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Adsorption of Nonpolar Solutes onto Neutral Polymeric Sorbents

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NOTE

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Abstract

Model nonpolar solutes were chosen to examine adsorption onto neutral polymeric sorbents. When *n*-hexane was used as the solvent, hydrogen bonding appeared to play a predominant role in adsorption. Hydrogen bonds were

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presumably established between the carboxylic ester groups of the sorbent and either the −OH or −NH groups of the solutes. These results suggest that the specificity of hydrogen bonding can be exploited to selectively adsorb solutes from nonpolar solvents. When water was used as the solvent, adsorption increased with decreasing solute polarity; while hydrogen bonding between the solute and sorbent appeared to be less important. These results suggest that hydrophobic interactions play a major role in adsorption from aqueous solutions, and thus the selectivity of adsorption may be limited by the nonspecific nature of hydrophobic interactions.

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INTRODUCTION

The separation of organics from dilute liquids containing many related compounds is common in the food and pharmaceutical industries. Examples include the recovery and purification of fermentation products and the removal of undesirable compounds from beverages. Because these biochemicals are often nonvolatile and found in low concentrations, traditional chemical engineering separations processes are not applicable for large-scale recovery/removal. Traditionally, solvent extraction and adsorption (carbon-based or ion exchange) have been employed for obtaining crude separations; however, these techniques generally suffer from low selectivities. At the other extreme are affinity based separations systems which are highly selective, but also quite expensive. Due to the need for alternative recovery techniques, considerable efforts have been made to develop separations processes based on supercritical fluid extraction and two-phase aqueous extraction. The authors believe that adsorption by neutral polymeric sorbents may offer some advantages for the recovery of biological molecules.

In previous studies, neutral styrene divinylbenzene and carboxylic ester sorbents were examined for the recovery of indole alkaloids. Initial studies demonstrated that adsorption was superior to extraction for concentrating these compounds from dilute aqueous solutions (*1*), while subsequent studies determined that these sorbents could be used to selectively adsorb specific indole alkaloids from dilute solutions containing several related compounds (*2*).

Although adsorption onto neutral sorbents has been reported to result from weak physical interactions (*3*, *4*), further improvements in selectivities, either through alteration of operating conditions or development of improved sorbents, will require a better fundamental understanding of adsorption mechanisms. The goal of this work was to use model solutes to determine the relative importance of hydrogen bonding and hydrophobic interactions for the adsorption of nonpolar solutes onto these neutral sorbents.

MATERIALS AND METHODS

All solutes (indole, methylindoles, benzene, phenol, and anisole) were obtained from Sigma Chemicals (St. Louis, Missouri). The neutral polymeric sorbents (XAD-4 and XAD-7 resins) were donated by Rohm and Haas (Philadelphia, Pennsylvania). Prior to their use in aqueous solutions, the sorbents were soaked in methanol for at least 24 h and then washed with several volumes of water. For studies in *n*-hexane, the sorbents were washed with *n*-hexane and dried prior to use.

Experiments were conducted by adding accurately weighed amounts of sorbent to a known volume of liquid. For studies with water as the solvent, moist resin was added, and the results are based on a wet resin weight. When *n*-hexane was the solvent, dry resin was added, and the results are reported on a dry resin basis. After adding the sorbent, the samples were equilibrated at 25°C.

Liquid phase solute concentrations were determined using ultraviolet (UV) adsorption, and the adsorbed levels were calculated from

$$q = (C_i - C)V/A \tag{1}$$

where q is the solid phase concentration (mmol/g resin); C_i and C are the initial (before adding the sorbent) and final (equilibrated) liquid phase concentrations (mmol/L), respectively; V is the liquid volume (mL); and A is the amount of resin (mg).

RESULTS AND DISCUSSION

Two major mechanisms for physical adsorption are hydrophobic interactions and hydrogen bonding. To assess the relative importance of these two mechanisms, adsorption studies employing model solutes and sorbents were conducted. Since hydrogen bonding is likely to be important for oxygenated and nitrogenated compounds, the model solutes chosen were related to phenol and indole (Fig. 1). The sorbents chosen for this study were neutral polymeric resins of either a styrene divinylbenzene (XAD-4) or a carboxylic ester structure (XAD-7).

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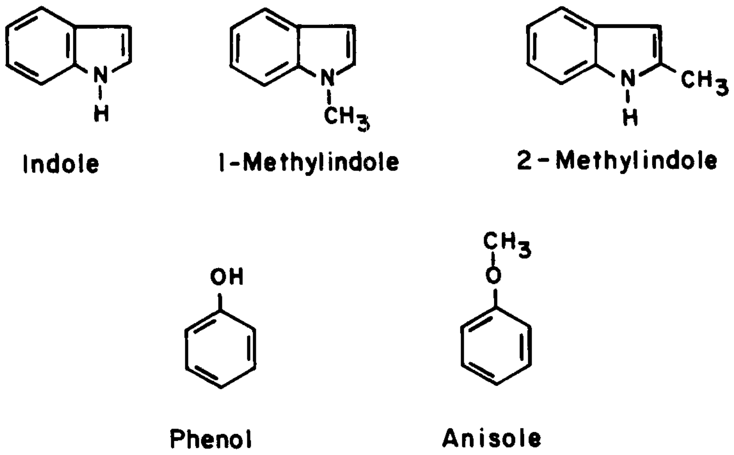

FIG. 1. Structures of model solutes.

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Adsorption from a Nonpolar Solvent

Figures 2 and 3 show the isotherms for the adsorption of the model solutes from *n*-hexane onto the carboxylic ester resin. The only compounds to adsorb were phenol, indole, and 2-methylindole. These solutes are the only compounds of those tested capable of forming hydrogen bonds between the —OH or —NH groups and the ester portions of the resin. This observation suggests hydrogen bonding to be a major mechanism for the sorption of solutes from nonpolar solvents. None of the model solutes adsorbed from hexane onto the styrene divinylbenzene resin (data not shown), which suggests that hydrogen bonding or other interactions with the π-electrons of the aromatic resin were not significant. These results agree with those of Paleos (*5*) who observed that phenol adsorbed onto the carboxylic ester from hexane but not onto the styrene divinylbenzene resin.

The slopes for the isotherms in Figs. 2 and 3 are reported as apparent equilibrium constants in Table 1. This table shows that phenol has a higher affinity for adsorption than the indoles. This greater affinity could be due to the larger electronegativity of oxygen which would be expected to enhance adsorption through hydrogen bonding mechanisms (*6*).

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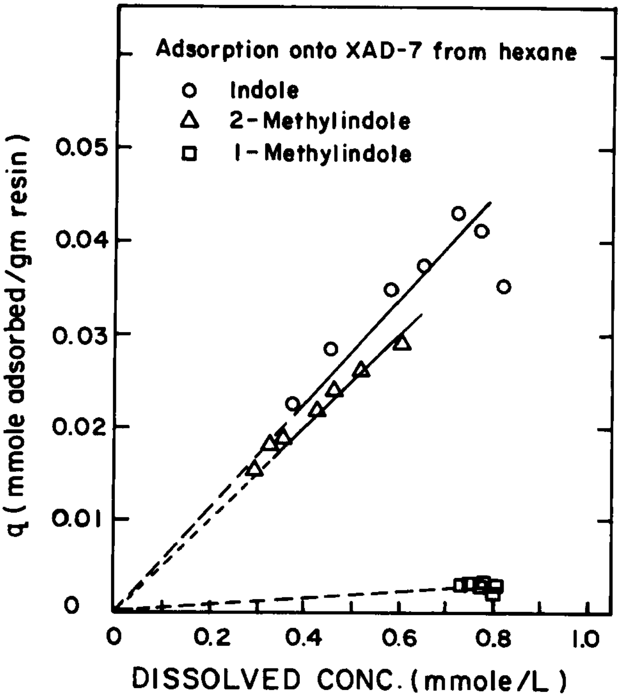

FIG. 2. Adsorption of indole, 1-methylindole, and 2-methylindole from *n*-hexane onto the carboxylic ester (XAD-7) sorbent.

TABLE 1
Apparent Equilibrium Constant for the Adsorption of Solutes from *n*-Hexane onto the Carboxylic Ester Resin (XAD-7).

Solute	Apparent equilibrium constant $\left(\frac{\text{mmol adsorbed/g resin}}{\text{mmol dissolved/L}}\right)^a$
Phenol	0.3
Indole	0.04
2-Methylindole	0.04

[a] Adsorbed concentrations are based on dry resin weight.

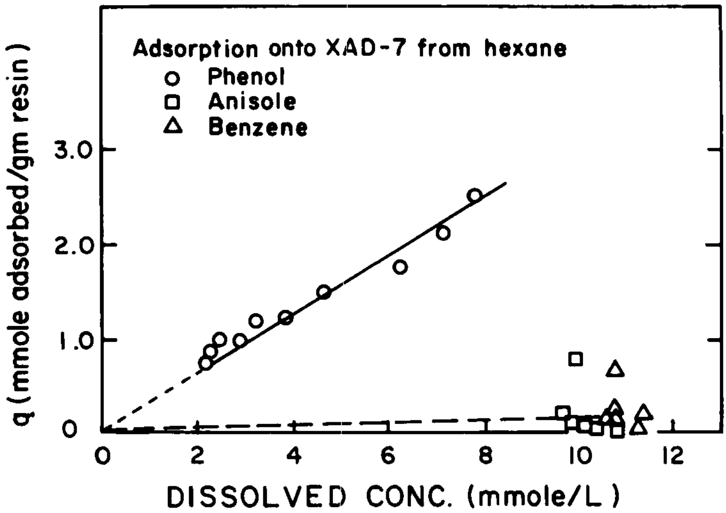

FIG. 3. Adsorption of phenol, anisole, and benzene from *n*-hexane onto the carboxylic ester (XAD-7) sorbent.

Adsorption from Aqueous Solution

Isotherms for the adsorption of these model solutes from aqueous solution are shown in Figs. 4 and 5. These figures show that the more hydrophobic styrene divinylbenzene resin, XAD-4, adsorbs more of these solutes on a mass basis. However, because of the larger surface area of the XAD-4 sorbent (*4*, *5*), adsorption per unit surface area was comparable for both types of sorbents. Paleos (*5*) also observed that adsorption per unit surface area was similar for these two sorbents.

The observation that 1-methylindole adsorbed at least as well as 2-methylindole (Fig. 4), and that anisole adsorbed better than phenol (Fig. 5), suggests that hydrogen bonding between the sorbents and the −OH or −NH groups of the solutes does not play a major role in the adsorption of these solutes from aqueous solution. The limited importance of hydrogen bonding mechanisms between the solutes and the sorbents in aqueous solution may be due to the strong hydrogen bonding characteristics of water (*7*).

Figures 4 and 5 show that the addition of methyl groups to the phenol and indole structures leads to enhanced adsorption from aqueous solution (i.e., anisole adsorbs better than phenol while the methylindoles adsorb better than indole). This result supports the suggestion that

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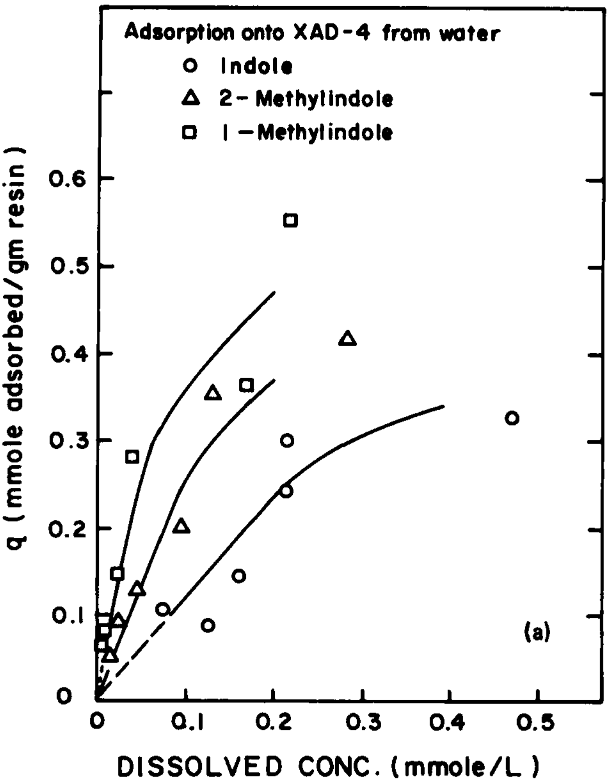

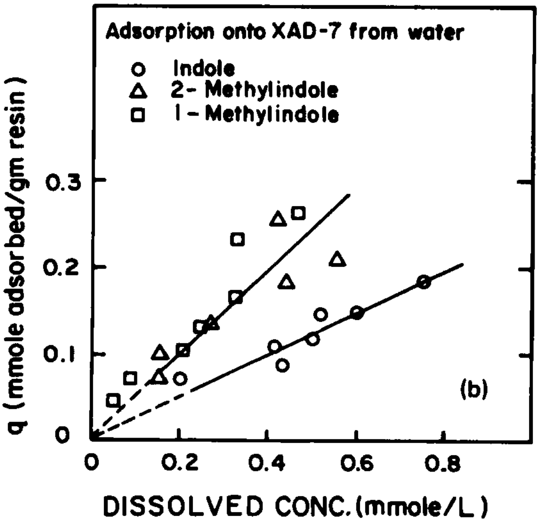

FIG. 4. Adsorption of indole, 1-methylindole, and 2-methylindole from aqueous solution onto the styrene divinylbenzene (XAD-4) (a), and carboxylic ester (XAD-7) (b) sorbents.

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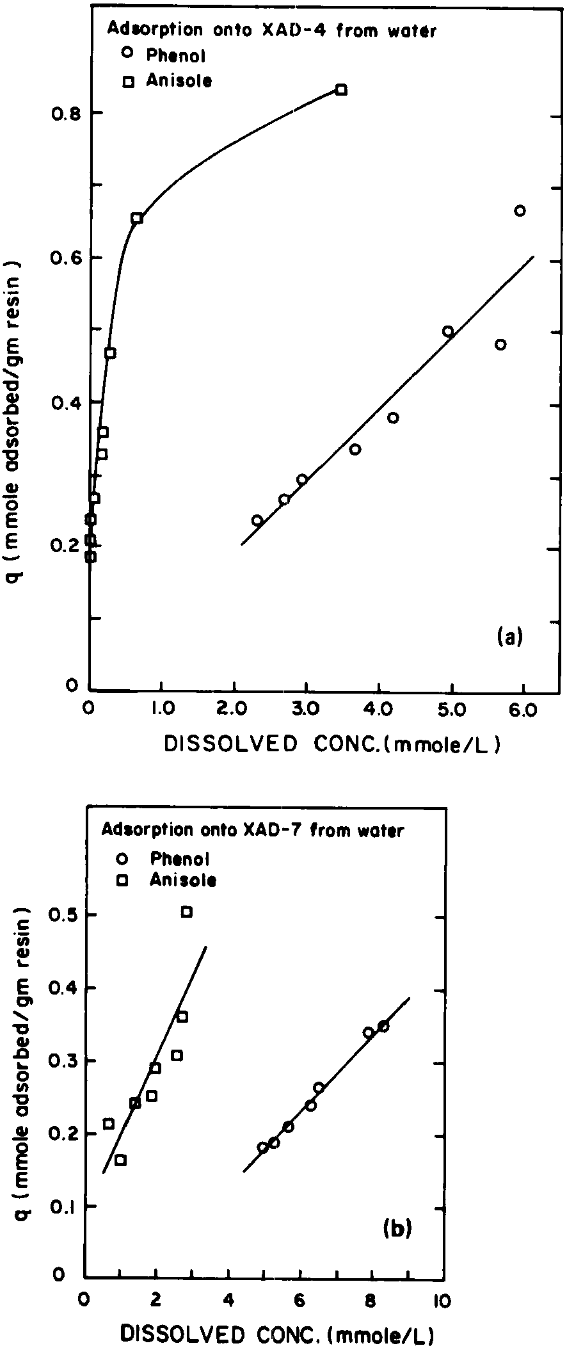

FIG. 5. Adsorption of phenol and anisole from aqueous solution onto the styrene divinylbenzene (XAD-4) (a), and carboxylic ester (XAD-7) (b) sorbents.

adsorption from aqueous solution onto these resins is due to hydrophobic interactions (*3–5*, *8*).

CONCLUSIONS

The first conclusion from this work is that from a nonpolar solvent (i.e., *n*-hexane), hydrogen bonding between the solute and the sorbent appears to be important for adsorption. Due to the specificity, it may be possible to exploit hydrogen bonding to achieve high separation factors for the selective adsorption of solutes from complex mixtures.

The second conclusion from these studies is that nonpolar solutes are adsorbed from aqueous solution onto these neutral sorbents by hydrophobic interactions. This conclusion is in agreement with those of previous workers (*3–5*, *8*). However, our data also suggest that hydrogen bonding between the solute and sorbent does not play an important part in adsorption from aqueous solution. Because of the limited specificity of hydrophobic interactions, this result suggests that separation factors for the adsorption of solutes from aqueous solutions may be limited by the polarity differences of the solutes.

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