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INTERACTION OF TETRAHYDROFURAN WITH ATHABASCA BITUMEN

By

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INTRODUCTION

Athabasca bitumen has been the subject of numerous investigations with attention usually focussing on the structure and chemical composition. Important works related to this subject have been extensively reviewed by Bunger et al. (1).

Separation of bitumen into a number of fractions is always the first step in these studies. Subsequently, the fractions are characterized by chemical and spectroscopic techniques. In most published work, the separations are based on different solubilities of bitumen fractions in various solvents. Combinations of solubility effects and chromatographic fractionation of bitumen are also frequently used.

Recently, Furinsky et al. (2) have fractionated an athabasca bitumen in tetrahydrofuran by gel permeation chromatography (GPC), which separates molecules on the basis of their molecular size. Structural parameters were determined from proton nmr. Elemental, nickel and vanadium analyses of the fractions were also reported. All of these fractions had exceptionally high oxygen content compared with that of the feed. As THF is known to form hydrogen bonded complexes with a number of compounds (3), this anomalous oxygen content could be caused by the interaction of THF with some bitumen components. We, therefore, undertook to investigate the interaction of tetrahydrofuran with bitumen both as an eluent in the GPC fractionation and as a solvent. The fractions have been characterized using elemental analyses and infrared and ^{13}C nmr spectroscopy.

EXPERIMENTAL

The sample of Athabasca bitumen was obtained from the Alberta Research Council sample bank. This was a standard bitumen sample used recently in a round robin study (4).

Gel Permeation Chromatography

Equipment - The liquid chromatographic system consisted of a microprocessor controlled solvent delivery system (series 3B), an auto sampler (model ISS-100), a variable wavelength scanning uv detector (LC 75/AC) and a refractive index (RI) detector (LC-25), all from the Perkin-Elmer Corp.

Column - Fractionation of bitumen was performed using a μ -styragel column (30 cm x 7.8 mm I. D., Waters Associates) of pore size 500Å.

Solvents - All solvents used in this study were of analytical grade or HPLC grade and were used without further purification.

Procedure - Bitumen solutions in THF were filtered using micro pore filters (Millipore; pore size $\sim 0.45\ \mu\text{m}$) prior to transferring into the vials. Concentration of bitumen solution was $\sim 4\%$. $50\ \mu\text{l}$ of the sample was injected using a flow rate of $1\ \text{ml}^{\text{L}}$ per minute. The fractionation in THF was carried out with the uv detector set at 254 nm and in toluene, at 290 nm.

Solvent Evaporation

The greater part of the solvent was removed in a Brinkman rotary evaporator at 50°C for THF, or 80°C for toluene, under reduced pressure. The remaining solvent was removed on a Brinkman model SC/24R sample concentrator, under nitrogen.

In a separate experiment, 0.5 g of bitumen was dissolved in 1 litre of THF. Solvent was then removed from half of this solution at 50°C and the other half at room temperature using the procedure outlined above.

Elemental Analyses

C, H and N analyses were performed using a Perkin-Elmer model 240 CHN analyzer. Sulfur was analyzed as total sulfur X-ray fluorescence spectroscopy. Oxygen was determined by

difference.

Instrumental Analyses

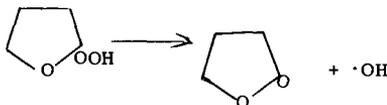
Infrared spectra were recorded using a Perkin-Elmer model 683 IR spectrometer. Samples were run as thin films on KBr plates.

^{13}C nmr spectra were obtained at 45.26 MHz on a Bruker CXPI80 nmr spectrometer under ^1H decoupling conditions and 5000-30,000 puses at intervals of 2 seconds.

RESULTS AND DISCUSSION

GPC elution curves of Athabasca bitumen in both tetrahydrofuran and toluene obtained using uv detector are shown in Figure 1. The sample was separated into two fractions as shown in the figure. Fraction 1 should contain the higher molecular weight material, which was confirmed by the molecular weights determinations on the two fractions. Polydispersity, the ratio of the weight average molecular weight to the number average molecular weight indicates a wider distribution of molecular sizes in fraction 1 compared with fraction 2.

Elemental composition of bitumen fractions, obtained from GPC and after treating with THF in both air and nitrogen, are given in Table I. Since oxygen content was determined by difference, all the errors in the determinations of carbon, hydrogen, nitrogen and sulfur will accumulate in the oxygen results. Elemental composition of GPC fractions in toluene indicates higher heteroatom (N, S, O) content of fraction 1 compared with fraction 2. This is again consistent with fraction 1 being a heavier fraction because heavier fractions of bitumen are known to contain higher heteroatom content (5). Elemental composition of the GPC fractions in THF cannot be rationalized simply on the basis of heavier and lighter fractions. Whereas there is no significant difference in the chemical compositions of fraction 2 in THF or toluene, the fractions 1 have very different chemical compositions. Most of the nitrogen is concentrated in fraction 1 for toluene solutions, whereas the corresponding fraction in THF has no detectable nitrogen. Also, the oxygen content of fraction 1 in THF is much higher than the corresponding fraction in toluene. THF is well known to form an unstable hydroperoxide which decomposes according to (6-8):



It has been previously reported that in the presence of free radical initiators THF and other ethers are not inert solvents and they act both as reactant and solvent (9). Incorporation of THF during the reductive alkylation of coal has also been noticed. The nature of the interaction between THF and the alkylated coal was said to be mysterious (10). Carson et al. (11) have reported the formation of trace quantities of an unidentified compound during the reaction of 1,2,3,4-tetrahydronaphthalene with THF. Cleavage of THF by benzene has long been observed (12). Therefore, in view of the reactivity of THF, particularly in the presence of free radical initiators, the interaction of THF or THF hydroperoxide decomposition products with bitumen components would not be surprising. Interaction of bitumen with THF was, therefore, investigated both in the presence of air and nitrogen. Elemental composition of bitumen treated with THF in the presence of air suggests the possibility of such an interaction. This bitumen has an unexpectedly high oxygen content that cannot be explained on the basis of experimental errors. The loss of nitrogen on heating bitumen with THF in air is consistent with the GPC results, where the absence of nitrogen was also found in the heavier fraction from THF solution.

HPLC grade THF used in this investigation contained no inhibitor. On treating with acidified KI, it liberated trace quantities of iodine indicating the presence of small quantities of hydroperoxide. Therefore, in a separate experiment, THF was freshly distilled from LiAlH_4 to remove hydroperoxide. This freshly distilled THF, when treated with bitumen under nitrogen, gave elemental analysis very similar to that of untreated bitumen. This demonstrates the significance of THF hydroperoxide during the interaction of bitumen with THF.

Infrared Spectra

Infrared spectra of Athabasca bitumen, its GPC fractions in THF and bitumen treated with THF in air, are shown in Figure 2. Infrared spectra of bitumen treated with freshly distilled THF in nitrogen and its GPC fractions in toluene were similar to that of the untreated bitumen. The infrared spectrum of GPC fraction 2 in THF is also similar to the infrared spectrum of untreated bitumen. However, the infrared spectra of GPC fraction 1 in THF and of bitumen treated with THF in

air contain characteristic absorption bands assignable to oxygen functions. Both exhibit a broad absorption band in the 3100-3500 cm^{-1} region due to the presence of hydrogen bonded -OH (13). Two sharp bands at 1725 and 1770 cm^{-1} present in the infrared spectra of GPC fraction 1 from THF and bitumen treated with THF in air have previously been assigned to six membered ring anhydrides (14, 15), acyl and aryl peroxides (16) and to α -hydroxytetrahydrofuran and butyrolactone (17), which are the decomposition products of tetrahydrofuran hydroperoxide (18). However, a definite assignment for the carbonyl absorption is difficult because a number of oxygen containing functions including aldehydes, ketones, acids and esters absorb in this region (19) and all of these species are said to be produced during the oxidation of bitumen and asphaltic materials (14, 15, 20-23).

TABLE I
CHEMICAL COMPOSITION OF BITUMEN FRACTIONS

Fraction	Elemental Analyses (Wt %)					Polydispersity ^e
	C	H	N	S	O ^d	
Athabasca bitumen (feed)	83.01	10.48	0.44	4.74	1.33	6.0
GPC-fraction 1 in toluene ^a	80.44	9.97	0.42	5.10	4.07	7.8
GPC-fraction 2 in toluene ^b	82.92	10.79	0.11	3.88	2.30	1.0
GPC-fraction 1 in THF ^a	76.08	9.80	-	4.58	9.54	4.3
GPC-fraction 2 in THF ^b	81.83	9.70	0.20	5.06	3.21	1.1
Bitumen treated with THF ^c at 30°C in air	70.88	8.83	0.32	3.48	16.49	N. D.
Bitumen treated with THF ^c at 50°C in air	65.21	8.60	-	4.5	21.69	N. D.
Bitumen treated with THF ^c at 50°C in N ₂	81.08	9.98	0.34	5.19	3.41	N. D.

- Collected between 0 and 26 minutes.
- Collected between 26 and 33.5 minutes.
- 0.5 g of bitumen dissolved in 1L of HPLC grade THF and then solvent removed under reduced pressure at 30°C in one case and 50°C in the other two cases.
- Determined by difference.
- Ratio of wt average molecular wt to no. average molecular wt determined by GPC.

N. D.: Not determined.

¹³C NMR
¹³C nmr spectra of Athabasca bitumen, its GPC fractions in toluene and THF, and bitumen treated with THF in air are shown in Figure 3. The ¹³C nmr spectrum of bitumen treated with freshly distilled THF under nitrogen was similar to the nmr spectrum of the untreated bitumen. Also, it is obvious from the spectra in Figure 3 that GPC fractions in toluene have similar spectra to that of untreated bitumen. GPC fraction 2 in THF has a much simpler spectrum resembling the spectrum of untreated bitumen except that the long chain methylene peak at ca. 29.7 ppm is less intense and the low field broad absorption in the aromatic region has disappeared. This suggests that GPC fraction 2 has much simpler aromatic systems with none or very few branched substituents.

The ¹³C nmr spectra of GPC fraction 2 in THF and bitumen treated with THF in air at 30°C and 50°C contain a number of resonances characteristic of oxygen functions (24-28). All three fractions exhibit signals over the ranges 60-68 and 98-109 ppm that can be assigned to the α -alkyl carbon of alcohols, ethers and esters. The sets of signals at 161-163 ppm, 175-178 ppm and 201-202 ppm exhibited by GPC fraction 2 in THF and by bitumen treated with THF in air at 50°C, are due to anhydrides, esters, acids, aldehydes, ketones and quinones. The resonances of 130-136 and 143-146 ppm exhibited by the bitumen treated with THF in air at 50°C are most likely due to the presence of peri- and cata-condensed systems.

The presence of butyrolactone, a decomposition product of THF hydroperoxide (18), is indicated by the resonances of 178, 69, 28 and 22 ppm in the spectra of GPC fraction 2 in THF and of the bitumen treated with THF in air at 50°C.

Based on the results of the spectroscopic studies and elemental analyses of the GPC fractions of bitumen and bitumen treated with THF, the following conclusions can be drawn.

1. Bitumen reacts with THF in presence of air producing considerable quantities of oxygen containing functional groups. Oxidation of bitumen by THF results in the initial formation of THF hydroperoxide which decomposes giving

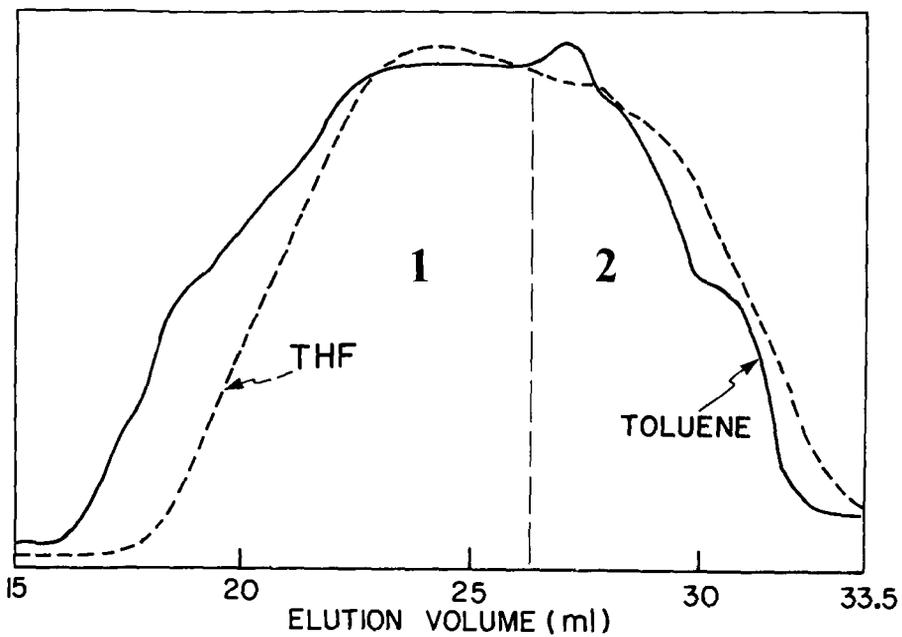


Figure 1. GPC chromatogram of Athabasca bitumen obtained using uv detector. — in toluene; - - - - in THF.

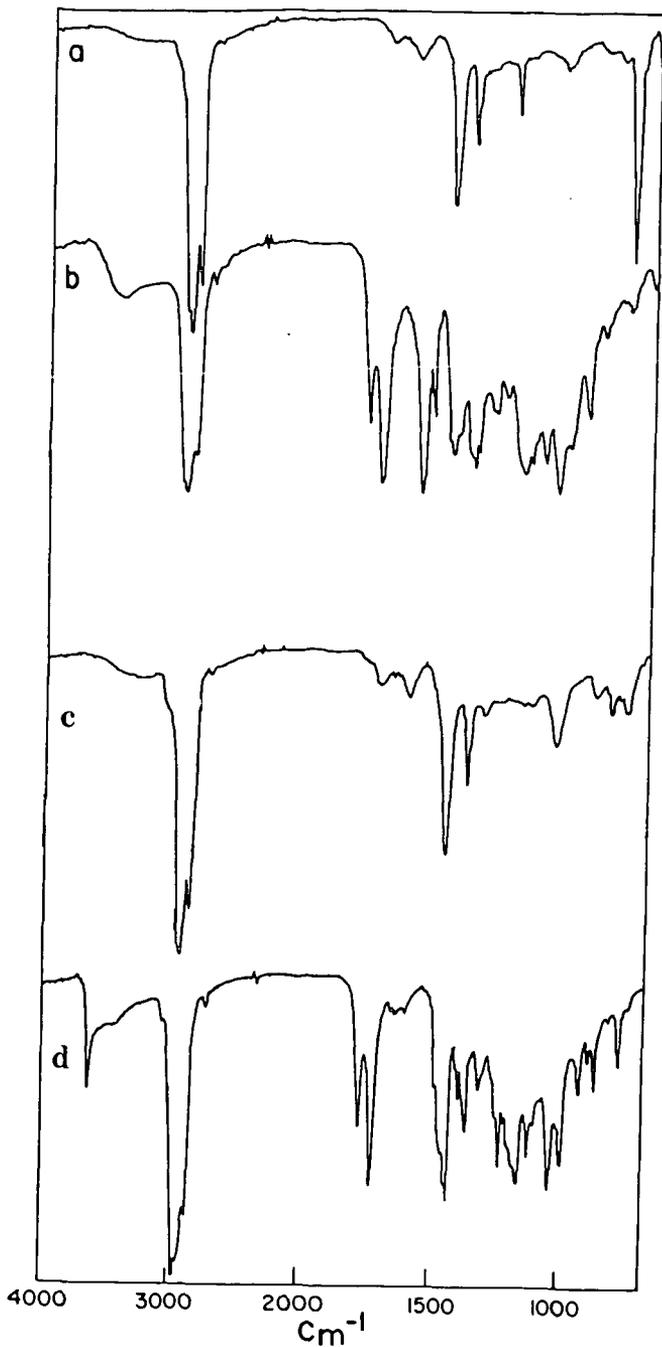


Figure 2. Infrared spectra of a) Athabasca bitumen; b) Bitumen dissolved in THF and solvent removed under reduced pressure; c) GPC fraction in THF collected between 26 and 33.5 minutes; d) GPC fraction in THF collected between 0 and 26 minutes.

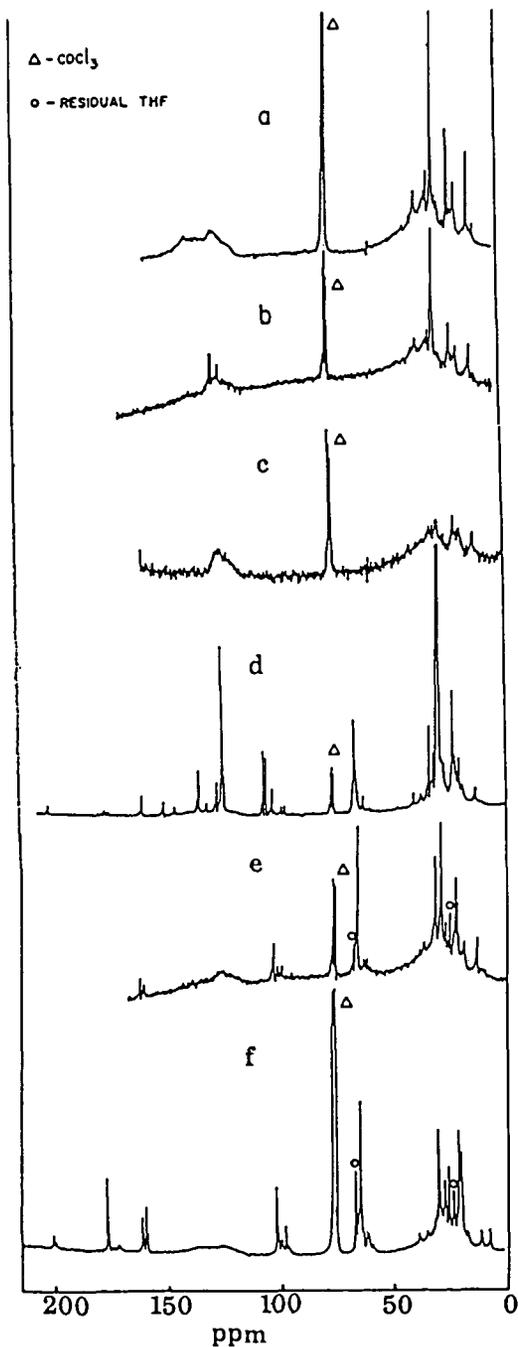


Figure 3. ^{13}C nmr spectra of a) Athabasca bitumen; b) a typical GPC fraction in toluene; c) GPC fraction in THF collected between 26 and 33.5 minutes; d) GPC fraction in THF treated with THF at 30°C in air and 26 minutes; e) Bitumen treated with THF at 30°C in air and f) Bitumen treated with THF at 50°C in air.



and $\cdot\text{OH}$ radicals that act as initiators.

2. Oxidation of bitumen by THF is faster at 50°C than at room temperature.
3. THF only oxidizes heavier fractions of bitumen which are rich in heteroatom content (N, O, S). This is consistent with the previous results for the oxidation of bitumen (29, 30).
4. Oxidation of bitumen by THF can be prevented by using freshly distilled THF containing no hydroperoxide.

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