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LOCALIZED ADSORBATE–ADSORBENT INTERACTIONS ON FLORISIL

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SUMMARY

   Localized adsorbate–adsorbent interactions were investigated by studying equilibrium adsorption of pyridine and *n*-butylamine on Florisil. The discontinuity of the Langmuir isotherms and heat of adsorption of pyridine were analyzed by the "patch" theory of adsorption on heterogeneous surfaces. Thus, at low surface coverages, the solutes appeared to be strongly localized on specific active sites. Final surface coverage appeared to result in a surface monolayer of adsorbed molecules. Because such differing results have been reported for localization on chromatographic grade silica gels, Florisil may be a model chromatographic adsorbent for studying strongly localized adsorbate–adsorbent interactions in liquid chromatography. This may be particularly useful since results of equilibrium adsorption isotherms are frequently used to develop liquid chromatographic theories.

INTRODUCTION

   There has been considerable discussion concerning mechanisms of adsorption in liquid chromatography with silica gel when strong adsorbate–adsorbent interactions occur[1-8]. Much discussion has involved results of equilibrium adsorption isotherms which exhibit two apparently distinct isotherm regions[1,6-9]. One conclusion is that the total isotherm represents bilayer (or at least excess of monolayer) adsorption[6-8]. Another is that the low concentration region represents localized, specific adsorption onto discrete active sites instead of initial monolayer formation[1,9].

   Chemical adsorption in liquid chromatographic systems represents the most extreme case of localized adsorbate–adsorbent interactions[1]. Such interactions have been shown to occur between nitrogen bases and exchangeable surface protons on magnesium silicates such as Florisil (Floridin®). These exchangeable surface protons are present to balance stoichiometrically the diffuse negative charge rising from isomorphous substitution of Mg^{2+} for Si^{4+} in the silicate matrix. Chemical adsorption of nitrogen bases on Florisil and similar magnesium silicates has been shown by

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chromatographic retention characteristics[10,11], spectrophotometric observations[12,13], and adsorption of Hammett indicators[14–16]. Chemisorption of nitrogen bases and other compounds on magnesium silicates is believed to result in "ion-pair" complexes between exchangeable surface protons (in contrast to silanol protons) and adsorbate[12,17]; adsorption of pyridine and 2,6-lutidine results in pyridinium ions[12].

 As part of our research on Florisil as a sampler for vapor-phase polynuclear aza-arenes in ambient air[18], we determined that Florisil could be effectively used for liquid chromatographic separations within classes of basic aza-arenes[19]. To investigate further the mechanisms of adsorption responsible for the chromatographic separations with Florisil, we conducted equilibrium adsorption studies of pyridine and n-butylamine on Florisil.

EXPERIMENTAL

 Specific surface area of Florisil (60–100 mesh), activated at 650°C and stored at 140°C, was determined by the BET method of nitrogen adsorption. For batch equilibrium adsorption studies, Florisil was cooled in a desiccator to room temperature. Portions (0.2–0.4 g to the nearest 0.1 mg) were transferred to stoppered 125-ml Erlenmeyer flasks. Adsorption experiments were conducted at 296°K for n-butylamine, and 296°K and 277°K for pyridine.

 For the preliminary kinetic experiments, 25.00 ml of a 27 mM solution of n-butylamine in pentane were added to flasks containing Florisil. Aliquots of the supernatants (10.00 ml) were then removed after specific periods of time. Concentrations of n-butylamine were determined by acidimetric titration.

 For the final equilibrium adsorption studies, 25.00 ml of various concentrations of either n-butylamine or pyridine in pentane were added to flasks containing Florisil. After at least 4 min and occasional swirling, supernatant concentrations of either n-butylamine or pyridine were determined by acidimetric titration or capillary column gas chromatography, respectively. Amounts adsorbed by Florisil were determined by difference. (Details of all experimental methods may be found in ref. 19.)

RESULTS AND DISCUSSION

Equilibrium adsorption isotherms

 A series of experiments was first conducted to determine the time for attainment of adsorption equilibrium. A plot of μmol m^{-2} adsorbed vs. time (Fig. 1) indicated that adsorption equilibrium for n-butylamine was attained in ca. 3 min. (Florisil specific surface area determined by the BET method of nitrogen adsorption was 203 m^2 g^{-1}.)

 The complete adsorption curves for pyridine (Fig. 2) and n-butylamine (Fig. 3) have the general appearance of type H (high affinity) curves[20,21]. Type H curves, with an apparent initial vertical rise at low solution concentrations, are typically associated with strong adsorption such as chemisorption. Type H curves at high solution concentrations appear similar to type L (Langmuir), with the y-intercept displaced upwards from the origin. Curves similar in appearance have been reported for adsorption of ethyl acetate, methyl ethyl ketone, and tetrahydrofuran on silica gel[6,7,22].
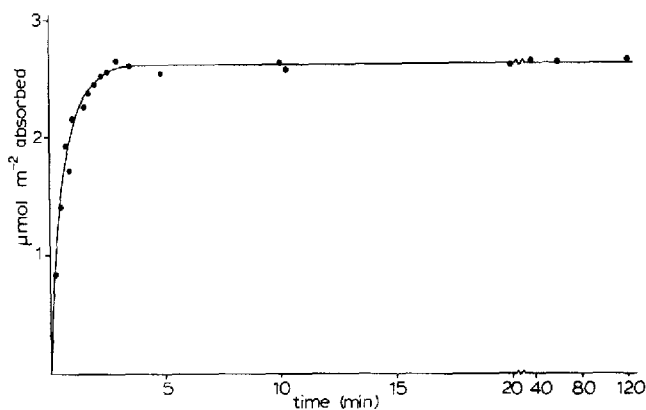
Fig. 1. Kinetics of adsorption of *n*-butylamine on Florisil (296°K).

Expansions of the "vertical" low concentration regions of the adsorption curves for pyridine (Fig. 4) and *n*-butylamine (Fig. 5) also have the general shape of Langmuir-type curves. Thus, the complete curves, high plus low concentration regions, appear to consist of two regions of adsorption, each characterized by Langmuir-type adsorption. This is more apparent when the overall adsorption data is plotted by the Langmuier adsorption isotherm[23,24]:

$$\frac{C_S}{C_A} = \frac{C_S}{N_0} + \frac{1}{KN_0} \tag{1}$$

where C_S is equilibrium solution concentration, C_A is equilibrium adsorption concentration, N_0 is monolayer capacity, and K is equilibrium constant of adsorption. For pyridine (Fig. 6), the Langmuir isotherm shows a change in slope at *ca.* 3–8 μmole ml^{-1} equilibrium solution concentrations. Similarly for *n*-butylamine (Fig. 7), a change in slope occurs at *ca.* 0.9–2 μmole ml^{-1} equilibrium solution concentrations.
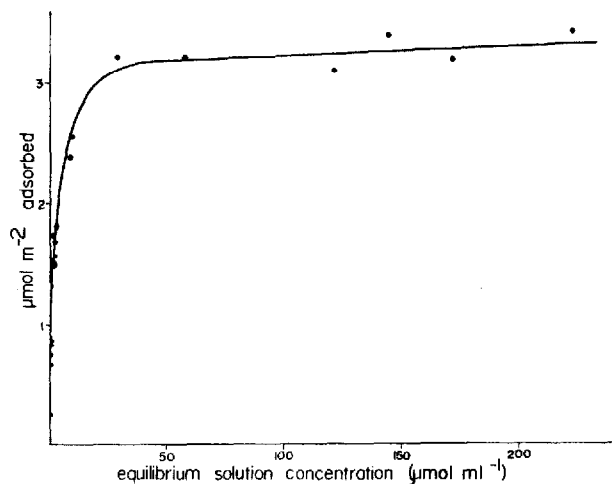

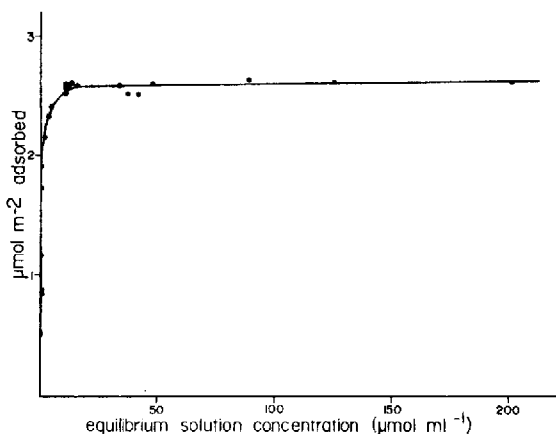Fig. 2. Equilibrium adsorption of pyridine on Florisil (296°K).

Fig. 3. Equilibrium adsorption of *n*-butylamine on Florisil (296°K).

Changes in slopes and intercepts for the two apparent regions of the Langmuir isotherms may be seen from the linear regression analyses (Table I). A similar discontinuous (broken) Langmuir isotherm has been reported for adsorption of dibenzyl on silica gel[9] and discussed more fully in ref. 1.

Heat of adsorption of pyridine

　　　The discontinuity of the Langmuir isotherms of pyridine and *n*-butylamine on Florisil would be consistent with "patch" adsorption on heterogenous surfaces[25]. The theory of "patch" adsorption assumes that there are different types of discrete adsorption sites on a heterogeneous surface. Therefore, each type of site or "patch" would be characterized by individual isotherms according to its specific affinity for the adsorbed compound. Thus, from the Langmuir isotherms, there appears to be at least two types of discrete sites responsible for adsorption of pyridine and *n*-butylamine on Florisil.
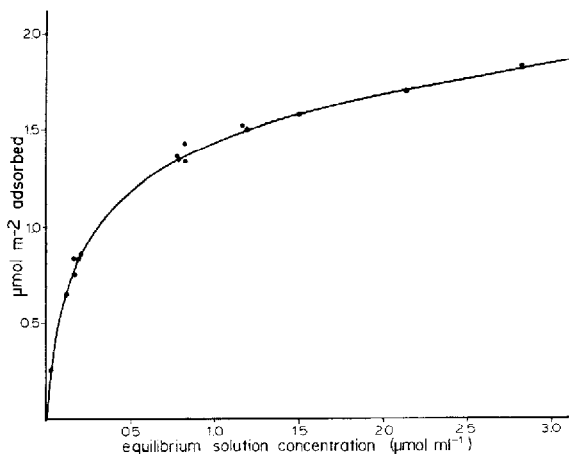

Fig. 4. Expansion of "vertical" low concentration region of pyridine adsorption curve (296°K).
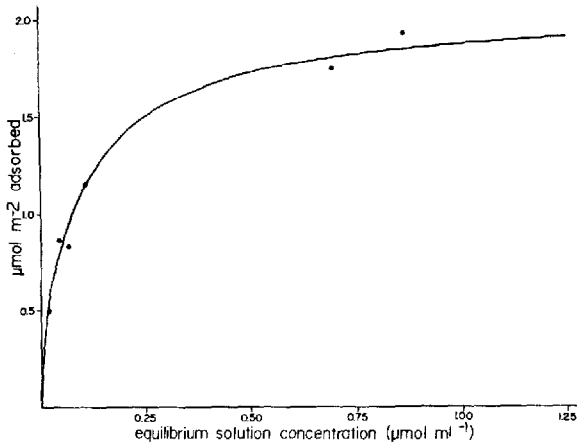
Fig. 5. Expansion of "vertical" low concentration region of *n*-butylamine adsorption curve (296°K).

If there were different "patches" of sites characterized by individual Langmuir isotherms, then those sites would also be characterized by corresponding heats of adsorption[25]. The relative difference between adsorptive strengths for the different sites could be estimated from Langmuir equilibrium constants of adsorption at two temperatures[23,26].

$$\Delta H = R \left[\frac{\ln K_2 - \ln K_1}{\dfrac{1}{T_1} - \dfrac{1}{T_2}} \right] \tag{2}$$

where ΔH = heat of adsorption, R = ideal gas constant, and K_1, K_2 = Langmuir equilibrium constants at temperatures T_1, T_2.

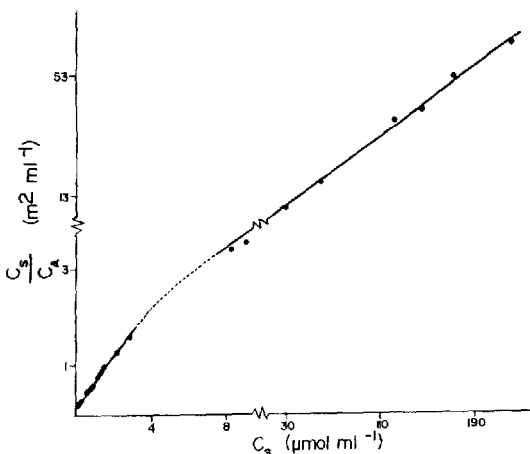For pyridine, adsorption experiments were conducted at 296°K and 277°K.

Fig. 6. Langmuir isotherm of pyridine adsorption on Florisil (296°K). From eqn. 1: C_S = equilibrium solution concentration; C_A = equilibrium adsorbed concentration.
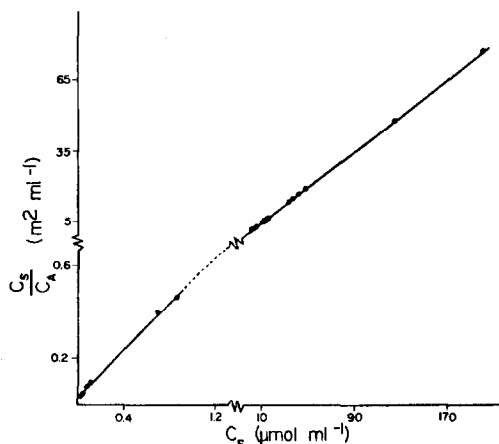
Fig. 7. Langmuir isotherm of n-butylamine adsorption on Florisil (296°K). From eqn. 1: C_S = equilibrium solution concentration; C_A = equilibrium adsorbed concentration.

(The linear regression analysis of the Langmuir isotherm at 277°K is listed in Table I.) The results give values of $\Delta H = -7.9$ and -1.2 kcal mol^{-1} for the low- and high-concentration regions of the Langmuir isotherms, respectively.

The relative difference between these two values suggests that two mechanisms of adsorption occur in the two regions of the overall Langmuir isotherm. For instance, the low concentration region may represent very strong adsorption, chemisorption, with the high region weaker adsorption or physisorption. In general, heat of adsorption is much greater for chemical than physical adsorption; however, ΔH for both may vary depending on adsorbate and adsorbent[27]. For gas-phase adsorption, enthalpy for physisorption may range from 0.07 to $ca.$ 4.8 kcal mol^{-1}; for chemisorption[26,27], the range may be from 10 to 100 kcal mol^{-1}.

Adsorption at low surface coverage

Localized adsorption (possibly chemisorption onto discrete Brönsted acid sites) in the low concentration regions is suggested by adsorption constants from the Langmuir isotherms for both pyridine and n-butylamine (Table II). For instance, the

TABLE I

LINEAR REGRESSION ANALYSES OF LANGMUIR ISOTHERMS

Compound	Temperature (°K)	Adsorption region	Regression equation*	Correlation coefficient
n-Butylamine	296	Low	$C_S/C_A = 0.500\ C_S + 0.0360$	0.998
		High	$C_S/C_A = 0.378\ C_S + 0.182$	1.000
Pyridine	296	Low	$C_S/C_A = 0.514\ C_S + 0.144$	0.998
		High	$C_S/C_A = 0.294\ C_S + 1.14$	0.998
Pyridine	277	Low	$C_S/C_A = 0.460\ C_S + 0.0153$	1.000
		High	$C_S/C_A = 0.317\ C_S + 1.05$	0.999

* From eqn. 1, C_S/C_A is m^2 ml^{-1}; C_S is μmol ml^{-1}.

TABLE II

ADSORPTION CONSTANTS FROM LANGMUIR ADSORPTION ISOTHERMS (296°K)

Solute and concentration region	Constants*		
	N_0	$\mathring{A}^2$	K
Pyridine, low	1.9	87	$3.6 \cdot 10^3$
n-Butylamine, low	2.0	83	$1.4 \cdot 10^4$
Pyridine, high	3.4	49	$2.6 \cdot 10^2$
n-Butylamine, high	2.6	64	$2.1 \cdot 10^3$

* From eqn. 1: N_0 = monolayer capacity (μmol m^{-2}); $\mathring{A}^2$ = surface area required for adsorption of one molecule of solute; K = equilibrium constant of adsorption (l mol^{-1}).

low concentration regions for both compounds result in surface coverages of 1.9–2.0 μmol m^{-2} or 87–83 $\mathring{A}^2$ per molecule. It is difficult to compare this data with other magnesium silicates because of differences in Brönsted surface acidity caused by magnesium oxide content, method of preparation, and aging time[15–17]. However, this is comparable with the concentration of Brönsted acid sites, 1.45–1.93 μmol m^{-2} or 110–86 $\mathring{A}^2$ per acid site, reported for magnesium silicates containing 10–20% magnesium oxide[16]. (Florisil is listed by the manufacturer to contain ca. 16% magnesium oxide[28].)

Adsorption at high surface coverage

In contrast to what may be strongly localized adsorption onto surface protons in the low concentration regions, the higher concentration regions may represent final formation of a monolayer of adsorbed molecules. From the Langmuir isotherm for pyridine, this results in final surface coverage of 3.4 μmol m^{-2} and an apparent molecular area of 49 $\mathring{A}^2$. This is identical to the apparent molecular area reported for liquid-phase adsorption of pyridine on alumina[20]. However, for n-butylamine, the Langmuir isotherm indicates a final monolayer coverage of 2.6 μmol m^{-2} and an apparent molecular area of 64 $\mathring{A}^2$. This value is identical to the apparent molecular area reported for liquid-phase adsorption of n-butylamine on silica gel[29]. [A similar value (67 $\mathring{A}^2$) has been reported for adsorption of n-butanol on silica[8].] However, this apparent molecular area (64 $\mathring{A}^2$) is significantly greater than expected from liquid density (ca. 34 $\mathring{A}^2$) and that observed for adsorption of diethylamine onto alumina (34 $\mathring{A}^2$)[5].

The large difference between apparent molecular area of n-butylamine on Florisil and that for diethylamine on alumina[5] may be the result of additional localization of n-butylamine on surface silanols[29]. That is, after strong localization onto strongly acidic exchangeable surface protons (pK_a 1.5[14]), n-butylamine also may be chemically adsorbed by less acidic silanol protons (pK_a 6–8[35] or 10[36]). After this further localization onto silanol protons, alignment and steric effects might restrict access to the remaining surface, thus resulting in the large apparent molecular area. (See refs. 1 and 5 for analogous discussions of·localization and delocalization with silica gel and alumina). This "two-site localization" may also account for the difference (0.8 μmol m^{-2}) in final surface coverage by pyridine and n-butylamine on Florisil. That is, pyridine may not be chemisorbed by the weaker silanol protons and thus is able to

cover more completely the surface through a weaker, more physical type of interaction. This is supported by experiments showing that pyridine only (physically) adsorbs by hydrogen bonding to surface silanols and does not chemisorb by proton-transfer[30-33]. In contrast, isolated silanol protons have been shown to protonate and, thus, chemically adsorb n-butylamine[34]. Though the chemistry supports this interpretation, it should be noted that another possible reason for the smaller monolayer capacity for n-butylamine compared with pyridine only may be physical differences in surface packing. For instance, liquid densities give molecular areas of ca. 34 Å^2 for both compounds. However, apparent molecular areas on adsorption have been shown to be frequently in excess of those calculated from liquid densities[37]. This may be the result, for instance, of more open packing in the adsorbed phase caused by thermal agitation and mutual repulsion[21].

CONCLUSIONS

At low surface coverage, pyridine and n-butylamine appear to be adsorbed on Florisil as specifically localized solutes, possibly chemisorbed on exchangeable surface protons. The strongly localized adsorption would be occurring on discrete active sites (1.9–2.0 μmol m^{-2}) which, for pyridine, are characterized by a greater enthalpy of adsorption than at higher surface coverages. According to the Langmuir isotherms, a monolayer of adsorbed molecules ultimately occurs at final surface coverage. The monolayer capacity of Florisil for pyridine resulted in an apparent molecular area of 49 Å^2. For n-butylamine, the apparent molecular area of 64 Å^2 may be caused by additional localization onto surface silanol protons.

In contrast with Florisil, localization on (pure) silica theoretically should be limited more by alignment and steric effects than the presence of strongly acidic adsorptive sites[1,5]. However, "two-phased" adsorption curves as seen here for adsorption of pyridine on Florisil might be comparable with those with silica gel if the silica gel had different strengths of adsorptive protonic sites. Chemisorptive localization would not be expected for silanol protons on pure silica gel (Cabosil) since such protons only have been shown to exhibit uniform hydrogen bonding toward such compounds as pyridine[38]. However, chromatographic grade silicas may contain metallic oxide impurities. Thus, as Florisil, such silicas may possess unusual Brönsted acidity in the form of exchangeable surface protons and be able to chemisorb such compounds as pyridine[38]. Because this may result in different mechanisms of adsorption for different silicas, chromatographers may wish to establish a standard grade of silica gel for studying localized interactions in liquid chromatography. This may be useful since silica gel, equilibrium adsorption isotherms, and interpretations about monolayer vs. bilayer formation are frequently used for developing liquid chromatographic theories[1,6-8]. However, over the solution concentration ranges studied here, adsorption of pyridine and n-butylamine on Florisil appeared to result in only monolayer coverage. Therefore, Florisil may be a quite useful model adsorbent for studying strongly localized adsorbate–adsorbent interactions in liquid chromatography, especially for comparison with silica and alumina.

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