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Chemical Characterization of Coal Tar–Water Interfacial Films

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Semigelatinous interfacial films, which may influence the fluid mechanic and mass transfer properties of coal tar in porous media, have been observed to form in coal tar–water systems when coal tars are aged in water under quiescent conditions for a few days. Samples of the interfacial film were isolated after aging for a period of 1 year and compared to the bulk coal tar using GC/MS, ¹³C-NMR, ¹H-NMR, and FTIR techniques. The results showed that these films were very similar in organic composition to the bulk coal tar with no significant enrichment, depletion, or polymerization of tar components. The notable difference in the composition of the film material was the presence of water bound to coal tar constituents by weak, reversible bonds. FTIR analysis of a sample of coal tar film kept in contact with deuterated water showed that the water molecules bound to the coal tar constituents would slowly interchange with water molecules that were not bound. Similar bonding of water molecules and coal tar constituents was observed in coal tar–water emulsions. These results suggest that the semigelatinous film formed at the coal tar–water interface is similar to a thin emulsion layer.

Introduction

Prior to the widespread use of natural gas, manufactured gas plants (MGPs) supplied gaseous fuel derived from coal, coke, and/or oil. A major byproduct of manufactured gas process was coal tar, which today is often associated with subsurface contamination at former MGP sites (1). Coal tar contamination of soil and sediments is found also at facilities that have engaged in coal tar refining and wood preserving. The slow dissolution of organic solutes from coal tar can cause long-term groundwater contamination. Coal tars are dense, nonaqueous phase liquids (DNAPLs)

primarily composed of polycyclic aromatic hydrocarbon (PAH) compounds. Various studies have summarized factors affecting the transport of DNAPLs in the subsurface (2–4). It is generally recognized that complete remediation of groundwater may be technically impractical at DNAPL-contaminated sites (5). This points to a need for more fundamental understanding of interfacial phenomena and mass transfer kinetics for both *in-situ* and *ex-situ* remediation technologies for DNAPL contamination.

Coal Tar Interfacial Films. Recent experiments have demonstrated that the coal tar–water interface undergoes a visible change as coal tar is aged in water. It is believed that these changes may influence the fluid mechanic and mass transfer properties of coal tar in porous media. Skin-like films may be observed at the coal tar–water interface when a coal tar is aged in water over a few days (6). The change in physical characteristics of the coal tar–water interface has been demonstrated by photographic observations using a pendant drop apparatus with free-phase coal tar recovered from the subsurface at two former MGP sites. In this test, a drop of coal tar was expressed through a syringe equipped with microthread threads with the tip of the syringe immersed in deionized water. The drop of coal tar formed at the tip of the syringe was spherical in shape and was kept suspended in deionized water for a period of 3 days or more (Figure 1A). When the coal tar drop was slowly retracted by operating the microthread, a wrinkled, skin-like texture was observed at the coal tar–water interface (Figure 1B). After the liquid coal tar had been drawn back into the syringe, the film or skin remained suspended from the tip of the syringe, suggesting a transformation and the existence of a material having a composition different from the bulk coal tar. In contrast, if the coal tar drop was retracted into the syringe without aging, the tar droplet would retract into the needle without any noticeable shape or textural change. A coal tar obtained from a different site showed a similar but less wrinkled film (Figure 1C). A sample of coal tar aged for 1 year in a beaker exhibits distinct textural features at the NAPL–water interface (Figure 2).

Time-dependent changes at the coal tar–water interface may significantly affect interfacial properties including interfacial tension and interphase mass transfer resistance. Changes in the coal tar–water interfacial tension may affect the wettability and capillary pressure and, thus, the migration of coal tar in the subsurface. The effect of aging on mass transfer has been inferred by measuring the rate of dissolution of naphthalene from coal tar aged in water using a flow-through slurry reactor with coal tar coated onto microporous silica beads (6, 7). The results showed that the time varying aqueous concentration of naphthalene in reactor flow-through tests was noticeably less when the experiment was performed after aging the coal tar-coated silica beads in water for 1 week. Calculations indicated that the pore diffusion rates were rapid compared to the particle boundary layer mass transfer rates. Thus, it was inferred that the decrease in the aqueous concentrations was caused by a reduction in the mass transfer rate as a result of changes in coal tar–water interfacial properties rather than diffusional constraints in the micropores. The decrease in the naphthalene mass transfer rate was notice-

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able in tests for which there was a large coal tar–water interfacial area, as with the microporous silica (8), but was not discernible in flow-through tests employing a single 0.7-mL tar globule. This was perhaps due to the change in mass transfer rates for the coal tar globule being so small that the techniques used did not provide the precision required to measure the small differences. The reduction in mass transfer of naphthalene from coal tar coated onto microporous silica was not of sufficient magnitude to affect the microbial mineralization rate of naphthalene in companion bioslurry tests, because of the much larger mass transfer rate in comparison to the biokinetic rate in those systems (9).

Crude Oil Interfacial Films. The occurrence of interfacial films in coal tar–water systems has not been reported prior to the work described above. However, the phenomena of interfacial film formation between water and certain crude petroleum oils was investigated as early as 1949 by Bartel and Niederhauser (10). Subsequent studies with a variety of crude oils have expanded these early investigations (11–14). Naturally occurring metal porphyrins (15–17) and high molecular weight carboxylic acids (18) and aromatic carboxylic esters (19) have been tentatively identified as interfacial film constituents. Strassner (12) and Pasquarelli *et al.* (20) have identified acidic resins and petroleum asphaltenes as a major component of such interfacial films. Recent work on the chemical and physical structure of asphaltenes and resins has been summarized by Speight (21). In general, asphaltenes consist of a collection of condensed aromatic nuclei that contain aliphatic and cycloaliphatic substituents, and heteroatoms such as nitrogen, oxygen, and sulfur are distributed throughout the structure. Resins have a lower molecular weight than asphaltenes, but contain similar heteroatomic distributions. Recently, Mohammed *et al.* (22) proposed that crude oil asphaltenes slowly form viscous, interfacial networks by structural reorganization when contacted with water. Collectively, these studies suggest that crude oil films are caused by ill-defined “asphaltenes” and “polar resins”, which are components of the whole crude. In the presence of water, crude oil interfacial films are stabilized by these components.

The coal tars used in work reported here are chemically different from crude oils in that the coal tars contain significant amounts of aromatic constituents such as PAH compounds. Some asphaltenic or polar compounds may be present in coal tars as well, and these compounds could play a significant role in the formation of the interfacial films. The wetting properties of coal tar also suggest the presence of some surface active agents (4).

Research Objective. The objective of this research was to characterize the chemistry of coal tar–water interfacial films. Knowledge of the composition of such films may assist in understanding the role of interfacial films in affecting the surface chemical behavior of coal tar. This paper describes the characterization of chemical differences between aged coal tar–water interfaces and bulk coal tar using nuclear magnetic resonance (NMR), Fourier transform infrared spectrometry (FTIR), and gas chromatography/mass spectrometry techniques (GC/MS). The GC/MS analysis was employed to assess whether there was a noticeable change in film composition with respect to bulk coal tar for semivolatile, lower molecular weight compounds. The ^{13}C -NMR and ^1H -NMR techniques were used to characterize the carbon and hydrogen atoms and their

TABLE 1

Characterization of Organic Compound Classes for Stroudsburg Coal Tar According to ASTM D2007^a

wt %	classification
34	asphaltenes— <i>n</i> -pentane insoluble fraction
17	polar compounds—material retained on adsorbent clay after percolation of sample in <i>n</i> -pentane eluent
41	aromatics—material that passes through column of adsorbent clay in <i>n</i> -pentane eluent but adsorbs on silica gel
8	saturates—material in <i>n</i> -pentane eluent that is not adsorbed on either clay or silica gel

^a From Peters and Luthy (23).

bonds, in both the bulk coal tar and the coal tar film samples. FTIR analyses were carried out to detect the presence of polar functional groups, such as carboxylic acids, esters, amides, phenols, and alcohols in the film and in bulk coal tar samples.

Experimental Methods

Coal Tars. Coal tar was obtained from free-flowing tar pools residing in the subsurface at a former MGP site located at Stroudsburg, PA. Liquid tar was pumped from DNAPL in a stratigraphic depression in the confining layer. Coal tar was collected from one of several wells that had been installed for remediation through coal tar pumping (23, 24). This coal tar was a byproduct of a carbureted water gas process, where anthracite coal was reacted with steam in a generator and the product gases were passed over hot checker brick in the presence of enriching oil in a carburetor and superheater. A medium BTU product gas (approximately 500 BTU) was produced, comprised of carbon monoxide, hydrogen, and methane. An aromatic coal tar liquid was produced as a byproduct from the enriching oil (1). The Stroudsburg coal tar was analyzed for volatile organic compounds, PAH compounds, and the percentage weight of characteristic groups fractionated according to compound classes as specified in ASTM D2007 using clay–gel adsorption chromatography. These analyses have been described in detail by Peters and Luthy (23). Results of the ASTM characterization are presented in Table 1.

A second coal tar sample was obtained from a monitoring well at a former MGP site at Baltimore, MD. As determined from characterization by ASTM D2007, aromatic compounds accounted for 98% (by weight) of this coal tar. Naphthalene was the most abundant constituent of the Baltimore coal tar, accounting for 10% (by weight) of the coal tar. BTEX and PAHs in this tar were analyzed by GC/MS for EPA priority pollutant volatiles and PAHs as per EPA Methods 8240 and 8270. Results from these analyses have been discussed by Ghoshal *et al.* (9).

As characterized by compound class according to ASTM Method D2007, the coal tar from Stroudsburg had a different composition compared to the Baltimore tar with aromatic compounds accounting for only 41% of the coal tar by weight. However, as typical for MGP coal tars, both the Baltimore coal tar and the Stroudsburg coal tar contained a significant fraction of PAHs with naphthalenes as the most abundant constituents (1, 25). The average molecular weight of the Baltimore coal tar was 226 g/mol while that for the Stroudsburg tar was 210 g/mol, based on vapor

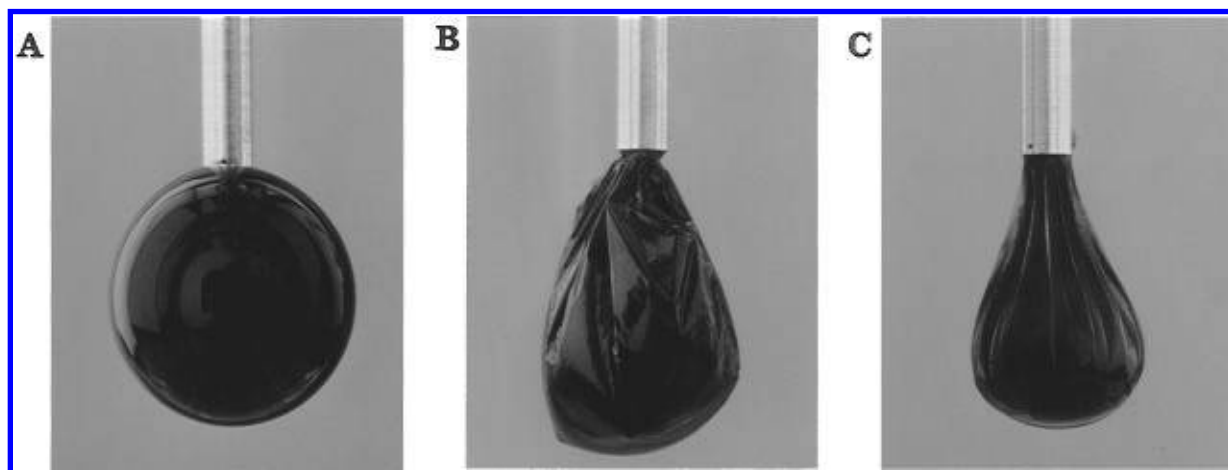


FIGURE 1. (A) Freshly formed Stroudsburg coal tar drop suspended in water from the tip of a syringe needle (ϕ), (B) Stroudsburg coal tar drop retracted after aging for 3 days (ϕ), and (C) Baltimore coal tar drop retracted after aging for 3 days. (Needle size for scale: o.d. = 0.8 mm.)

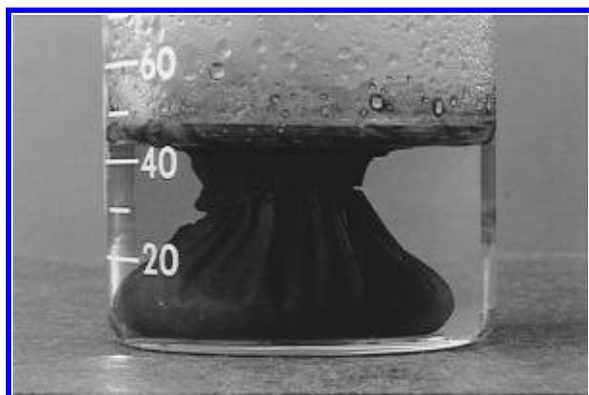


FIGURE 2. Coal tar aged in water in a beaker for 1 year.

pressure osmometry. Both coal tars were free-flowing brown/black liquids and were denser than water. The Stroudsburg tar had a kinematic viscosity of 9.94 cSt and a specific gravity of 0.994 (both measured at 30 °C). The kinematic viscosity of the Baltimore tar was 9.5 cSt (at 37 °C), and the specific gravity was 0.99 (at 25 °C).

Formation and Isolation of Coal tar Films. Photographs of the interfacial films observed from the pendant drop test are shown in Figure 1 for both the Stroudsburg and Baltimore coal tars. Visual observations suggested that the Stroudsburg tar had a more substantial film compared to the Baltimore tar. The interfacial film formed on the Baltimore coal tar had a more fluid texture and thus was more difficult to isolate from the bulk coal tar. Thus, the following suite of analyses was performed with the Stroudsburg coal tar only, in as much as the composition of the film material would likely be more identifiable with this coal tar. In order to obtain the quantity of interfacial film material required for chemical analyses, large coal tar–water interfacial areas were created in 100-mL glass beakers. The beakers were filled with 40 mL of deionized water, and 30 mL of coal tar was pipetted to the bottom of the beaker. Care was taken to prevent the coal tar from touching the air–water interface, as otherwise some lighter fraction of coal tar would tend to separate from the bulk phase and spread at the air–water interface. After dispensing, the coal tar mass attained an elongated configuration, partially rising to the water surface as a column of coal tar in the beaker. Yet by this technique there was no spreading of coal tar material at the air–water interface. Duplicate

beakers were covered with parafilm and aluminum foil, stored in the dark, and aged in the beakers for 1 month and 1 year. No evidence of biological activity, such as turbidity of the aqueous phase or formation of biofilms was visible. Figure 2 shows a beaker containing a coal tar sample aged in water for 1 year. This beaker contained smaller volumes of tar and water, but in the same ratio as described above. This sample was prepared for photography, not for isolation of the interfacial film material. The interface shows convolutions and irregular surface features, and such interfaces were observed in all the samples regardless of volume. The interfacial films formed after 1 month of aging were more viscous than the parent tar, having a semigelatinous texture. The film material had a tendency to spread at the air–water interface if lifted through the water column in the beaker. In the case of Stroudsburg coal tar aged for 1 year, parts of the interfacial films were more solid-like in texture showing brown or black clumps that could be lifted through the water column. To isolate these films, the coal tar in the beaker was first pipetted out. As a result, the interfacial film collapsed onto the bottom of the beaker. The water in the beaker was then pipetted out, and the film material and a small amount of coal tar that could not be pipetted out remained in the beaker. Any liquid coal tar was drained off to the extent possible, and the film material was scraped off the bottom of the beaker with a spatula. However, it is possible that small amounts of inseparable liquid coal tar were associated with the film material. Samples of the film material were weighed out in glass vials. The film material isolated from these samples was dissolved in either chloroform, methanol, or methylene chloride according to the requirements of the analysis. Samples were used without further drying.

Coal Tar Emulsion Preparation. An emulsion of bulk coal tar and water was prepared by vigorously shaking 10 mL of Stroudsburg coal tar and 10 mL of deionized water in a glass vessel for 1 h. After standing for several weeks, a semisolid, brown emulsion was physically separated from residual water by pipet and used without further drying. This material had a texture and appearance different from the film material.

Gas Chromatography/Mass Spectrometry Spectra. For analysis of the semivolatile compounds in the film material, a 0.2-g sample of the Stroudsburg tar film material from the beaker aged for 1 year was diluted to 3 mL in methanol.

A total of 600 μ L of this solution, 1 mL of a surrogate spiking solution, and 30 mL of methylene chloride were combined and concentrated to a final volume of 1 mL. Six deuterated compounds were used as internal standards, and six other compounds were used as matrix spikes. Based on a preliminary analysis, the concentrate was diluted 10 times and analyzed. For the bulk coal tar, a 4-g sample of unaged Stroudsburg coal tar was diluted with methanol to a final volume of 10 mL. Six hundred microliters of this sample and identical amounts of the surrogate spiking solution and methylene chloride, as described above, were combined and concentrated to a final volume of 1 mL. Samples appeared to dissolve completely in the solvents. A dilution of 60 times was necessary based on a preliminary analysis. Samples were analyzed on a HP 5890 GC, fitted with a 0.53 mm \times 105 m capillary column. The GC was connected to an HP 5970 mass selective detector. The analysis was performed according to U.S. EPA Method SW846 8270, with the temperature program running from 40 to 270 $^{\circ}$ C with the MS scanning from 35 to 500 amu. Volatile compounds were analyzed by the GC purge-and-trap method according to U.S. EPA Method 8240. Three internal standards and five matrix spikes were used. Approximately 100-fold dilutions were necessary for both the film material and the bulk coal tar. The temperature program for analysis of the volatiles was from 35 to 225 $^{\circ}$ C and the MS scanned from 30 to 300 amu. Mass spectral analyses were performed for Priority Pollutant List volatiles, semivolatiles, including xylenes, as well as 1- and 2-methylnaphthalene. A library search was done using the NIST spectral library to identify the compounds that are nontarget analytes and represent the 20 most prominent peaks in the total ion count chromatogram from the mass spectral analysis.

Nuclear Magnetic Resonance Spectra. NMR experiments were performed on a Varian VXR-300 operating at a frequency of 299.948 MHz for ^1H and 75.429 MHz for ^{13}C . Samples of 1-year-old Stroudsburg film or bulk Stroudsburg coal tar (50–200 mg) were dissolved in 1–2 mL of deuterated chloroform (CDCl_3) and placed in a 5-mm NMR tube. No second phase was observed, and the distinct line shapes observed suggest that the sample was a solution containing no large aggregates. The probe used was a 5-mm-Varian 4-Nucleus probe tuned simultaneously to ^1H , ^{13}C , ^{19}F , and ^{31}P . Reference (0 ppm) for both ^1H and ^{13}C was TMS (tetramethylsilane). For the ^1H spectra, the acquisition time was 1.87 s, and a recycle delay of 1 s was used. Spectra were collected by applying a 4- μ s pulse width, corresponding to a 20 $^{\circ}$ tip angle. The temperature was ambient, and 80 transients were collected. Line broadening of 0.2 Hz was applied upon Fourier transformation. For the ^{13}C spectra, the acquisition time was 0.75 s, and a recycle delay of 2 s was used. Spectra were collected with a 5-ms pulse width, corresponding to a 30 $^{\circ}$ tip angle. Temperature was ambient, a spectral width of 40 kHz was used, and 20000 transients were collected. During the acquisition, the spins were waltz decoupled. Line broadening of 8 Hz was applied. Published spectra (26) and tables of characteristic chemical shifts (27) were used to analyze spectra obtained. Chemical shift data were used to distinguish carbon and hydrogen atomic types present in the mixtures of coal tar-derived materials, e.g., aromatic carbons, aliphatic carbons, carbonyl carbons, and aromatic protons. Quantitative determinations of the atomic percentages of these atomic types were made by integration of the peak areas according to standard techniques.

Fourier Transform Infrared Spectra. FTIR spectra were taken as solutions in CDCl_3 (Aldrich Chemical, 99.8 atom %) in demountable solution cells (Spectra Tech, 0.2 mm spacer, sodium chloride disks). Solutions of Stroudsburg coal tar, 1-year-old film or coal tar emulsions were prepared by dissolving 5–10 mg in glass vials. Solutions were transferred by glass pipet into N_2 -flushed cells. A Nicolet 520 FTIR spectrometer was used for analysis. A resolution of 4.0 cm^{-1} and 25 scans were used for all samples. Spectra were recorded in the absorbance mode with a background of CDCl_3 solvent. Analyses of the spectra were carried out by reference to published FTIR spectra (28) and tables of characteristic frequencies (29). Deuterium exchange experiments were carried out by adding enough D_2O (Aldrich Chemical, 99.9 atom %) to CDCl_3 solutions of the film or bulk coal tar to produce a second phase of D_2O in glass vials. These two phase mixtures were shaken to ensure saturation of the CDCl_3 phase with D_2O . Periodically, samples of the organic phase were separated by glass pipet and transferred to N_2 -flushed solution cells.

Results

Gas Chromatography/Mass Spectrometry. The results of the GC/MS analyses of the bulk coal tar sample employed in these experiments and the interfacial film sample are shown in Table 2 and in Figure 3. The mass fractions of the bulk coal tar constituents listed in Table 2 differ by a small extent from those reported previously (23). This is a result of the analytical techniques and equipment employed to characterize the bulk coal tar and film samples being modified somewhat from those procedures used in the previous investigation. The most prevalent compounds in both the bulk coal tar and the interfacial film sample were naphthalene and 1- and 2-methylnaphthalene. Most compounds were present at essentially identical concentrations in both bulk coal tar and the interfacial film except for the volatile compounds (i.e., toluene, ethylbenzene, and xylenes) for which concentrations in the coal tar film were lower in comparison to the bulk coal tar (Table 2). Toluene, ethylbenzene, and xylenes comprised 0.49% by weight of the bulk coal tar and 0.1% of the film sample. The decrease in concentration of these compounds in the film material in comparison to the bulk coal tar may be attributed to loss by volatilization during the period of formation of coal tar films or during transfer and isolation of coal tar film material. Chromatograms of relative ion counts for the volatile compound analyses of the bulk coal tar and the coal tar film samples showed prominent peaks at identical retention times, suggesting that the same compounds were present in the bulk coal tar and the film. The total ion counts for nontarget analyte compounds obtained from GC/MS analysis by EPA Method SW846 8270 of the bulk coal tar and the coal tar film samples are presented in Figure 3A,B. The chromatograms are very similar, and a peak-to-peak match for the 20 most prominent peaks from the nontarget analytes is obtained, suggesting that the chromatographable fraction in the two samples are very similar. An unknown hydrocarbon (C_9H_{12}) with a concentration of 3200 mg/kg was the only compound noted in the bulk coal tar but not in the film material, and methyl-9H-fluorene (1800 mg/kg) was present in the film samples but not detected from the coal tar.

Carbon Nuclear Magnetic Resonance Spectra. ^{13}C -NMR spectra were used to detect for the presence of

TABLE 2

Concentrations of Volatile and Semivolatile Organic Compounds and of Tentatively Identified Compounds Comprising the 20 Largest Peaks for Nontarget Analytes in Total Ion Chromatograms for Bulk Coal Tar and 1-Year Aged Coal Tar Film Samples

compounds	coal tar film (mg/kg)	bulk coal tar (mg/kg)
Volatile Organic Compounds		
benzene ^a	<75	15
toluene	<75	220
ethylbenzene	350	2 100
<i>m</i> -, <i>p</i> -xylenes	370	1 700
<i>o</i> -xylenes	260	830
methylethyl benzene isomer ^{a,b}	200	490
Semivolatile (PAH) Compounds		
naphthalene	26 000	29 000
2-methylnaphthalene	25 000	26 000
1-methylnaphthalene ^{a,b}	15 000	16 000
acenaphthylene ^a	1 800	2 100
acenaphthene	5 800	5 900
fluorene	4 400	4 400
phenanthrene	10 000	10 000
anthracene ^a	2 400	2 500
fluoranthene ^a	2 000	2 000
pyrene	2 700	2 900
benz[a]anthracene	<1 500	850
bis(2-ethylhexyl) phthalate ^a	540	930
chrysene ^a	660	650
benzo[b]fluoranthene	<2 500	<2 500
benzo[k]fluoranthene	<2 500	<2 500
benzo[a]pyrene	<2 500	<2 500
dibenz[a,h]anthracene	<2 500	<2 500
benzo[g,h,i]perylene	<2 500	<2 500
indeno[1,2,3-c,d]pyrene	<2 500	<2 500
Tentative Identification of 20 Largest Peaks from Nontarget Analytes^c		
unknown C ₉ H ₁₂		3 200 (1)
unknown C ₉ H ₈	2 500 (1)	4 000 (2)
unknown C ₁₀ H ₁₀	2 300 (2)	3 200 (3)
unknown C ₁₀ H ₁₀	2 300 (3)	3 000 (4)
1-methylnaphthalene	15 000 (4)	16 000 (5)
unknown C ₁₂ H ₁₀	2 300 (5)	2 800 (6)
ethylnaphthalene	5 800 (6)	6 000 (7)
dimethylnaphthalene	7 800 (7)	7 800 (8)
dimethylnaphthalene	7 800 (8)	8 000 (9)
dimethylnaphthalene	4 200 (9)	4 200 (10)
unknown C ₁₂ H ₁₂	4 000 (10)	4 000 (11)
unknown C ₁₃ H ₁₄	1 500 (11)	1 500 (12)
trimethylnaphthalene	2 500 (12)	2 800 (13)
trimethylnaphthalene	1 500 (13)	1 800 (14)
trimethylnaphthalene	2 000 (14)	2 800 (15)
trimethylnaphthalene	1 500 (15)	1 800 (16)
unknown	1 500 (16)	1 800 (17)
methyl-9H-fluorene	1 800 (17)	
unknown C ₁₅ H ₁₂	2 000 (18)	2 000 (18)
unknown C ₁₅ H ₁₂	2 000 (19)	2 000 (19)
unknown	2 800 (20)	2 800 (20)

^a Tentatively identified compound. ^b Compound identified and quantified during library search. ^c Peak numbers are shown in parentheses. Peaks are marked in the total ion chromatograms in Figure 3.

phenolic and carbonyl carbon and to distinguish the various types of carbon atoms present in the mixtures. The abscissa of the spectra represents the chemical shift, δ , a dimensionless number, which is equal to the ratio of the difference in the frequencies of the signal and the reference to the operating frequency. The chemical shift is expressed in parts per million (ppm), and the frequency scale decreases from left (upfield) to right (downfield). The area under the

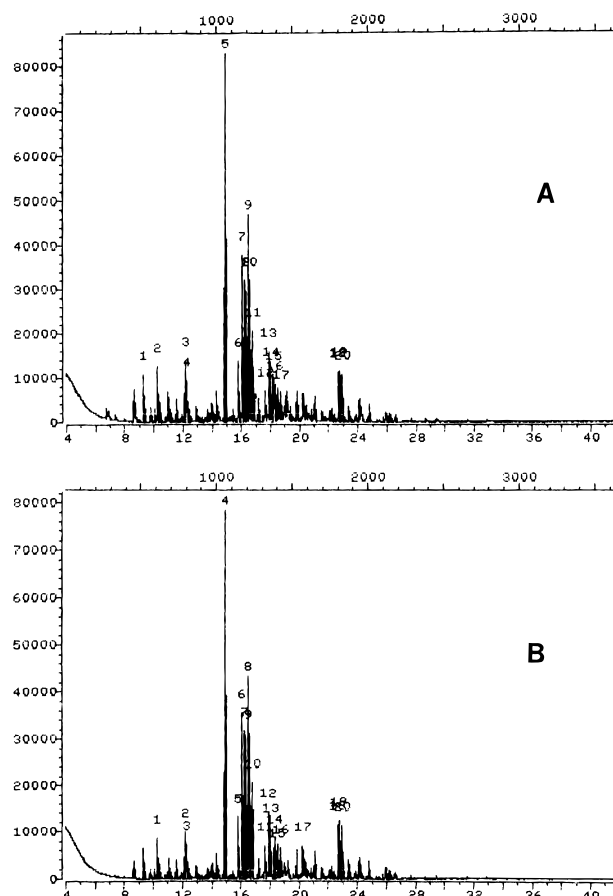


FIGURE 3. Chromatogram showing total ion counts for (A) samples of bulk coal tar and (B) samples of coal tar film isolated from coal tar aged in water for 1 year. The 20 most prominent nontarget analyte peaks are numbered.

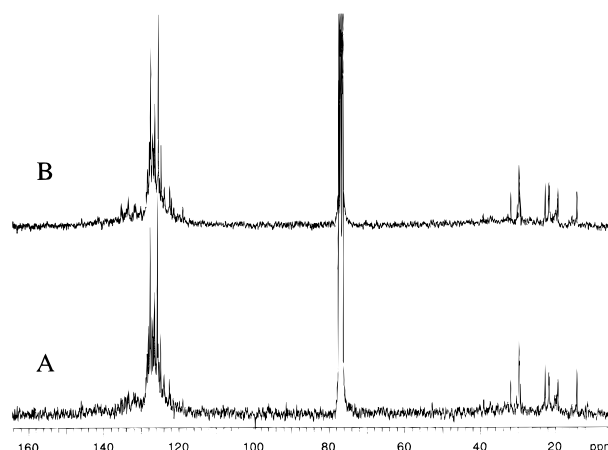


FIGURE 4. ¹³C-NMR spectra of (A) a sample of the bulk coal tar dissolved in CDCl₃ and (B) a sample of the coal tar film dissolved in CDCl₃. Almost identical peak-to-peak correspondence is obtained.

observed peaks can be correlated with the relative concentration of a functional carbon type.

¹³C-NMR spectra of the bulk coal tar and the coal tar film in CDCl₃ are compared in Figure 4. This comparison shows nearly identical peak-to-peak correspondence between the bulk coal tar and the coal tar film (Figure 4). Peaks were clustered into the aromatic/olefinic region (160–100 ppm) and aliphatic regions (100–0 ppm). Resonances typical of phenolic (30) or carbonyl (31) moieties were not detected over the region from 150 to 210 ppm. A small

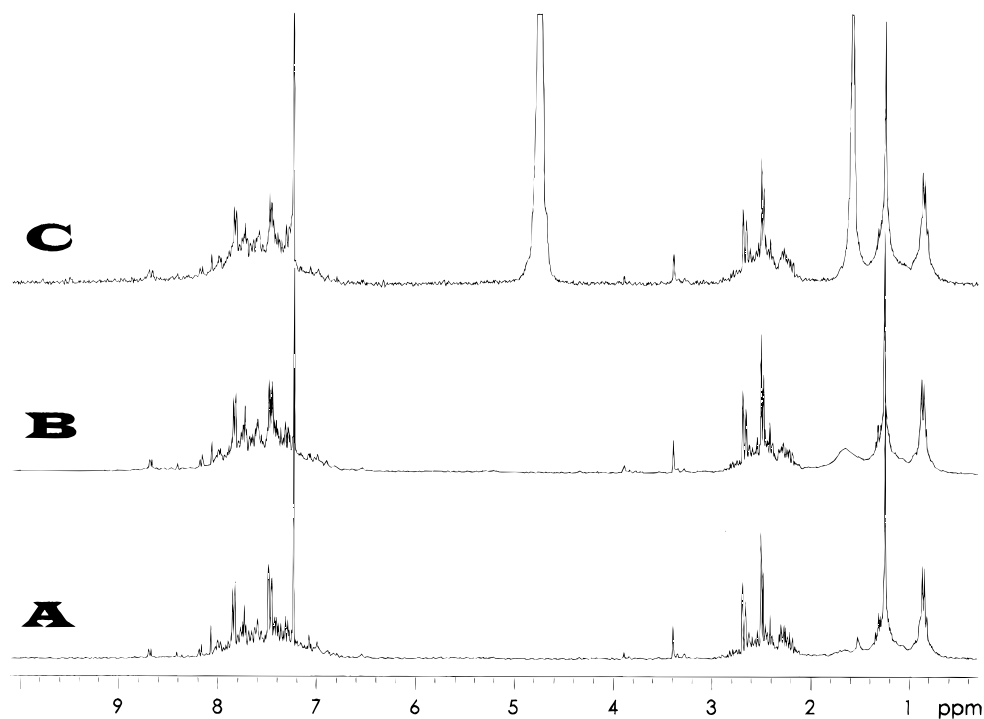


FIGURE 5. ^1H -NMR spectra of (A) a sample of the bulk coal tar dissolved in CDCl_3 , (B) a sample of the coal tar film dissolved in CDCl_3 , and (C) a sample of a coal tar emulsion in CDCl_3 . The significant difference between (A) and (B) is the broader peak stretching from 1.5 to 1.8 ppm in the spectrum for the coal tar film sample compared to the sharp peak at 1.53 ppm in the spectrum for the bulk coal tar sample. The peak at 4.8 ppm in spectrum C for the coal tar–water emulsion corresponds to free-phase water, i.e., water surrounded by adjacent water molecules.

difference in the intensity of two methyl peaks at 19.9–22.2 ppm was noted between the bulk coal tar and coal tar film samples. A comparison of summed integrations for the aliphatic and aromatic regions showed that the coal tar film contained approximately 75% aromatic and 25% aliphatic carbon atoms. Samples of the bulk coal tar were nearly identical with 74% aromatic and 26% aliphatic carbon atoms. Within the limits of detection (*ca.* 1%) the bulk coal tar and the coal tar film contain substantially the same atomic compositions of organic carbon. Table 1 indicates that approximately 41% of the material is “aromatic” by a clay adsorption technique (ASTM D2007). However, ASTM D2007 classifies mixtures more or less by their bulk polarities. ^{13}C -NMR techniques measure percentages of atomic carbon, which do not correlate well with such bulk characterization techniques.

Proton Nuclear Magnetic Resonance Spectra. ^1H -NMR was used to determine the types and relative ratios of carbon–hydrogen connectivities present in the coal tar mixtures. Characteristic carbon–hydrogen groupings, e.g., aromatic methine or aliphatic methyl, are detected as peaks at characteristic chemical shifts. Integration of the peak areas in these groupings can be used to determine relative atomic percentages of the various types of hydrogen atoms in the mixtures. Interactions between hydrogen atoms on adjacent carbons give rise to characteristic peaks or “multiplets”. Similarities in peak chemical shift and multiplicity may be used to characterize mixtures of compounds.

^1H -NMR spectra of the bulk coal tar and the coal tar film samples are shown in Figure 5. These spectra are consistent with the ^{13}C -NMR results. Peak-to-peak match is nearly identical for both the coal tar film and the bulk coal tar. The large number of signals observed was grouped into three distinct regions: aromatic (9.0–6.0 ppm), methine/methylene adjacent to electron-withdrawing groups (4.5–2.0

ppm), and methyl/methylene (2.0–0.5 ppm). Integration of the total peak areas for these three regions of the coal tar film afforded relative ratios of 2.14/1.00/1.67 for aromatic/methine, substituted methylene/methyl, and methylene. Similarly, integration of the same areas for the bulk coal tar gave relative ratios of 2.10/1.00/1.63. These results suggest only small relative differences between film and bulk coal tar samples in the distribution of these proton types.

The only significant difference in the ^1H -NMR spectra between the coal tar film and bulk coal tar samples was observed in a region where water solvated in chlorinated solvents is typically observed (32). In general, the spectrum of a two-phase mixture of water in CDCl_3 will display a sharp resonance at 1.53 ppm for dissolved-phase water, i.e., water surrounded by adjacent CDCl_3 molecules, and a resonance at 4.8 ppm for free-phase water, i.e., water surrounded by adjacent water molecules. For both bulk coal tar and coal tar film samples dissolved in CDCl_3 , it was observed that the CDCl_3 contained small, dissolved-phase water peaks at 1.53 ppm, but as shown in Figure 5, no free-phase water peak could be detected in an otherwise silent area of the spectrum at 4.8 ppm. The region corresponding to dissolved-phase water in the ^1H -NMR spectra is highlighted in Figure 6 to emphasize the finding that the coal tar film showed a broad resonance envelope stretching from 1.5 to 1.8 ppm.

The broader resonance in the ^1H -NMR spectrum for the coal tar film sample at 1.5–1.8 ppm is attributed to water molecules that are weakly bound to the freshly dissolved coal tar film material. Since these water molecules are in a relatively nonpolar environment, CDCl_3 , or coal tar, they have a chemical shift characteristic of water in nonpolar environments (32). However, broadening of the resonance suggests that the water is present in a collection

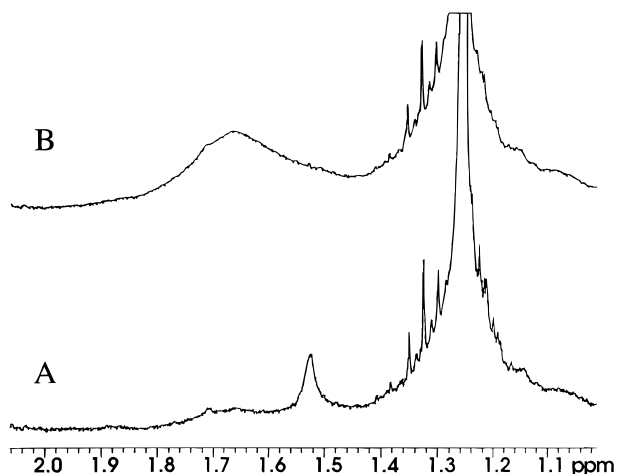


FIGURE 6. ^1H -NMR spectra of the region containing dissolved-phase water proton resonances for (A) bulk coal tar in CDCl_3 and (B) coal tar film in CDCl_3 .

of slightly varying chemical environments rather than in a uniform nonpolar environment. Deshielding of the dissolved-phase water protons by weak binding to coal tar components or to adjacent, entrapped water molecules may produce the observed resonance envelope. Support for these two models is found in the work of Germani *et al.* (32), Atwood *et al.* (33), and Suzuki *et al.* (34). Germani *et al.* observed a gradual downfield shift of water protons in CD_2Cl_2 from 1.9 to 4.1 ppm as progressively greater amounts of water were incorporated in "water pool micelles". They attributed this downfield shift in water proton resonance to increased hydrogen bonding between water molecules in surfactant-stabilized water pool micelles. Alternatively, Atwood *et al.* and Suzuki *et al.* demonstrated that weak hydrogen bonding between water protons and aromatic π -electrons is possible. Since the coal tar contains a variety of polycyclic aromatic hydrocarbons, this latter kind of weak hydrogen binding may provide the cross linking needed to stabilize film formation.

After allowing the coal tar film to stand for several weeks in CDCl_3 solution, the broad envelope at 1.5–1.8 ppm originally observed in the film sample was replaced by a narrow peak centered at 1.53 ppm. This change is attributed to slow dissolution of water into the CDCl_3 solvent from the coal tar film material. These results suggest that the water in the coal tar film is bound only weakly to the coal tar film components and that such water will dissociate to a dissolved-phase state in the presence of the CDCl_3 solvent.

Infrared Analysis of Coal tar Film. IR analysis provided additional evidence of the presence of bound water in the coal tar film. Spectra for a sample of bulk coal tar, a sample of coal tar film dissolved in CDCl_3 , and a sample of bulk coal tar in water-saturated CDCl_3 are presented in Figure 7. Spectrum A for the bulk coal tar in CDCl_3 shows aromatic and aliphatic C-H stretching ($3100\text{--}2800\text{ cm}^{-1}$), aromatic ring-breathing vibrations ($1800\text{--}1550\text{ cm}^{-1}$), and C-H bending ($1550\text{--}1350\text{ cm}^{-1}$) (35). These results are consistent with previously described GC/MS and NMR spectral data, which show that coal tar is mostly a mixture of alkyl aromatic and polycyclic aromatic hydrocarbons. Typical strong absorbance associated with the polar carbonyl ($1650\text{--}1800\text{ cm}^{-1}$) or sulfonyl ($1000\text{ to }1375\text{ cm}^{-1}$) groups (36) were not observed in either film or bulk coal tar spectra.

Spectrum C of Figure 7 for the coal tar film is similar to the bulk coal tar spectrum in most respects except that

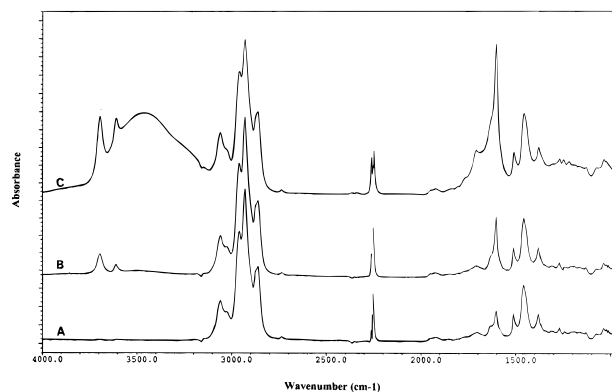


FIGURE 7. FTIR spectra for (A) bulk coal tar dissolved in CDCl_3 , (B) bulk coal tar dissolved in water-saturated CDCl_3 , and (C) coal tar film dissolved in CDCl_3 . The broad envelope of peaks in spectrum C is caused by bound water in association with the coal tar film constituents.

several strong absorbances are noted at 3691 , 3606 , 3455 , and 1603 cm^{-1} . The peaks at these wavenumbers are attributed to dissolved-phase water and bound water. Peaks at 3691 and 3606 cm^{-1} are assigned, respectively, to asymmetric and symmetric O-H stretching of water dissolved in CDCl_3 . Schioberg and Luck (37) have reported similar absorbance for water dissolved in CCl_4 . These absorbances are apparent in Figure 7, spectrum B, the IR spectrum for bulk coal tar dissolved in water-saturated CDCl_3 . This spectrum demonstrates the presence of dissolved-phase water at 3691 and 3606 cm^{-1} , confirming the assignments for dissolved-phase water in spectra of the coal tar film. However, in contrast to spectrum B, a broad peak or envelope of peaks for coal tar film was centered at 3455 cm^{-1} as shown in spectrum C. Hydrogen-bonded phenolic and hydroxylic OH stretching may cause such peaks (38), but GC/MS, ^{13}C -NMR, and ^1H -NMR data do not support the presence of these moieties. Instead, based on the findings from the ^1H -NMR studies, this envelope of peaks is attributed to bound water that has been reduced in stretching frequency by intermolecular interactions with components of the coal tar or by hydrogen bonding with adjacent entrapped water molecules (38). Also shown in spectrum C is greater absorbance near 1600 cm^{-1} , which is ascribed to water bending vibrations, and as might be expected is most intense in the coal tar film sample, which contains water.

Deuterium Exchange Studies. Further experiments were carried out to confirm the assignments of the water peaks at 3691 , 3606 , and 3455 cm^{-1} . This was done by observing if the bound water present in the coal tar film was exchangeable with D_2O . Under these conditions, protons in H_2O should exchange upon introduction of deuterons of D_2O . Thus, stretching frequencies attributed to O-H bonds would be expected to diminish, and new, lower stretching frequencies attributed to O-D stretching are likely to appear (39). This result is shown in Figure 8. A comparison of spectrum A and spectrum B shows that treating a CDCl_3 solution of the coal tar film with D_2O caused an almost immediate reduction in symmetric (3606 cm^{-1}) and asymmetric (3691 cm^{-1}) dissolved-phase water peaks and the appearance of a new peak at 3621 cm^{-1} . These changes may be attributed to the exchange of dissolved water with D_2O and the formation of HDO. The H-O bond of HDO is assigned a stretching frequency at 3621 cm^{-1} (37). As shown in spectrum C of Figure 8, over a period of

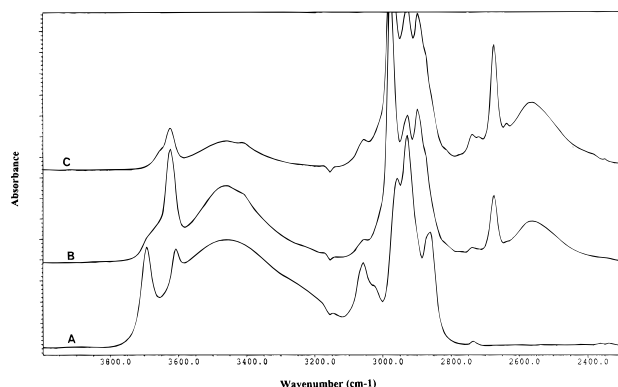


FIGURE 8. FTIR spectra for (A) a sample of coal tar film dissolved in CDCl_3 , (B) a sample of coal tar film in CDCl_3 contacted with D_2O for 20 min, and (C) a sample of coal tar film in CDCl_3 contacted with D_2O for 19 h.

19 h the broad envelope centered at 3455 cm^{-1} slowly diminished in intensity, as might be expected for water that is weakly bound in some way to coal tar substituents. In addition, several new peaks appeared at 2739, 2674, 2637, and 2564 cm^{-1} that are attributed to deuterium-oxygen stretching from D_2O and HDO in the bound or dissolved phases.

Coal Tar–Water Emulsion Studies. Combined NMR and IR studies suggested that the coal tar film shared some similarities with coal tar–water emulsions. ^1H -NMR of coal tar–water emulsions (Figure 5C) in CDCl_3 solutions were nearly identical in peak shape and intensity with bulk coal tar in CDCl_3 . However, the coal tar–water emulsions contained peaks at 4.8 and 1.6 ppm. The substantial peak at 4.8 is attributed to free-phase water. Other spectra showed that a two-phase mixture of water in CDCl_3 contains peaks at 4.8 ppm and 1.55 ppm, while, in contrast, CDCl_3 saturated with dissolved-phase water only shows a peak at 1.55 ppm. The peak at 1.6 ppm in the coal tar emulsion was attributed to a mixture of water bound to the coal tar film constituents and dissolved-phase water in CDCl_3 . Bound water appears over the region 1.5–1.8 ppm in the coal tar film spectrum, and dissolved-phase water appears as a sharp peak at 1.53 ppm in the bulk coal tar spectrum. These results suggest that the chemical environment of the bound water in the coal tar film is similar to the chemical environment of a fraction of the water present in the coal tar–water emulsion. In addition, the intensity of the peak at 1.6 ppm, relative to the hydrocarbon matrix, was greater in the emulsion than in the coal tar film spectrum. The ratio of the integrated peak areas of the region of the spectrum (2.0–1.4 ppm) containing water resonances to that for the integrated peak areas of the region of the spectrum (1.4–0.4 ppm) containing hydrocarbon resonances was calculated to compare the mass of bound water in the coal tar emulsion and the coal tar film sample. The result indicated that the coal tar emulsion contained 3.3 times more bound water than the coal tar film, suggesting that bound water present in the coal tar film is less abundant than bound water in the coal tar–water emulsion.

The IR spectrum of an emulsion of the bulk coal tar dissolved in CDCl_3 is characterized by sharp stretching absorbances at 3693 and 3606 cm^{-1} due to dissolved water, a broad stretching absorbance centered at 3409 cm^{-1} caused by bound water, and a strong absorbance at 1603 cm^{-1} due to water bending. Except for a reduced frequency for the

absorbance assigned to bound water, this IR spectrum is very similar to the IR spectrum of the coal tar film.

Discussion

The analysis of the coal tar film and the bulk coal tar by GC/MS, NMR, and FTIR techniques did not reveal any significant differences in the organic composition of the two samples. The primary difference was that only the film material contained bound water. GC/MS analysis showed small differences in composition between film and bulk coal tar samples, which do not appear sufficient to explain the formation of a prominent film. The NMR and IR spectra are consistent with this GC/MS data and previously published compositional analyses (23), which conclude that the coal tar materials are mixtures of alkyl aromatic and polycyclic aromatics. The lack of evidence for phenolic, carbonyl, or sulfonyl-containing compounds in the GC/MS, ^{13}C -NMR, ^1H -NMR, and FTIR spectra suggests that typical surfactant compounds containing these functional groups are not present in appreciable quantities in the bulk coal tar. If film formation was caused by migration of surfactant molecules to the interface, typical surfactant moieties should have been detected in film samples. However, differences in composition between the film and the bulk coal tar samples of less than 1% for NMR analyses and less than 0.1% for FTIR analyses might not be detected by these analytical techniques. Therefore, for the tar examined, only small amounts of interfacially active, nonvolatile compounds may have been concentrated in coal tar films. ASTM D2007 analysis shows that approximately 17% of the coal tar is classified as 'polar', i.e., components that are soluble in pentane but sorb firmly to clays. Alkyl heterocyclic compounds might display sufficient polar characteristics to fall into this category of the ASTM D2007 without displaying the strong interfacial activity of typical surfactant molecules. Previous work (23) demonstrated that at least one heterocyclic compound, dibenzothiophene, is present in the coal tar. Therefore, it is possible that higher molecular weight alkyl heterocyclics are present in the 'polar' fraction of the ASTM D2007 test. No evidence was obtained suggesting an accumulation of these types of molecules in the coal tar films. Nevertheless, the preponderance of the data suggests that the primary chemical difference between the coal tar film and the bulk coal tar is the presence of small amounts of bound water.

NMR and FTIR techniques allowed the identification of water in three different environments: (i) dissolved-phase water (water molecules surrounded by CDCl_3), (ii) free-phase water (water molecules surrounded by other water molecules in CDCl_3), and (iii) water weakly bound with coal tar components in CDCl_3 . Intermolecular interaction between water and coal tar components caused bound water molecules to appear as broad peaks or an envelope of peaks. In the FTIR and ^1H -NMR spectra, similar broad peaks were seen on analyzing samples of coal tar–water emulsions. Deuterium exchange studies with coal tar film material in CDCl_3 showed that over a period of 1 day bound water molecules exchanged with dissolved-phase water molecules. On standing for several weeks in CDCl_3 , bound water dissolved from the coal tar film material to the slightly polar solvent phase. This observation suggests that weak organizational structures are responsible for film formation, i.e., weak intermolecular interactions between coal tar components or between water and coal tar components.

Based on these findings and the findings reported in the literature (32–34), we hypothesize that the coal tar–water interface is stabilized by the formation of an organized, semigelatinous film or thin emulsion-like layer.

The mechanism for coal tar film formation appears to depend more on the interaction of the coal tar with water and less with the composition of the coal tar itself. Thus, a plausible mechanism for the reduction in mass transfer of naphthalene from ‘aging experiments’ with coal tar coated on microporous silica beads (7, 8) was possibly due to increased interfacial resistance resulting from increased surface viscosity of an emulsion-like layer. Although the experiments show film formation for two specific coal tars, we suspect that the same phenomena may occur in other coal tar liquids and possibly in other NAPLs in contact with water. Bound water interfacial film phenomena may be important in other systems for which surface active substances or surface chemical redox reactions are not predominant.

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