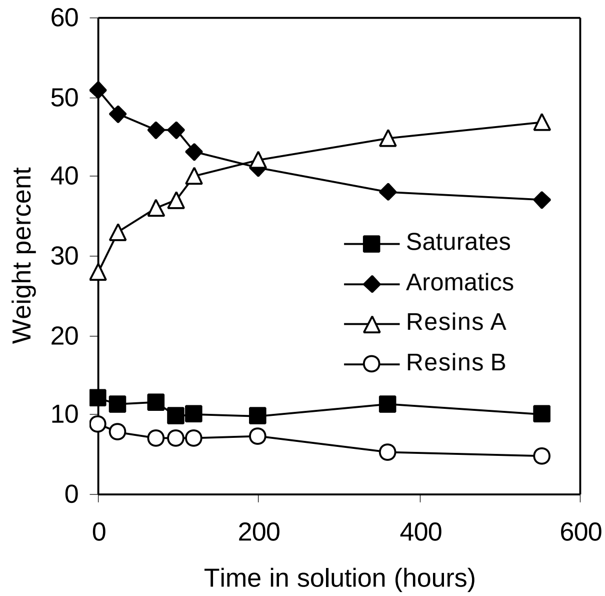

Figure 3. Evolution in the composition of bitumen B dissolved in trichloroethylene as obtained on new chromarods.

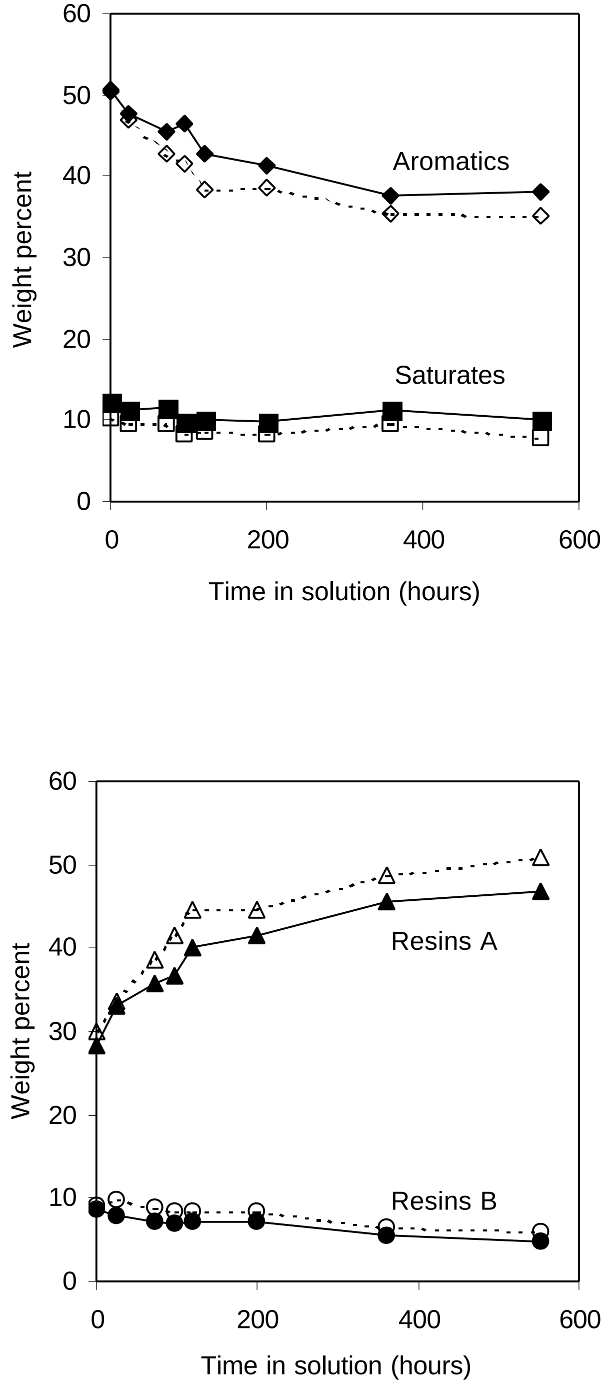

Figure 4. Composition of bitumen B obtained on new (full line) and old (dotted line) chromarods.

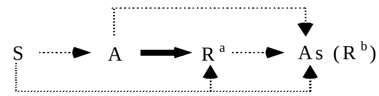

Figure 5. Upon oxidative aging, bitumen composition evolves as shown by the arrows. In solution, the transformation is limited to that shown by the full line. S, saturates; A, aromatics; R^a, resins A; As, asphaltenes or R^b, resins B.

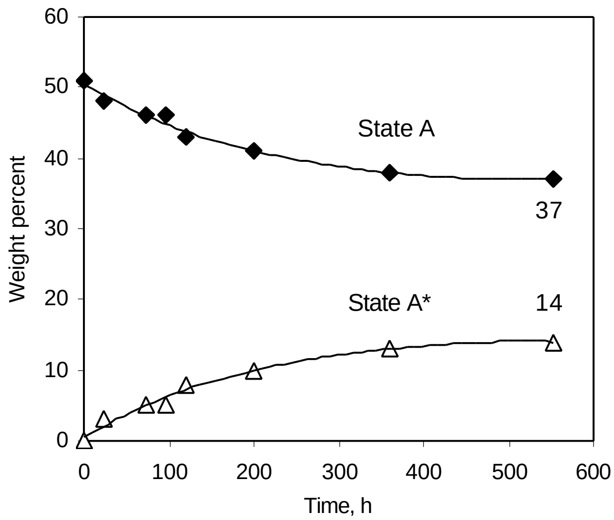

Figure 6. Modeling the decrease in aromatics and its conversion into specie A* after equation 1. The values for the aromatics are those from Figure 3. The concentration of A* is A_o-A. The equilibrium values (indicated) allow for calculating the equilibrium constant K_{eq}. See text for details.

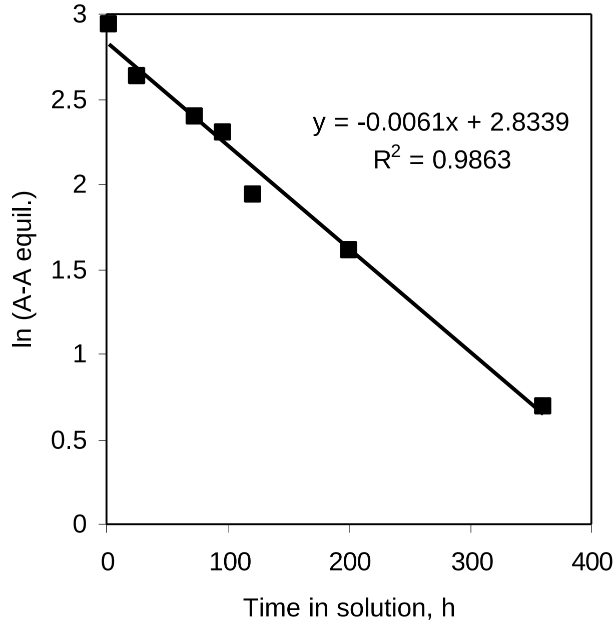

Figure 7. Plot from equation 2. The slope, k+k', is 0.0061 h^{-1} or 1.7 x 10^{-6} s^{-1}.

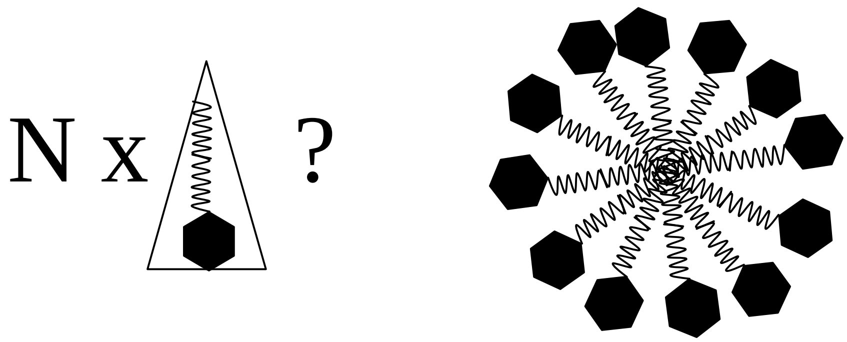

Figure 8. 2D representation of the flocculation of some aromatics into a micelle. Molecules with a triangular shape, such as monoalkylated-aromatic molecules, provide the right geometry for the formation of a sphere. The polar shell formed by the aromatic rings can be stabilized by a solvent with a dielectric constant higher than that of bitumen.