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LIQUID CHROMATOGRAPHIC SYSTEMS FOR THE SEPARATION OF POLYCYCLIC AROMATIC HYDROCARBON AND NITROGEN HETEROCYCLE COMPOUNDS PRESENT IN COAL LIQUIDS

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SUMMARY

Normal-phase and reversed-phase high-performance liquid chromatography were compared for the separation of compounds known to be present in solvent refined coal liquids. Several commercially available stationary phases were investigated with standards and compared for their ability to separate polycyclic aromatic hydrocarbons from nitrogen heterocycle compounds. The normal-phase columns investigated were μPorasil, Nucleosil NO_2, basic alumina, μBondapak NH_2, and μBondapak CN. μBondapak C_{18} and μBondapak CN packings were investigated under reversed-phase conditions. Utilizing normal-phase chromatography only the μPorasil system was able to resolve polycyclic aromatic hydrocarbons from the nitrogen heterocycles investigated. Both reversed-phase systems studied were able to resolve these functional classes, but the solubility of solvent refined coal liquids in aqueous systems limits the usefulness of this approach.

INTRODUCTION

Non-distillable solvent refined coal (SRC) liquids are complex organic mixtures ranging from polycyclic aromatic hydrocarbons (PAHs) to very polar multifunctional compounds. The complexity of these coal liquids normally necessitates compound class separation prior to detailed chemical characterization. As a result, considerable attention has been focused on preliminary separation steps[1–6]. Most of the preliminary separation schemes involve open column chromatography which require large volumes of high purity solvents. Although these approaches are useful, they are time consuming to apply to routine analysis.

Both reversed-phase and normal-phase high-performance liquid chromatography (HPLC) can provide a fast and relatively detailed characterization of these complex mixtures. Holstein and Severin[7] and Matsunaga[8] have used normal-phase HPLC to obtain profiles for fossil fuel liquids. Holstein and Severin[9] were able to identify the major compound types in a recycle oil by normal-phase HPLC–mass spectrometry (MS). Wise *et al.*[10] reported the normal-phase separation of PAHs in crude oil using μBondapak NH_2. Boduszynski *et al.*[11] also used μBondapak NH_2 to

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separate PAHs isolated from coal liquids according to the number of double bonds. Liphard[12] reported using an amino bonded phase to separate hydrocarbon groups from a distillable coal liquid. Suatoni and Swab[13] reported determining hydrocarbon types in crude oils using μPorasil. Galya and Suatoni[14] were able to separate saturates, aromatics, resins and asphaltenes from *n*-hexane-soluble portions of liquid fuel materials. This separation approach involved three different columns for the preparative step and a μBondapak NH_2 for the analytical separation. Alfredson[15] reported a column switching technique for hydrocarbon group separations of gas oils, gasolines and *n*-hexane-soluble portions of solvent refined coal. Dark[16] and Dark *et al.*[17] reported the separation and characterization of coal liquids by HPLC–MS using both normal-phase and reversed-phase chromatography. These studies are very informative but do not consider specific functional classes which can overlap with high-molecular-weight PAHs such as hindered nitrogen heterocycles. Mobile phase additives have been reported by Green and Grizzle[18] to enhance selectivity for various functional classes on plain silica. A reversed-phase HPLC system was successfully used to separate several aromatic and hydroaromatic hydrocarbons in coal derived liquids by Schabron *et al.*[19]. Reports on the reversed-phase chromatography of nitrogen heterocycles thought to be in coal-derived liquids were published by Schronk *et al.*[20] and Colin *et al.*[21]. These workers concluded that the retention of these heterocycles was dependent on the steric accessibility of the nitrogen atom. Schmitter *et al.*[22] reported the use of reversed-phase HPLC combined with gas chromatography (GC)–MS to identify triaromatic nitrogen heterocycles in crude oils.

Although both normal-phase and reversed-phase HPLC have been used to study coal liquids, there have been few reports involving a comparison of a wide variety of stationary phases or dealing with specific overlap of nitrogen compounds into the PAH region of elution. Blumer and Zander[23] used a Nucleosil NO_2 stationary phase to separate PAHs from nitrogen heterocycles with heptane–chloroform mobile phases. Recently Chmielowiec[24] used dimethyl sulfoxide–carbon tetrachloride mobile phases and a μPorasil stationary phase to separate a wide variety of compounds known to be in coal liquids, petroleum, and bitumen samples. Matsunaga[8] did a comparative study of several stationary phases for their ability to separate aromatic and polar compounds in coal liquids. Miller[25] investigated several liquid chromatography bonded phases for their selectivity toward functional group types in the separation of hydrocarbon mixtures in petroleum crude, shale oil and coal oil. These studies are informative but lacked important standards such as large (ten rings) PAHs or sterically hindered, weakly retaining nitrogen heterocycles which are known to be in coal-derived liquids.

The purpose of this work was to evaluate a wide variety of stationary and mobile phases for their ability to separate PAHs from nitrogen heterocycles and to investigate the extent of overlap of these classes of compounds. Model compounds were chosen based upon a separation and characterization procedure developed in this laboratory[5,6]. Emphasis was placed on normal-phase chromatography for two reasons: (a) the retention and selectivity in normal-phase systems are mainly dependent upon specific functional group–stationary phase interactions; (b) the solubility of coal-derived liquids is a problem with the water-based solvent systems normally employed in reversed-phase chromatography[26].

EXPERIMENTAL

High-performance liquid chromatograph

The liquid chromatograph used was a Waters Model ALC/GPC 244 equipped with a Model 6000A pump, a U6K injector, a dual-channel UV detector set at both 254 nm and 280 nm, and a dual channel 10 mV strip chart recorder.

Columns

All columns were 30 cm × 3.9 mm I.D. and contained 10-μm particles. Basic alumina and Nucleosil NO_2 columns were purchased from HPLC Technology/Phenomonex, Palos Verdes Estates, CA, U.S.A. All other columns were obtained from Waters Assoc., Milford, MA, U.S.A.

Reagents

Model compounds were obtained from Aldrich. 1,2-Benzperylene and 1,2,4,5-dibenzperylene were donated by Dr. John McKay of the Western Research Institute, Laramie, WY, U.S.A. HPLC-grade chloroform and 2-propanol were obtained from J. T. Baker, Phillipsburg, NJ, U.S.A. MCB Omnisolve grade *n*-heptane ($\leq$0.02% water) was degassed with helium prior to use. Dioxane was obtained from Burdick & Jackson, Muskegon, MI, U.S.A. Methanol was obtained from Fisher Scientific, Fair Lawn, NJ, U.S.A. All solvents were filtered through a Millipore type F-H 0.45-μm filter prior to use. HPLC-grade chloroform was used to dissolve model compounds.

All normal-phase separations were carried out at ambient temperature (26 ± 1°C) with a flow-rate of 2.0 ml/min. Reversed-phase separations were carried out at 1 ml/min at ambient temperature. Solutes were dissolved in HPLC-grade chloroform and between 0.01 μg and 20 μg injected, depending on the molar absorptivity and retention characteristics of the solute. The capacity factor (k') was calculated from the relationship $k' = (V_R - V_m)/V_m$, where V_R (ml) is the measured retention volume and V_m (ml) is the column void volume. Values of V_m were determined for normal-phase systems by the small baseline disturbance of chloroform in which the solutes were dissolved. V_m for reversed-phase systems was measured by injecting methanol and measuring the first baseline disturbance.

Following a change in mobile phase, 1–2 h of equilibration time with the new mobile phase was allowed. Equilibrium conditions were confirmed by repetitive injection of the same sample, until constant k' values were obtained. The Nucleosil NO_2 column was flushed with 100% chloroform overnight at 0.2 ml/min after every 4 days of operation.

Chromatographic systems studied

Normal phase (2 ml/min). (1) μBondapak NH_2 with *n*-heptane; (2) μBondapak NH_2 with *n*-heptane–2-propanol; (3) μBondapak CN with *n*-heptane; (4) basic alumina with *n*-heptane–chloroform; (5) basic alumina with *n*-heptane–2-propanol; (6) basic alumina with *n*-heptane–dioxane; (7) μPorasil with *n*-heptane; (8) μPorasil with *n*-heptane–2-propanol; (9) μPorasil with *n*-heptane–chloroform; (10) Nucleosil NO_2 with *n*-heptane; (11) Nucleosil NO_2 with *n*-heptane–2-propanol; (12) Nucleosil NO_2 with *n*-heptane–chloroform.

TABLE I

MODEL COMPOUNDS, COLUMNS, MOBILE PHASES, AND CAPACITY FACTORS FOR NORMAL-PHASE CHROMATOGRAPHY

Compound	*Nucleosil NO_2*			*μBondapak NH_2*			*μPorasil*			*μBondapak CN*
	n-Heptane	*95:5**	*75:25**	*n-Heptane*	*5:1**	*25:1**	*n-Heptane*	*99:1***	*99:1**	*n-Heptane*
1 Acenaphthene	0.80	0.26	0.32	0.43	0.06	0.27	0.59	0.03	0.19	0.03
2 1,2,3,4-Dibenzanthracene	13.1	3.00	0.48	4.20	0.63	2.33	2.29	0.03	0.70	0.76
3 1,2-Benzperylene	15.3	3.13	0.61	2.70	0.33	2.46	1.97	0.04	0.54	0.53
4 3,4-Benzofluoranthene	7.66	2.00	0.32	2.40	0.50	1.66	2.46	0.04	0.53	0.41
5 Coronene	12.3	3.66	0.71	3.80	0.77	2.66	1.79	0.13	0.54	0.50
6 Perylene	9.60	2.33	0.48	2.20	0.29	2.01	1.50	0.15	0.54	0.41
7 Diindeno[1,2,3-*c-d*:1′,2′,3′--*im*]perylene	***	5.01	1.72	4.75	1.80	7.21	13.3	0.30	1.97	2.26
8 Decacyclene	55.1	5.66	2.54	4.75	2.03	9.02	13.6	0.30	1.86	2.76
9 5,6-Benzoquinoline	***	31.6	3.80	8.21	1.63	7.30	***	1.97	***	2.47
10 7,8-Benzoquinoline	31.0	4.33	0.72	2.39	0.46	1.56	***	0.13	47.0	0.47
11 Acridine	***	23.1	3.52	5.48	1.06	4.22	***	1.02	***	1.23
12 4-Azafluorene	***	22.3	3.19	6.63	2.06	4.82	***	1.86	***	1.26
13 Carbazole	***	19.7	2.87	***	8.60	36.1	***	0.73	***	5.47

* Heptane–chloroform, v/v.
** Heptane–2-propanol, v/v.
*** Very strongly retained.

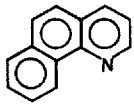
Reversed-phase (1 ml/min). (13) μBondapak C_{18} with methanol–water; (14) μBondapak CN with methanol–water.

RESULTS AND DISCUSSION

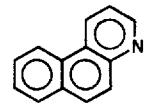
Normal-phase chromatography

Table I summarizes the retention data of the model PAHs and nitrogen heterocycles on each of the stationary phases investigated. The model PAHs ranged in size from two to ten rings. The model nitrogen heterocycles were chosen because of their presence in coal liquids and also their relatively weak retention. Typically these less polar aromatic nitrogen heterocycles are mono-aza types of low molecular weight and are sterically hindered. These types of weakly retaining nitrogen compounds are thus the most likely to overlap a PAH fraction in an SRC separation. 7,8-Benzoquinoline was included as a model nitrogen compound in this work after a normal-phase chromatographic study of several nitrogen compounds with the columns in Table I. The study revealed that this nitrogen heterocycle was in all cases the least retained of the nitrogen compounds, indicating that this type of compound was thus the most likely to overlap a PAH fraction. Using an open column procedure developed in this laboratory[5,6], Boduszynski *et al.*[27] have reported elemental analysis results on the hydrocarbons in oils of a non-distillable Wyodak SRC sample. A major fraction of the hydrocarbons would appear in the oil fraction of an SRC sample. The following elemental analysis results were obtained for the hydrocarbons in oils: carbon, 91.6%; hydrogen, 7.1%; nitrogen, 0.1%; oxygen, 1.4%; sulfur, 0.1%. Generally sulfur is present in relatively small amounts in SRC samples; thus sulfur compounds were not investigated extensively. Oxygen is present in sizeable amounts in SRC samples, but it is incorporated mainly in hydroxyl aromatics which can be readily separated from hydrocarbons[5,6]. The oxygen in the hydrocarbon fraction is most likely found in aromatic ethers. The overlap of oxygen compounds into a hydrocarbon fraction is currently being investigated. In this work, the separation of PAH from nitrogen heterocycles and the extent of overlap of nitrogen compounds into a hydrocarbon fraction were of interest.

Throughout Table I the effect of steric hindrance to the nitrogen atom upon retention can be seen if the isomers 5,6-benzoquinoline and 7,8-benzoquinoline are compared.



7,8- benzoquinoline



5,6- benzoquinoline

In all cases, the hindered 7,8-isomer eluted prior to the 5,6-isomer. This retention difference is most notable for the Nucleosil NO_2 stationary phase utilizing the heptane–chloroform mobile phase (95:5, v/v). A separation factor of 7.3 was observed for these isomers. In all cases 7,8-benzoquinoline eluted prior to any other nitrogen heterocycle. Because of its retention characteristics, this compound is a good indicator of nitrogen heterocycle overlap with PAHs.

Upon inspection of the data in Table I, it is shown that the most effective

stationary phase for the group separation of nitrogen heterocycles from PAH is μ-Porasil. Utilizing a mobile phase of *n*-heptane–chloroform (99:1, v/v), the longest retained PAH (diindeno[1,2,3-*c*-d:1′,2′,3′-*im*]perylene) gave a k' of 1.97, while the least retained nitrogen heterocycle (7,8-benzoquinoline) yielded a k' of 47.0. This strong nitrogen heterocycle retention can be attributed to the strong acid–base interaction of the nitrogen atom with the silanol groups on silica gel. The interaction between the basic nitrogen atom and acidic silanol group is demonstrated by the dramatic decrease in nitrogen heterocycle retention upon the addition of a protic solvent such as 2-propanol to the mobile phase (see Table I). A 1% solution of 2-propanol in *n*-heptane is sufficient for the alcohol to compete for the silanol groups via hydrogen bonding and interact with the basic nitrogen heterocycles as a proton donor. This results in a large decrease in retention for nitrogen heterocycle compounds. It should be noted that the addition of 1% chloroform (a very weak hydrogen donor) to the *n*-heptane–μPorasil system has a moderate effect upon retention of the compounds in Table I. This type of strong interaction between basic nitrogen heterocycles and silica has been reported by others[8,21,28] and provides a good basis for the separation of these compounds from PAHs.

Basic alumina is another stationary phase capable of acid–base interactions and is known for its ability to preferentially adsorb pyrrolic and basic nitrogen compounds[29]. The ability of basic alumina to separate these and other compound classes has been used recently in this laborastory to investigate coal-derived liquids with an open column procedure[5,6]. Since this approach yields relatively clean fractions of PAHs and nitrogen heterocycles it was decided to investigate this stationary phase using HPLC. It was found that the basic alumina retained the model compounds longer than any of the other stationary phases investigated. Utilizing 100% heptane, only acenaphthene was observed to elute from the column. The other PAHs remaining on the column were later eluted by switching to *n*-heptane–chloroform (95:5, v/v). This mobile phase and 1% dioxane in heptane eluted the model compounds, but overlap of 7,8-benzoquinoline with the larger PAHs demonstrated that the separation of these compounds classes was not complete. While 7,8-benzoquinoline eluted rapidly, the other less hindered nitrogen standards were more strongly retained. It was found that acridine and 4-azafluorene were retained significantly longer than 7,8-benzoquinoline, allowing a separation of these compounds from the PAHs. In general, basic alumina cannot completely resolve basic nitrogen compounds from PAHs, but does allow the separation of pyrrolic compounds from the other two classes of compounds due to the acid–base interaction of this functional group with the stationary phase. The order of elution is PAHs < basic nitrogen heterocycles < acidic nitrogen heterocycles.

The μBondapak NH_2 column showed similar preferential adsorption of pyrrolic types. Using *n*-heptane–chloroform (25:1, v/v) it can be seen in Table I that carbazole is retained considerably longer than the nitrogen heterocycles. This can be attributed to hydrogen bonding interactions between the lone pair electrons of the bonded NH_2 group and the pyrrolic hydrogen of carbazole. μBondapak CN also interacted with carbazole, but to a lesser extent than the μBondapak NH_2 column (Table I). As with basic alumina, μBondapak NH_2 has the ability to separate carbazole from PAHs and nitrogen heterocycles and generally showed the same elution order for these three compound classes. In addition, μBondapak NH_2 showed similar

nitrogen heterocycle overlap with PAHs with only 7,8-benzoquinoline overlapping when using the pure heptane mobile phase (Table I).

The weakly polar nature of both the NH_2 and CN stationary phases is evident if one compares the k' values for these columns with the Nucleosil NO_2 and μPorasil columns utilizing 100% heptane as the eluent. Only with the NH_2 and CN stationary phases are the nitrogen heterocycles 9, 11, and 12 eluted with the *n*-heptane (Table I). It can also be seen that μBondapak CN yields the smallest k' values and the most compound class overlap for the *n*-heptane mobile phase. Due to the weak interaction with basic nitrogen heterocycles, the selectivity for these compounds is inferior with the two columns. Since the CN column displayed the most overlap with the weakest mobile phase, organic modifiers were not considered with this column.

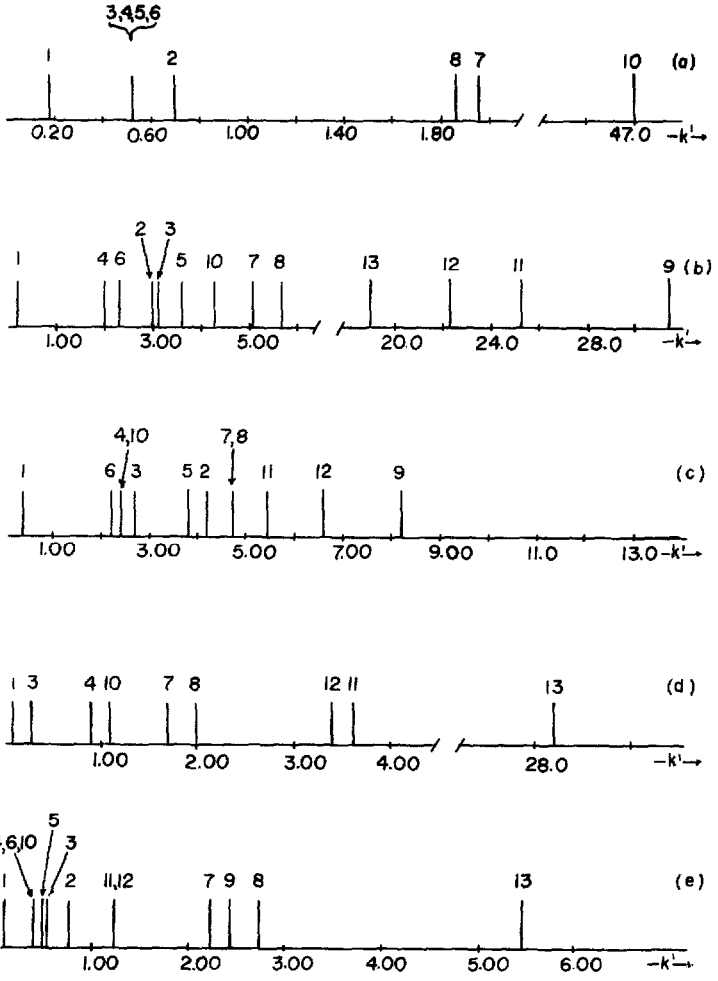


Fig. 1. Retention characteristics of model compounds on the stationary phases investigated with selected mobile phases. (a) μPorasil, *n*-heptane–chloroform (99:1, v/v); (b) Nucleosil NO_2, *n*-heptane–chloroform (95:5, v/v); (c) μBondapak NH_2, *n*-heptane; (d) basic alumina, *n*-heptane–chloroform (95:5, v/v); (e) μBondapak CN, *n*-heptane.

Nucleosil NO_2 was utilized by Matsunaga[8] to fingerprint chromatographically coal liquids and to separate model PAHs from nitrogen heterocycles. Blumer and Zander[23] and Ray and Frei[30] proposed electron donor–acceptor complex formation as the retention mechanism for bonded nitrophenyl stationary phases. The data for *n*-heptane in Table I indicates that very strong solute–stationary phase interactions are occurring for both PAHs and nitrogen heterocycles with the Nucleosil NO_2 stationary phase. Only basic alumina retained these compounds more strongly, indicating that in the absence of an organic modifier a strong solute–nitrophenyl interaction was occurring. It should be noted that the Nucleosil NO_2 column does not have the residual silanol groups capped[31], which presents the possibility of a dual retention mechanism. Although a dual retention mechanism may be possible, the bulkiness of the nitrophenyl group would suggest that a solute molecule would encounter substantial steric hindrance to these uncapped silanol groups decreasing this type of interaction. Table I does support the theory of stronger donor–acceptor complexes for solutes with larger numbers of π-electrons. Donor–acceptor interactions are also supported by the very strong retention of hindered and low-molecular-weight nitrogen heterocycles when using *n*-heptane as the mobile phase.

Due to the relatively long retention times of some PAHs on Nucleosil NO_2, overlap with small nitrogen heterocycles such as 7,8-benzoquinoline can occur, but in general this bonded phase separates PAHs and nitrogen heterocycles reasonably well. The Nucleosil NO_2 column displayed the same general elution order for the standards as the basic alumina and μBondapak NH_2 systems investigated. Fig. 1 diagramatically illustrates the retention of the model compounds on each stationary phase with selected mobile phases.

Reversed-phase chromatography

Table II lists the retention characteristics of the model compounds investigated under reversed-phase conditions. It is clear from this data that reversed-phase chromatography offers better selectivity for separating PAHs from nitrogen heterocycles than the normal-phase systems in Table I. With both the C_{18} and CN columns, the polar nitrogen heterocycles are eluted prior to the PAH compounds, in agreement with solvophobic theory[32,33]. Larger PAH compounds tailed extensively in methanol–water mixtures weaker than 70:30, (v/v). This indicated the low solubility of these condensed ring systems in aqueous mobile phases. μBondapak C_{18} retained the model compounds significantly longer than the μBondapak CN, so higher percentages of methanol in the mobile phase were required to elute the PAHs and reduce peak tailing. No overlap of these functional classes is observed under these conditions, suggesting that reversed-phase chromatography is the optimal approach to separate these standards. Unfortunately, many coal liquid samples are not very soluble in methanol–water mixtures. Because of the inherent solubility problem, few reports have appeared involving reversed-phase HPLC of coal-derived liquids[26]. Although some workers such as Schabron *et al.*[19,34] have had success with the distillable fractions of coal liquids, non-distillable fractions of higher molecular weight can present solubility problems in aqueous mobile phases. While analytical amounts of these heavier fractions may be chromatographed to obtain a profile of the sample, this yields limited information. Problems in reversed-phase systems have been reported by Schmitter *et al.*[22] who were unable to use NMR analyses on crude oil

TABLE II

MODEL COMPOUNDS, COLUMNS, MOBILE PHASES, AND CAPACITY FACTORS FOR REVERSED-PHASE CHROMATOGRAPHY

Compound	*μBondapak C_{18}*		*μBondapak CN*	
	CH_3OH–H_2O (80:20, v/v)	*CH_3OH–H_2O (70:30, v/v)*	*CH_3OH–H_2O (50:50, v/v)*	*CH_3OH–H_2O (45:55, v/v)*
1 Acenaphthene	0.76	2.03	2.70	4.09
2 1,2,3,4-Dibenzanthracene	3.70	13.1	15.0	*
3 1,2-Benzperylene	4.12	14.8	15.4	*
4 3,4-Benzofluoranthene	2.73	8.76	15.4	*
5 Coronene	6.94	13.7	14.6	*
6 Perylene	2.65	8.41	12.6	*
7 Diindeno[1,2,3-*c*-*d*:1′,2′,3′-*im*]perylene	6.59	23.7	15.1	*
8 Decacyclene	6.36	24.0	15.2	*
9 5,6-Benzoquinoline	0.35	0.76	2.10	2.96
10 7,8-Benzoquinoline	0.35	0.94	2.00	2.54
11 Acridine	0.30	0.88	2.15	3.00
12 4-Azafluorene	0.28	0.58	1.80	2.12
13 Carbazole	0.23	0.76	2.50	3.60

* Very strongly retained.

samples because of low sample capacity. Amateis and Taylor[35] reported similar solubility problems while attempting to chromatograph a coal-derived liquid with aqueous mobile phases. Thus, even though Table II appears to present an attractive method for separating PAHs from nitrogen heterocycles it can not be easily applied to non-distillable coal-liquid samples. Table II does illustrate, however, the potential for reversed-phase systems in other applications where solubility does not present a problem.

CONCLUSIONS

With the normal-phase systems, the μPorasil column was most selective for the separation of PAHs from nitrogen heterocycles due to the acid–base interaction of the nitrogen lone-pair electrons with the surface silanol groups. This interaction retained basic nitrogen-type compounds very strongly thereby permitting the separation of them from the non-polar PAHs. All other normal-phase packings investigated showed overlap of sterically hindered nitrogen heterocycles into the PAH fraction. Acid–base retention mechanisms are also responsible for the separation of pyrrolic compounds from nitrogen heterocycles and PAHs on the basic alumina and μBondapak NH_2 stationary phases. Reversed-phase systems offer a superior method for the separation of PAHs from nitrogen types but the low solubility of non-distillable coal derived liquids in aqueous mobile phases limits the use of this technique with actual coal samples.

The results of these studies demonstrate the potential for separating PAHs from nitrogen heterocycles in coal-derived liquids and the extent of overlap of the com-

pound classes. Normal-phase HPLC should provide an effective means to collect compound class fractions which will provide a basis for evaluating the PAH and nitrogen heterocycle character of these highly complex samples.

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