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### PPA-Modified Bitumen: Disruption of the Asphaltenes Network Based on the Reaction of Non-Basic Nitrogen with Polyphosphoric Acid

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Abstract

Relatively little is known about the effect of polyphosphoric acid (PPA) on bitumen chemistry and structure. In an effort to increase this understanding, the reaction of indole with PPA was studied by Fourier-transform infrared spectroscopy (FTIR). Indole contains a pyrrole functional group very common in bitumen. The results revealed that both the amine and the double bond of indole can be reactive, and that indole concentration affected the reaction pathway. All reactions began with the protonation of the indole double bond, which provided two reactive carbocation intermediates. When the concentration of indole was high, each carbocation coupled with unprotonated indole and two products were obtained. In one case two N–H groups produced a N–N bond, and in the other case two indole double bonds to produced a cyclobutane ring. When the concentration of indole was reduced by dilution, N-H coupling proceeded without double bonds coupling, and a reaction with the PPA anion was found to occur instead. These findings indicate that the effect of PPA in bitumen may be to raise molecular stiffness through N–N bridging, while at the same time disrupt the hydrogen bond network where the N–H function of pyrrole groups is involved and reduce the effective molecular weight of asphaltenes.

#### Introduction

Polyphosphoric acid (PPA) is often reacted with bitumen in an effort to modify its flow characteristics.<sup>1,2</sup> Work on some PPA-modified bitumen has allowed for a glimpse of the possible reactions between the two components,<sup>1,3</sup> but the complexity of bitumen composition and its variation with petroleum crude source precludes a detailed understanding of these reactions. It is therefore essential to resort to the reaction of bitumen model compounds with PPA to improve this understanding.

In earlier work, we postulated that PPA reacted with bitumen in domains rich in heteroatomic functional groups.<sup>4</sup> Accordingly, we showed that model compounds with basic pyridine or pyridinone functional groups formed ionic-pairs with PPA.<sup>5</sup> Here, we present work on the reactivity of the non-basic pyrrole function, which is often the most common of the heteroatomic functional groups of bitumen.<sup>6</sup> In this respect, we show by means of infrared spectroscopy that both the double bond and the amine group of the pyrrole ring can lead to coupling (dimerization), and that the amine group is subject to phosphorylation.

#### Experimental

Reactants were selected in an effort to reproduce the mixing conditions used to prepare PPA-modified bitumen, i.e., mixing at 150°C to 180°C. Consequently, indole (Sigma-Aldrich, b.p. 253°C), which contains a pyrrole ring was selected for reaction with PPA, instead of pyrrole (b.p. 131°C). Their structure can be compared in Figure 1. PPA with a 115% H<sub>3</sub>PO<sub>4</sub> content was supplied by ICL Performance Products LP. Its P<sub>2</sub>O<sub>5</sub> content

was 83.3.%, in other words, the H<sub>3</sub>PO<sub>4</sub> content/1.38.<sup>4</sup> In the experiment, PPA was mixed with indole in a 1:5 weight ratio. This ratio allowed for an excess of indole and enough products for analysis by infrared spectroscopy. To prevent undue oxidation of reactants or products during heating, the reaction vessel was flushed with argon prior to heating,<sup>5</sup> after which the mixture was stirred 1h at 150°C. After the reaction mixture had cooled to room temperature, it was dissolved in acetone to separate the products and PPA, which is insoluble in acetone. A drop of the soluble products was applied to a KBr crystal for analysis by Fourier-transform infrared spectroscopy (FTIR) as described earlier.<sup>5</sup> The reaction yield was calculated based on the loss of N–H absorbances.

Diluted indole was also heated with PPA. The PPA:indole:diluent weight ratio was 1:5:25. Both indan (Sigma-Aldrich, b.p., 176°C) and butyl phenyl ether (Sigma-Aldrich, b.p., 210°C) were used as a diluent. The reaction vessel was flushed with argon prior to heating.<sup>5</sup> Products were fractionated from reactants by flash chromatography<sup>7</sup> with toluene followed by ethyl acetate, and then analyzed by infrared spectroscopy.<sup>5</sup>

The intensity of all the infrared spectra was normalized to the common aromatic absorbance at  $1457\pm2$  cm<sup>-1</sup>. The infrared frequencies of the double bond in indole and its products were assigned based on its comparison with indan, indene, and thianaphthene (Figure 1). Other infrared frequencies were assigned based on compilations.<sup>8-10</sup>

#### **Results and discussion**

#### Reaction of indole with PPA

At room temperature, crystalline indole did not dissolve in PPA. Upon heating to 150°C, indole melted and formed an immiscible layer above PPA. After ten minutes of heating with PPA, the upper indole layer had turned to a transparent yellow, which indicated that indole was not immune to the effect of PPA despite the immiscibility.

Figure 2 shows the FTIR spectrum of the indole layer (R) after one hour of heating with PPA. Unheated indole is used for comparison. Most conspicuous was a large decrease in the amine (N–H) absorbance of the product at 3403 cm<sup>-1</sup>. From this decrease, the transformation of indole was estimated at 70%. This decrease was consistent with that of other N–H absorbances at 1505 cm<sup>-1</sup> and 429 cm<sup>-1</sup>. There was also a decrease in double bond (C=C) absorbances at 1353 cm<sup>-1</sup>, 766 cm<sup>-1</sup>, 724 cm<sup>-1</sup>, 613 cm<sup>-1</sup>, and 503 cm<sup>-1</sup> and new C–H absorbances at 2989 cm<sup>-1</sup>, 2870 cm<sup>-1</sup> and 1142 cm<sup>-1</sup>.

The change in indole upon its reaction with PPA was consistent with the reaction sequence shown in Figure 3. As expected from electrophilic addition onto indole,<sup>11</sup> the sequence begins with protonation of the double bond at the carbon furthest from the nitrogen. This leads to a carbocation stabilized by two resonance structures (B and C in Figure 3). The nucleophilic addition of the nitrogen lone electron pair of indole onto the charged nitrogen of carbocation C produces nitrogen head-to-head coupling as in compound D. Such coupling was obtained before by electrochemical synthesis<sup>12</sup>, and interestingly, it occurs through the aromatic lone pair of electron on nitrogen. In contrast,

the electrophilic addition of carbocation B onto the double bond of unprotonated indole leads to intermediate F from which the loss of a hydrogen ( $H_a$  or  $H_b$ ) can produce E and G.

The spectrum of the product in Figure 2 provides evidence for compounds D and G. Nitrogen head-to-head coupling is consistent with the decrease of N–H absorbances of compound D. Electrophilic addition of compound B onto the indole double bond produces the cyclobutane ring in compound G, which is consistent with C–H stretching frequencies at 2989 cm<sup>-1</sup> and 2870 cm<sup>-1</sup>, notably higher than those in normal alkanes because of ring strain.<sup>8-10</sup> Such rings are very common in natural products, and the structure of G is reminiscent of that in lumicolchicine alkaloids.<sup>13</sup>

Thin-layer chromatography of the reaction mixture showed only two products. Given the absence of evidence for compound E in the FTIR spectrum of reacted indole, i.e., the absence of a new absorbance near 800 cm<sup>-1</sup> for its triply substituted double bond,<sup>10</sup> it was concluded that indole produced two compounds, D and G, upon heating with PPA, both of which were the result of intermolecular coupling.

#### Reaction of diluted indole with PPA

Nitrogen concentration in bitumen is usually below 1%. It is therefore uncertain that indole coupling as shown in Figure 3 would occur in bitumen when pyrrole functional groups are far apart, dispersed in a sea of alkyl aromatics. To better simulate this reality, indole was first diluted separately with indan and then with butyl phenyl ether (Figure 1).

When the diluents were heated alone with PPA, no change was visible in their respective infrared spectrum. As they were alkyl aromatics typical of bitumen compounds and they were immune to the effect of PPA, the diluents allowed for a more effective assessment of the true nature of the reaction between PPA and the pyrrole rings in bitumen.

Upon the heating of diluted indole with PPA, the extent of the reaction was as before about 70%, which indicated that indole diffusion was effective within the diluent. In this case, the mixture was fractionated on a flash column, and a major and a minor fraction were obtained. Their respective yields were estimated at 55% and 15%. The premise was that they were compounds D and G obtained earlier with undiluted indole (Figure 2), but FTIR showed the premise to be false.

Like undiluted indole (Figure 2), the FTIR of the major fraction showed a decreased N–H band at 3403 cm<sup>-1</sup>. However, it did not show the typical cyclobutane C–H absorbances at 2989 cm<sup>-1</sup> and 2870 cm<sup>-1</sup> (not shown). Consequently, this fraction did not contain compound G. This left compound D as a possible product in the major fraction. The production of compound D with its N–N bridge was consistent with the loss of N–H at 3403 cm<sup>-1</sup> and 426 cm<sup>-1</sup> (Figure 4), but decreases in the absorbances typical of orthoaromatics and cis double bonds, respectively at 725 cm<sup>-1</sup> and 746 cm<sup>-1</sup>, could not readily be accounted by the reactions illustrated in Figure 3. Given that absorbance is governed by both concentration and molar absorptivity,<sup>8</sup> the decrease in the intensities of the typical ortho aromatic and the cis alkene absorbances were tentatively assigned to a decrease in molar absorptivity.

To confirm that a change in molar absorptivity was responsible for the decreased absorbances in indole at 725 cm<sup>-1</sup> and 746 cm<sup>-1</sup>, compounds with a structure analogous to that of indole were compared. Table 1 lists the relative absorptivities of the double bond below the ortho-aromatic band in indole, indene, and thianaphthene whose structures are shown in Figure 1. These compounds only differ in the size and mass of the group between the benzene ring and the cis double bond, namely, NH, CH<sub>2</sub>, or S. As shown in the table, the group affects the molar absorptivity and the frequencies of both the double bond and the ortho-aromatic absorbances. The variation was consistent with the results in Figure 4. The greatest change was shown by the typical absorbances for ortho aromatics and cis alkenes, with respective coefficients of variation of 30% and 40%. The decrease in the intensity of the indole absorbances after its reaction with PPA was therefore attributed to a change in mass between the aromatic ring and the cis double bond, that is to say, to a coupling reaction of the amine group.

With these results, the composition of the major fraction of the reaction of diluted indole with PPA was clear. It was compound D with some unreacted indole (Figure 3), with the indole being responsible for the residual NH absorbance in the spectrum.

Based on the above results with diluted and undiluted indole, the minor fraction was expected to be compound G (Figure 3). The FTIR spectrum of this fraction did show C–H absorbances (Figure 5), but the frequencies were not those in Figure 2. At 2855 cm<sup>-1</sup>

and 2960 cm<sup>-1</sup>, they were typical of  $CH_2$  and  $CH_3$  absorbances in alkyl segments. Consequently, this fraction was not compound G.

The FTIR spectrum of the minor fraction showed broad and overlapping O–P=O absorbances between 800 cm<sup>-1</sup> and 1600 cm<sup>-1</sup> (Figure 5). These absorbances arise from PPA, H[O–P(=O)(OH)]<sub>n</sub>OH.<sup>5</sup> Consequently, the minor fraction was produced by a reaction between PPA and indole. The spectrum demonstrated that reactions occurred onto both the amine and the double bond. There was a very large loss in N–H at 3403 cm<sup>-1</sup>, and the complete disappearance of C=C bands at 1337 cm<sup>-1</sup>, 764 cm<sup>-1</sup> and 726 cm<sup>-1</sup> (Figure 5). The ortho aromatic band was retained, but its intensity was reduced, which was consistent with that in the major fraction.

The total loss of double bond absorbance, the large reduction in NH and the new O–P=O absorbances are all explained by a reaction between PPA anions  $(H[OP(=O)(OH)]_nO^-$ , henceforth written as PPAO<sup>-</sup>) and protonated indole resonance structures (Figure 6). From successive protonation and nucleophilic attacks by the anion, four phosphorylated products are possible, with H and I being single PPA adducts, and J and K being double adducts. Given that PPA is a chain with several OH groups,<sup>5</sup> the first phosphorylation is likely followed by cascading intramolecular phosphorylation that leads all the way to K. Such a cascade was consistent with a single product in thin-layer chromatography (TLC), and new CH<sub>2</sub> and CH<sub>3</sub> signals from an ethyl group in compound K. Notwithstanding the TLC results, this fraction was not entirely pure. The infrared spectrum showed residual NH signals, which indicated that the conversion all the way through to compound K was

not quite complete. A low yield of 15% indicated that the second reaction step, the nucleophilic addition of the anion onto the carbocations, is likely rate determining. In other words, the PPAO<sup>-</sup> anion is a weak nucleophile.

#### Intermolecular associations and molecular stiffness in PPA-modified bitumen

Given that PPA is used to modify bitumen, it is useful to reflect on the significance of the above findings on the chemistry and the intermolecular associations of different compounds in bitumen. In this respect, the results are of particular significance when the high molecular weight asphaltenes are considered. The asphaltenes fraction is nitrogenrich<sup>14</sup> and it is the fraction most likely to contain the non-basic pyrrole functional groups tested here in indole.

Regardless of dilution, the major product of the reaction between PPA and indole was a compound with an N–N bridge (compound D, Figure 3). In this respect, two issues must be highlighted, firstly, the effect of bridging, and secondly, the loss of the starting amine groups. Bridging increases molecular weight. This reduces molecular mobility and raises glass transition temperatures  $(T_g)$ .<sup>15</sup> In bitumen, asphaltenes have a  $T_g$  above room temperature,<sup>16</sup> in the vicinity of 50 to 70°C.<sup>17,18</sup> This is the temperature region where a stiffening effect of PPA is observed.<sup>1,3</sup> Nitrogen bridging may be partly responsible for this stiffening.

The loss of N–H groups would reduce the network of hydrogen bonds in domains rich in heteroatoms,<sup>4</sup> especially in asphaltenes. Pyrroles and indoles are non-basic because the

nitrogen lone pair of electron is part of an aromatic system.<sup>11</sup> The nitrogen electrons cannot bond to a hydrogen, but the nitrogen proton can associate with free electron pairs in neighbouring pyridines, phenols, ketones, carboxylic acids, and other groups capable of sustaining a hydrogen bond. The loss of amine groups due to PPA thus translates into a loss of hydrogen bonding capabilities, which means that compounds no longer held together by these forces have a lower effective molecular weight (and a lower  $T_g$ ), in accordance with result of gel permeation chromatography.<sup>1,3</sup> Consequently, it would promote the dispersion of asphaltenes in maltenes, in accordance with the idea set forth by Orange et al.<sup>1</sup> The loss of hydrogen bonds may also lead to a softening that would compete with the stiffening provided by bridging.

The effect of two bond couplings such as that in compound G would provide for the greatest restriction of molecular motion and the greatest rise in  $T_g$ . However, based on our findings, it can only occur when indole double bonds concentration is high. Given that indoles are diluted in bitumen in a sea of other compounds, the likelihood that such coupling would occur is low. Coupling reactions with analogs such as indenes and thianaphthenes cannot be excluded, but the study of cross-coupling was outside the scope of this work.

In its reaction with indole, PPA was found to be both a reaction catalyst and a reactant. As a reactant, it added (slowly) onto the amine. In bitumen, the phosphorylation of the NH group would affect intermolecular association, as indicated above, and it would induce some softening by affecting the  $T_g$  and the molecular backbone. The effect on Tg would be like random copolymerization.<sup>15</sup> The  $T_g$  of PPA is  $-10^{\circ}$ C,<sup>19</sup> so its reaction with asphaltenes would in principle drag the  $T_g$  of asphaltenes down towards  $-10^{\circ}$ C. The concentration of PPA in bitumen is most often below 1%, and the yield of phosphorylation is low, so the decrease in  $T_g$  due to phosphorylation of the NH group may be subtle. The effect might be compounded by internal plasticization,<sup>15</sup> however. In going from indole to the final double PPA adduct (compound K), the 5-membered ring opened to give a benzene ring with two pendant chains that have a greater degree of motion than the original ring. As greater molecular motion provides for lower  $T_g$ ,<sup>15</sup> the net effect of phosphorylation may be a softening of bitumen. Clearly, a true appreciation of the effect of PPA on bitumen can only be obtained after the reactivity of other model functional groups have been studied, and after a detailed analysis of  $T_g$ s in PPA-modified bitumens. We will address these issues in future publications.

#### Conclusion

The reaction of diluted and undiluted indole with PPA was studied by FTIR and the changes in the structure of indole were explained by a mechanistic analysis of the reaction pathways. Upon heating undiluted indole with PPA, two products were obtained. FTIR of the reaction mixture showed new bands related to cyclobutane and the loss of N–H and C=C in the pyrrole ring. This was consistent with the head-to-head coupling of two indole molecules into a compound with a N–N bond, and with the coupling of double bonds from two indoles to form a strained cyclobutane ring. Upon heating indole diluted with an inert alkyl aromatic and PPA, head-to-head coupling still occurred, but double bond coupling did not occur. Instead, the indole reacted with the

PPAO<sup>-</sup> anion in a cascade of reactions that led to the opening of the 5-membered ring and the production of a tertiary nitro-phosphorylated product.

On the basis of this study, PPA would disrupt the hydrogen bond network in bitumen, where pyrrole or indole N–H functions are involved. In this respect, it would reduce the effective molecular weight of asphaltenes aggregated through hydrogen bonds and disrupt the asphaltenes–maltenes equilibrium. Based on competing N–N bridging and ring opening reactions, PPA would also increase the stiffness of some molecular segments, while at the same time reduce that of others. This is consistent with the current inability to predict the stiffening effect of PPA on bitumen and its variation with bitumen sources. In attempts to predict this effect, we will explore in later publications the relationship between the work on model compounds and the actual reactivity of bitumens with PPA.

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(19) Shen, M. C.; Ensenberg, A. Glass transitions in polymers, *Rubber Chem. Technol.* **1970**, *43*, 95-155. **Table 1.** Relative absorptivity<sup>a</sup> of some aromatic and alkene infrared absorbances<sup>b</sup> in similar ring systems

Figure 1. Aromatic compounds referred to in this work.

Figure 2. FTIR spectra of indole before and after its reaction (R) with PPA.

**Figure 3.** Potential coupling reactions of indole (A) with its cations (B, C). For clarity of presentation, not all hydrogens are shown.

**Figure 4.** FTIR spectrum of the major product of the reaction (Rx) of diluted indole with PPA. The lighter shaded labels indicate noteworthy absorbance losses.

**Figure 5.** FTIR spectrum of the minor product (Rx') from the reaction of diluted indole with PPA. The normalization band is shown with a star at  $1456 \text{ cm}^{-1}$ .

**Figure 6.** Mechanistic analysis of the transformation of indole into PPA adducts through successive phosphorylation. The PPA anion is written as PPAO<sup>-</sup>.

Compounds	Group <sup>c</sup>	Ortho	Cis C=C	C=C	C=C
Indole	NH	2.9 (746)	1.9 (726)	0.8 (612)	0.9 (503)
Indene	$CH_2$	1.5 (718)	1.0 (697)	0.6 (550)	none
Thianaphthene	S	1.9 (737)	2.3 (693)	0.6 (559)	1.0 (471)
Indan <sup>d</sup>	$\mathrm{CH}_2$	2.3 (749)	none	none	none
COV <sup>e</sup> (%)		30	40	20	10

**Table 1.** Relative absorptivity<sup>a</sup> of some aromatic and alkene infrared absorbances<sup>b</sup> in similar ring systems

<sup>a</sup> With respect to normalized aromatic absorbances at 1457±2 cm<sup>-1</sup> <sup>b</sup>Frequency is in parenthesis. <sup>c</sup> Group between the benzene ring and the cis double bond. <sup>d</sup> Indan does not have a double bond. <sup>e</sup>The coefficient of variation is the mean absorptivity over its standard deviation.



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Figure 2. FTIR spectra of indole before and after its reaction (R) with PPA.



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