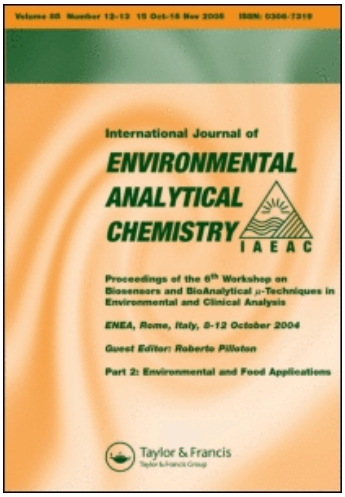

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Chromatographic Retention of Azaarenes on Florisil

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Chromatographic Retention of Azaarenes on Florisil

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Various substituted pyridines, quinolines, and other azaarenes were applied on Florisil and eluted with ether saturated with ammonia. The relationships between chromatographic retention and aqueous basicity suggested that the mechanism of adsorption involved the exchangeable protons on the surface of Florisil. Thus, retention of azaarenes on Florisil was mainly influenced by the Brönsted basicity of the heterocyclic nitrogen atom(s). In contrast with adsorption on silica and alumina, steric interactions had minimal effects on retention. The results suggested that Florisil might be a good adsorbent for separating azaarenes in environmental and other samples.

KEY WORDS: Azaarenes, Florisil, liquid chromatography, adsorption.

INTRODUCTION

Nitrogen heterocyclic bases (azaarenes), such as pyridine, quinoline, and acridine, may be ubiquitous environmental contaminants. Many have been identified in ambient air, sediments, ground water, and biota.[1–4] Their presence in the environment has been mainly

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attributed to the use of fossil fuels.[2] However, many of these biologically active compounds may also enter the environment from such sources as hazardous wastes.[5]

The determination of azaarenes in environmental and other samples requires methods to selectively isolate and characterize nitrogen bases. As part of our research on the use of Florisil (®Floridin) to isolate vapor-phase azaarenes from ambient air,[1] we began a study of the chromatographic adsorptivities of nitrogen bases on Florisil.[6] We found, for instance, that liquid chromatography on Florisil could effectively isolate azaarenes from a coal liquid.[7] To further study the applications of Florisil for such analyses, we conducted a series of experiments to examine the chromatographic interactions of environmentally important azaarenes on Florisil. This report describes some of our results.

EXPERIMENTAL

The basic procedure, described in detail elsewhere,[7] consisted of applying standard mixtures of heterocyclic bases on 50.0-g columns of activated Florisil (60/100 mesh). *n*-Tridecane was also applied to determine column void volume. The compounds were eluted with ether saturated with ammonia (NH_3Et_2O) at flow rates of 1–2 mL min^{-1}. Eluents were collected and analyzed by capillary column gas chromatography for *n*-tridecane and the heterocyclic bases: a Varian-3700 gas chromatograph equipped with a 15-m SE-54 or CAM fused silica capillary column was used. The retention factor (k') for each heterocyclic amine was determined by:

$$k' = \frac{V_R - V_m}{V_m}, \tag{1}$$

where V_R equals retention volume of nitrogen heterocycle and V_m equals column void volume or retention volume of *n*-tridecane.

RESULTS AND DISCUSSION

Retention of substituted pyridines

Values of $\log k'$ (retention factors) for substituted pyridines on Florisil and their aqueous free energies of protonation (ΔG_{prot}) are

listed in Table I. A plot of $\log k'$ vs $-\Delta G_{prot}$ (Figure 1) shows that twelve compounds (closed squares) gave the following linear (free energy) relationship (LFER):

$$\log k' = 0.180\ (-\Delta G_{prot}) - 0.642. \quad (2)$$

The linear regression gave a correlation where $r = 0.994$, std. dev. $= 0.03$, and SD/RMS $= 0.11$. (Ideally, good precision for structure-reactivity relationships has SD/RMS $\leqq 0.1$.[10] This statistical parameter gives a measure of the deviation for which the linear correlation does not account. More detailed discussions may be found in ref. 7 and 10.)

The LFER between chromatographic retention (measure by $\log k'$) and aqueous free energy of protonation indicated that the major factor influencing adsorption of pyridine bases was transmission of

TABLE I

Log k' (retention factors) and ΔG_{prot} (free energies of protonation) for substituted pyridines

no.	substituent	log k'	$-\Delta G_{prot}$[a]
1	3-Cl	0.049	3.83
2	2-MeO	0.19	4.40[b]
3	4-Cl	0.24	5.22
4	2-Phenyl	0.53	6.50
5	H	0.62	7.09
6	2-Et	0.66	8.03
7	3-Et	0.67	7.58
8	4-Phenyl	0.73	7.44[b]
9	3-Me	0.77	7.77
10	2-Me	0.81	8.13
11	4-Et	0.82	8.00
12	4-Me	0.85	8.17
13	3,5-diMe	0.85	8.39
14	2,5-diMe	0.86	8.73
15	3,4-diMe	0.86	8.81
16	2,4-diMe	0.86	9.04
17	2,6-diMe	0.86	9.16

[a]Aqueous free energy of protonation (kcal mol^{-1}) at 25°C from either ref. 8 or 9.

[b]Aqueous free energy of protonation (kcal mol^{-1}) at 20°C.

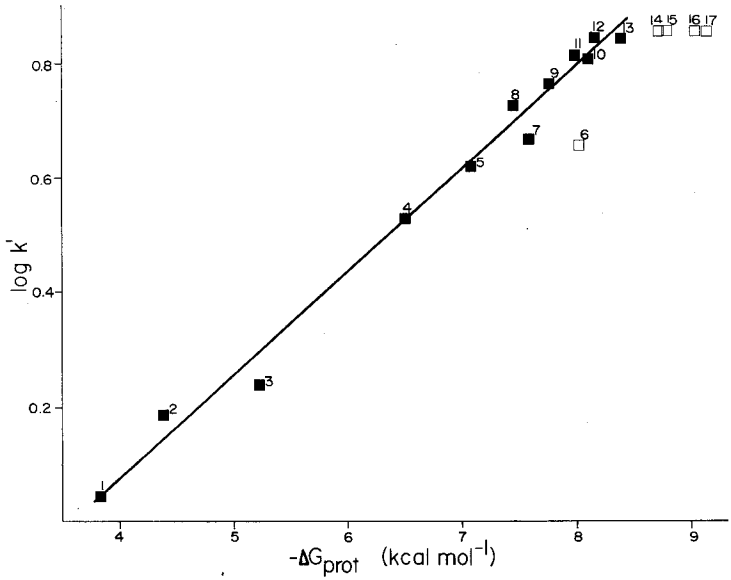


FIGURE 1. Plot of $\log k'$ (retention factors) vs $-\Delta G_{prot}$ (aqueous free energies of protonation) for substituted pyridines on Florisil: ■ = data used in linear correlation; □ = data omitted from linear correlation. Numbers refer to substituents listed in Table I.

substituent effects to the heterocyclic nitrogen atom. Except for 2-ethylpyridine, there appeared to be minimal steric hindrance to retention. The deviation between retention and aqueous basicity exhibited by 2-ethylpyridine (compound 6) might have been caused by extra substituent interference with interaction of the ring nitrogen atom and the adsorbent surface. For instance, a weakly or nonadsorbed alkyl chain might be free to undergo rotational movements.[11] This might reduce interaction energy by preventing the aromatic ring from adopting a preferred planar configuration.[12]

The deviation exhibited by 2-ethylpyridine was not exhibited by either 2-methoxy- or 2-phenylpyridine. However, for both compounds, added (electrostatic) interactions of the methoxy or phenyl substituents with the adsorbent surface[13] might have overcome possible substituent interference with adsorption.

There appeared to be no increase in the values of the retention factors ($\log k'$) for the last four dimethyl-substituted pyridines

(compounds 14–17), although $-\Delta G_{prot}$ increased. This was possibly due to "solvent demixing" of the NH_3Et_2O on Florisil: a concentrated front of NH_3 formed which may have displaced the more strongly retained lutidines (including 2,6-dimethylpyridine) as essentially a single band. (It should be noted that ether without ammonia was ineffective in eluting the azaarenes. More details may be found in ref. 7.).

The chemistry of the adsorptive mechanism on Florisil is clearly different from that of other metal oxide adsorbents. On alumina, a limited LFER between retention and the Hammett σ-function[14,15] was observed.[16,17] However, notable exceptions occurred with α-alkyl-substituents: 2-methylpyridine and 2-substituted lutidines were retained considerably less than pyridine.[16,17] While a limited relationship was seen with alumina, no clear LFER between retention and basicity of substituted pyridines was observed with silica.[18] One author suggested that retention of pyridine and its 2-alkyl derivatives on silica, alumina, and alumina impregnated with cobalt was influenced by steric accessibility rather than basicity.[19] Similarly, no correlation between retention and basicity was observed in liquid chromatography of pyridine and its methyl derivatives on silver impregnated silica.[20]

The relationship between $\log k'$ and free energy of protonation of substituted pyridines suggested a mechanism of adsorption involving the exchangeable (proton) acid sites on the surface of Florisil.[6,7] For instance, as predicted from aqueous basicity, both 2-picoline and 2,6-lutidine were more strongly retained on Florisil than pyridine. Others showed that adsorption of 2,6-lutidine on a similar synthetic magnesium silicate only involved Brönsted (proton) acid sites.[21] If adsorption had involved Lewis acid sites, the α-alkyl-substituted pyridines would have been expected to be eluted before pyridine, as typically occurs with alumina and silica. For instance, steric inhibition to interaction has been observed in reactions between 2-methyl- or 2,6-dimethylpyridine and various Lewis acids.[22–24] Thus, adsorption of 2,6-lutidine has been used to determine Brönsted (proton) acidity of solid catalysts.[25]

Retention of polynuclear diazaarenes

Values of $\log k'$ (retention factors) for five polynuclear diazaarenes on Florisil and their aqueous free energies of protonation (ΔG_{prot}) are

listed in Table II. These five compounds gave a limited relationship between $\log k'$ and $-\Delta G_{prot}$ (Figure 2):

$$\log k' = 0.554\,(-\Delta G_{prot}) - 0.880, \qquad (3)$$

with $r = 0.976$, std. dev. $= 0.12$, and SD/RMS $= 0.26$. The main deviations from the relationship were exhibited by phenazine (No. 18) and quinoxaline (No. 19). That is, phenazine was adsorbed to a lesser extent and quinoxaline to a greater extent than aqueous basicities would predict.

TABLE II

$\log k'$ (retention factors) and ΔG_{prot} (free energies of protonation) for polynuclear diazaarenes

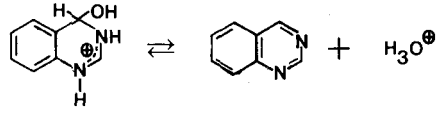
no.	compound	$\log k'$	$-\Delta G_{prot}$[a]
18	phenazine	−0.12	1.65[b]
19	quinoxaline	0.0043	1.38[b]
20	quinazoline	0.58	2.61[c]
21	benzo[c]cinnoline	0.80	2.95
22	cinnoline	0.89	3.24

[a]Aqueous free energy of protonation (kcal mol^{-1}) at 20°C from either ref. 8 or 9.

[b]Aqueous free energy of protonation (kcal mol^{-1}) at 25°C from ref. 26.

[c]In absence of covalent hydration.

Although phenazine and quinoxaline exhibited deviations from the linear correlation, it was interesting to note that retention of quinazoline (No. 20) corresponded to its "true" free energy of protonation in absence of covalent hydration. That is, in aqueous solution, the overall free energy of protonation (−4.71 kcal mol^{-1}) includes the following equilibrium:[27]



1

The carbinolamine *1*, covalently hydrated across the 3,4-bond, is the most stable of the two quinazolinium cations (*1* and *2*) in aqueous solution. The other cation, the "anhydrous" species *2*, which is

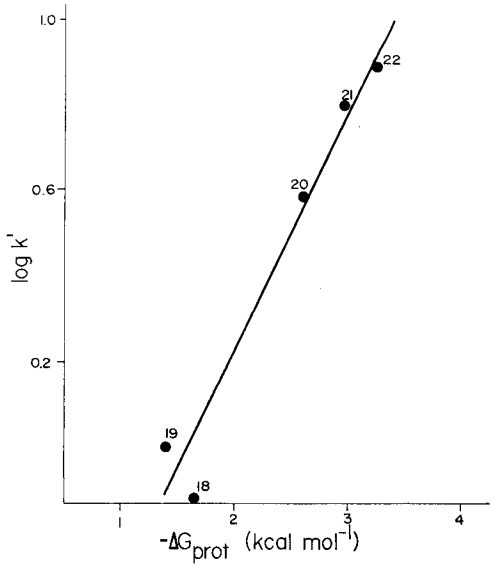
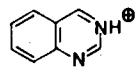


FIGURE 2. Plot of $\log k'$ (retention factors) vs $-\Delta G_{prot}$ (aqueous free energies of protonation) for polynuclear diazaarenes on Florisil. Numbers refer to compounds listed in Table II.

unstable in aqueous solution, has ΔG_{prot} of $-2.61\,kcal\,mol^{-1}$. It was the free energy of protonation of the "anhydrous" species *2* which most accurately related to retention of quinazoline on Florisil.



2

Retention of Benzo-substituted quinolines

Values of $\log k'$ (retention factors) for four benzoquinolines on Florisil and their aqueous free energies of protonation (ΔG_{prot}) are listed in Table III. These four compounds gave a LFER between $\log k'$ and $-\Delta G_{prot}$ (Figure 3):

$$\log k' = 0.228\ (-\Delta G_{prot}) - 0.817, \qquad (4)$$

with $r = 0.993$, std. dev. $= 0.02$, and SD/RMS $= 0.11$.

TABLE III

Log k' (retention factors) and ΔG_{prot} (free energies of protonation) for benzo-substituted quinolines

no.	compound	log k'	$-\Delta G_{prot}$[a]
23	7,8-benzoquinoline	0.49	5.70
24	phenanthridine	0.54	6.06
25	5,6-benzoquinoline	0.78	6.90
26	acridine	0.88	7.51

[a]Aqueous free energy of protonation (kcal mol^{-1}) at 20°C from either ref. 8 or 9.

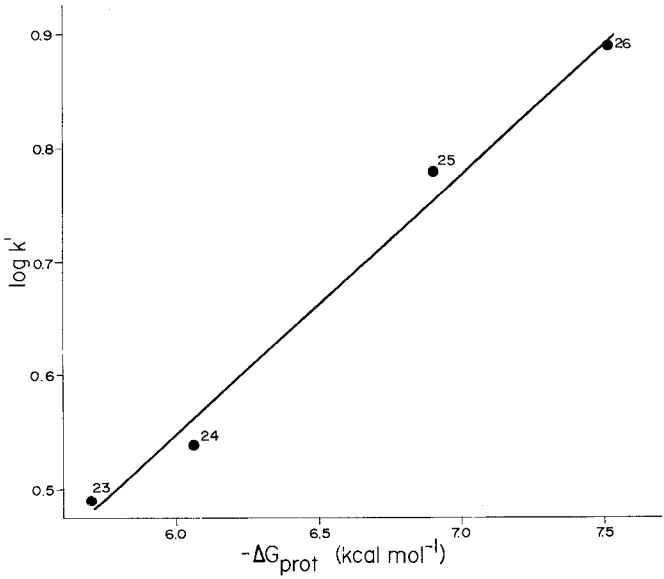


FIGURE 3. Plot of log k' (retention factors) vs $-\Delta G_{prot}$ (aqueous free energies of protonation) for benzo-substituted quinolines on Florisil. Numbers refer to compounds listed in Table III.

The chemistry governing the adsorption of these compounds on Florisil also appears significantly different from that of other metal oxide adsorbents. For instance, acridine (No. 26) was adsorbed more strongly on Florisil than the other benzoquinolines, as predicted by its greater aqueous basicity. However, with alumina,[17,28–31] silica gel,[18,32,33] and other chromatographic adsorbents,[34,35] acridine was

one of the least adsorbed of the benzo-substituted quinolines. As with the α-alkyl-substituted pyridines, the decreased retention on alumina of acridine relative to other polynuclear azaarenes was explained through steric hindrance.[28] With Florisil, however, such steric hindrance is minimal and retention is mostly influenced by the (Brönsted) basicity of the heterocyclic nitrogen atom.

Retention of alkyl-substituted quinolines and isoquinoline

Interpreting the relationship between retention on Florisil and aqueous free energy of protonation for these compounds was dependent on availability of consistent aqueous dissociation constants. However, values of $\log k'$ (retention factors) for eight alkyl-substituted quinolines and isoquinoline on Florisil and their aqueous free energies of protonation (ΔG_{prot}) judged to be best available are listed in Table IV. Five compounds (quinoline, isoquinoline, 8-methyl-, 4-methyl-, and 2-methylquinoline) gave a LFER between $\log k'$ and $-\Delta G_{prot}$ (Figure 4):

$$\log k' = 0.314\,(-\Delta G_{prot}) - 1.60, \qquad (5)$$

with $r = 0.998$, std. dev. $= 0.01$, and SD/RMS $= 0.06$.

TABLE IV

Log k' (retention factors) and ΔG_{prot} (free energies of protonation) for alkyl-substituted quinolines and isoquinoline

no.	compound	$\log k'$	$-\Delta G_{prot}$[a]
27	quinoline	0.49	6.65
28	8-methylquinoline	0.52	6.77
29	isoquinoline	0.69	7.24
30	4-methylquinoline	0.79	7.60
31	2,7-dimethylquinoline	0.80	6.84[b]
32	7-methylquinoline	0.83	7.16
33	2-methylquinoline	0.85	7.82
34	2,6-dimethylquinoline	0.88	7.45[b]

[a]Aqueous free energy of protonation (kcal mol^{-1}) at 20°C from either ref. 8 or 9 (optical methods).

[b]Aqueous free energy of protonation (kcal mol^{-1}) at 25°C (from hydrolysis of perchlorates; quinhydrone electrode).

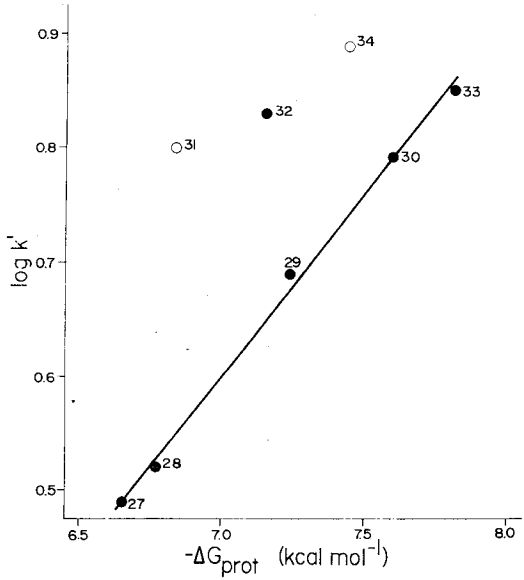


FIGURE 4. Plot of $\log k'$ (retention factors) vs $-\Delta G_{prot}$ (aqueous free energies of protonation) for alkyl-substituted quinolines and isoquinoline on Florisil. Numbers refer to compounds listed in Table IV. Acid dissociation constants determined by: ● optical methods; ○ hydrolysis of perchlorates, quinhydrone electrode.

The deviation exhibited by 2,7- and 2,6-dimethylquinoline (Nos. 31 and 34, respectively) might have resulted from the different method used to determine their aqueous dissociation constants. The deviation exhibited by 7-methylquinoline (No. 32), however, might not be similarly explained. The general inconsistencies of the aqueous dissociation constants may be seen when $\log k'$ is plotted against the range of available aqueous free energies of protonation for these compounds (Figure 5).

Despite the limitations of the linear correlation, the general relationship again suggests a mechanism of adsorption mainly involving the exchangeable Brönsted acid sites on Florisil. This is especially suggested by the retention of the α-alkyl-substituted quinolines: 2-methyl-, 2,6-dimethyl-, and 2,7-dimethylquinoline were all more strongly retained than either quinoline or 4-methylquinoline. As with the substituted pyridines, a mechanism involving Lewis acid sites should have resulted in a decrease in retention of 2-

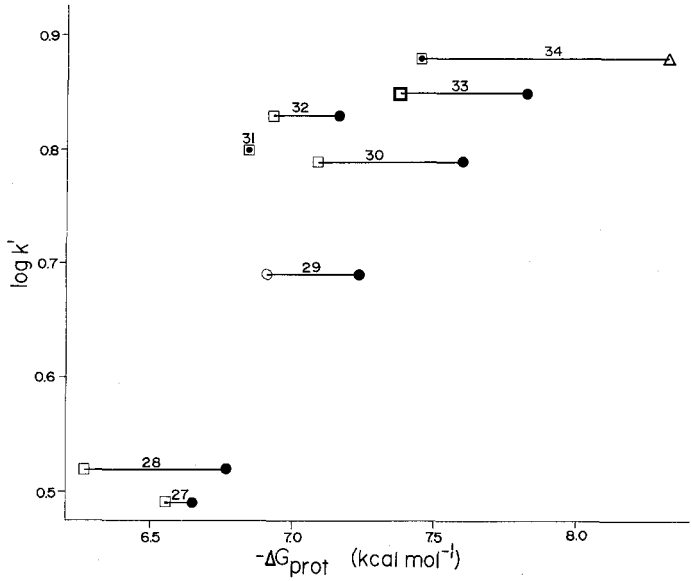


FIGURE 5. Plot of $\log k'$ (retention factors) vs $-\Delta G_{prot}$ (aqueous free energies of protonation) for alkyl-substituted quinolines and isoquinoline on Florisil using range of available aqueous free energies of protonation: ● = from Table IV; □, ○, △ = from other data in either ref. 8 or 9.

methyl-compared to 4-methylquinoline.[36] Thus with Florisil, the main influence on retention of substituted quinolines was their Brönsted basicity. This again contrasts with other chromatographic systems where retention is strongly influenced by steric effects. With alumina,[16,17,28] silica,[18,37] and silver impregnated Zipax,[34] the α-alkyl-substituted quinolines were all retained less than quinoline.

CONCLUSIONS

Because of its strong Brönsted surface acidity, Florisil traditionally has been considered unsuitable for chromatographic separations of nitrogen bases.[38,39] In contrast, our results suggest that the chemistry of the adsorption process on Florisil might provide some ideal separations for analyzing azaarenes. For instance, it might be an excellent method for confirming the identity of azaarenes (or other nitrogen bases) based on predictable retention characteristics.

Although these initial results represent limited classes of compounds with some limitations in the linear correlations, the technique has significant potential application in analyses of environmentally important azaarenes.

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