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Gregory F. Payne[a]; Yuko Ninomiya[b]
[a] DEPARTMENT OF CHEMICAL AND BIOCHEMICAL ENGINEERING, CENTER OF AGRICULTURAL BIOTECHNOLOGY UNIVERSITY OF MARYLAND—BALTIMORE COUNTY, BALTIMORE, MARYLAND [b] DEPARTMENT OF CHEMICAL AND BIOCHEMICAL ENGINEERING, UNIVERSITY OF MARYLAND—BALTIMORE COUNTY, BALTIMORE, MARYLAND

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Selective Adsorption of Solutes Based on Hydrogen Bonding

GREGORY F. PAYNE

DEPARTMENT OF CHEMICAL AND BIOCHEMICAL ENGINEERING
CENTER OF AGRICULTURAL BIOTECHNOLOGY
UNIVERSITY OF MARYLAND—BALTIMORE COUNTY
BALTIMORE, MARYLAND 21228

YUKO NINOMIYA

DEPARTMENT OF CHEMICAL AND BIOCHEMICAL ENGINEERING
UNIVERSITY OF MARYLAND—BALTIMORE COUNTY
BALTIMORE, MARYLAND 21228

Abstract

Current evidence suggests that adsorption of solutes from a nonpolar solvent onto a polycarboxylic ester sorbent involves the formation of a hydrogen bond. This bond appears to be formed between a hydrogen atom of the solute and the carbonyl group of the sorbent. From studies involving single solutes it was observed that the primary amine aniline adsorbed nearly twice as much as the secondary amine *N*-methylaniline. The tertiary amine *N,N*-dimethylaniline, which does not contain a nitrogen-bonded hydrogen atom, was unable to bind to the sorbent. In studies involving mixtures, solutes were observed to be selectively adsorbed based on their hydrogen bonding abilities. A simple thermodynamic model which was developed to explain this adsorption was capable of accurately predicting separation factors for the selective adsorption of solutes from solute mixtures.

INTRODUCTION

Adsorption is a low energy separations technique which is becoming more widely used for bulk liquid separations (*1–4*). However, the development of liquid-phase adsorptive processes is plagued by two major problems. First, our current understanding of solid–liquid equilibria is insufficient to permit the accurate prediction of multicomponent adsorption. Despite recent advances (*5–7*), our ability to accurately describe the behavior of condensed phases (either solid or liquid) is limited. In addition, typical sorbents (e.g., activated carbon) have heterogeneous surfaces, and

adsorption can involve a number of different types of binding mechanisms and a range of adsorption energies (*8*, *9*). As a result of our limited theoretical understanding of adsorption, the development of improved sorbents or the design of large-scale adsorption systems requires considerable experimental study and empirical correlation.

A second problem with adsorption-based separations is that separation factors are often low. Although common in many separation areas, low separation factors are particularly troublesome for adsorption-based systems because of the difficulties in the countercurrent contacting of a solid phase. Thus most adsorption-based systems are operated batchwise and operational flexibility is quite limited. When the goal is to remove solutes from a solvent, then a sorbent with a high affinity for the solutes is often used in a fixed bed mode. In this case, solutes of similar polarity are often adsorbed indiscriminately. Thus, although offering high adsorptive capacities, there is little capability for isolating individual solutes from a mixture. On the other hand, when the goal is to isolate an individual solute from a mixture of solutes, then it is necessary either to use multiple equilibrium stages or to develop sorbents with high selectivities. The approach of using multiple staged contacting to isolate a single solute from a mixture of solutes is best illustrated by chromatographic separations. Despite the ability to isolate solutes from complex mixtures, chromatographic separation techniques often have low capacities. It should be noted that large-scale systems which simulate countercurrent contacting have recently been employed commercially for bulk liquid separations (*1*, *2*). However, if sorbents can be developed which offer higher adsorptive selectivities, then the requirements for, and difficulties associated with multistaged contacting will be reduced.

Over the past twenty years polymer-based adsorbents have become available (*10–13*). The often cited advantages of these sorbents is that they have well controlled physical properties such as particle size and pore size distribution. However, the capability of using the well-defined chemical structure of the polymeric backbone to enhance sorption selectivities has not been fully exploited. In our work we are investigating the use of sorbents which appear to bind solutes through only a single type of mechanistic interaction. Thus these sorbents selectively adsorb only those solutes which can bind through this single mechanism. Initial studies (*14*) identified that hydrogen bonding appears to be the sole mechanism responsible for the binding of model solutes from a nonpolar solvent onto a polycarboxylic ester sorbent. Here we report that this sorbent can be used to selectively adsorb solutes based on their ability to form a hydrogen bond with the sorbent. In addition, simple thermodynamic expressions were observed to be capable of explaining the adsorption of individual solutes as well as

being capable of predicting separation factors for the adsorption of solutes from mixtures.

MATERIALS AND METHODS

The polycarboxylic ester sorbent, XAD-7, was donated by Rohm and Haas. Prior to use, this sorbent was soaked and thoroughly washed with methanol, and residual methanol was evaporated by heating in a vacuum oven.

As previously described (*14*), experiments were conducted by adding accurately weighed sorbent to hexane solutions containing either a single solute or a solute mixture. After equilibration, samples were removed and liquid-phase concentrations were determined. For single solutes studies, UV absorption was used to measure dissolved concentrations. Absorption for aniline, *N*-methylaniline, and *N,N*-dimethylaniline were measured at 288, 294, and 298 nm, respectively. When solute mixtures were studied, gas chromatography was used to measure liquid concentrations. A Hewlett-Packard (model 5880) chromatograph was used with a HP-SE30 column at 67°C.

Adsorbed concentrations were calculated from

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

where q is the adsorbed concentration, C_i and C are the dissolved solute concentrations prior to and after adsorption, V is the liquid volume, and A is the mass of sorbent.

THERMODYNAMIC DESCRIPTION

Adsorption of the Tertiary Amine *N,N*-Dimethylaniline

Previous results (*14*) suggest that hydrogen bonding is the major mechanism for the adsorption of solutes from nonpolar solvents onto the polycarboxylic ester sorbent. Since we believe the carbonyl group of the sorbent is the hydrogen accepting group, and since a tertiary amine does not contain a hydrogen donating group, then the tertiary amine, *N,N*-dimethylaniline, is not expected to adsorb.

Adsorption of the Secondary Amine *N*-Methylaniline

Using a typical Langmuir approach, the adsorption of a secondary amine (RR'NH) via a hydrogen bond can be represented by the reaction

$$RR'NH + O{=}C{-}A \leftrightarrow RR'NH{---}O{=}C{-}A \tag{2}$$

where O=C– represents the carbonyl group, or hydrogen bonding site of the sorbent. It should be noted that this approach differs from treatments in which adsorption is viewed as an exchange process where the solute replaces a previously adsorbed solvent molecule. We believe this approach is justified in this case because it is unlikely that the solvent hexane can hydrogen bond to this carbonyl site. Assuming equilibrium, then the standard free energy change (ΔG°) for Reaction (2) is given by

$$\Delta G^\circ = -RT \ln K \tag{3}$$

The equilibrium constant, K, can be represented as

$$K = \frac{a_{RA}}{a_R a_A} \tag{4}$$

where the activities (a) can be related to the mole fractions (X) and activity coefficients (γ) of the various species by

$$a = \gamma X \tag{5}$$

By rearranging the above equations, it can be seen that

$$\frac{X_{RA}}{X_R} = \frac{\gamma_R \gamma_A X_A}{\gamma_{RA}} e^{-\Delta G^\circ/RT} \tag{6}$$

Combining the above equation with the thermodynamic relationship

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{7}$$

it can be seen that

$$\frac{X_{RA}}{X_R} = \left(\frac{\gamma_R \gamma_A X_A}{\gamma_{RA}}\right)(e^{\Delta S^\circ/R})e^{-\Delta H^\circ/RT} \tag{8}$$

If the liquid- and solid-phase concentrations are sufficiently dilute with respect to the solute (in this case the secondary amine), then the first term on the right-hand side of Eq. (8) will be constant. It should be noted that this assumption is valid only in the linear region of the adsorption isotherm where the number of sorption sites which are occupied is so small relative to the total number of sites that X_A is essentially unchanged by the adsorption. Further, if the standard entropy change of adsorption is constant,

then the second term on the right-hand side would also be constant. Finally, if data are presented with respect to absolute concentrations and not mole fractions, then the above equation can be simplified, and the adsorption of the secondary amine can be described by

$$(q/C)_{SEC} = \kappa e^{-\Delta H^{\circ}/RT} \tag{9}$$

where q and C are the solid- and liquid-phase solute concentrations in mmol adsorbed/g sorbent and mmol dissolved/L, respectively. If the above assumptions are valid, then κ in Eq. (9) is expected to be constant.

Adsorption of the Primary Amine Aniline

To develop an equation to describe the adsorption of a primary amine, certain assumptions are required. In our case we believe the following assumptions are most reasonable and best supported by the data which will be presented. These assumptions are:

1. Only a single (and not both) nitrogen-bonded hydrogen atom is responsible for adsorption via hydrogen bonding.
2. Each nitrogen-bonded hydrogen atom is equally capable of hydrogen bonding such that either of the following reactions can lead to adsorption:

$$HN(R)H^* + O{=}C{-}A \leftrightarrow HN(R)H^*{---}O{=}C{-}A \tag{10a}$$

$$HN(R)H^* + O{=}C{-}A \leftrightarrow A-C{=}O{---}HN(R)H^* \tag{10b}$$

where the asterisk is used to distinguish between the two possible hydrogen atoms.

With these two assumptions, our physical understanding of how the primary amine aniline is absorbed onto the polycarboxylic ester sorbent is illustrated in Fig. 1.

To test these assumptions, we compared the adsorption of the primary amine aniline and the secondary amine *N*-methylaniline. For our comparisons we made one further assumption—that the activity coefficients and entropy change for the adsorption of aniline and *N*-methylaniline are similar. If this latter assumption is valid, then the differences between the adsorption of these two solutes would be due solely to the fact that the primary amine has two possible adsorption reactions (Reactions 10a and 10b) while the secondary amine has only one adsorption reaction (Reaction

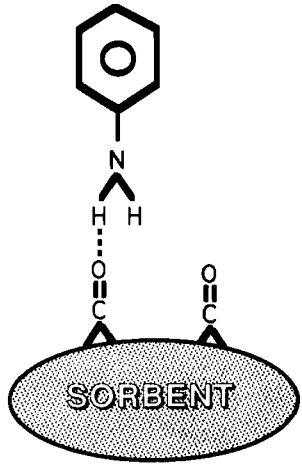

FIG. 1. Postulated mechanism for aniline adsorption from a nonpolar solvent onto the polycarboxylic ester sorbent.

2). Thus the adsorption equilibrium for this primary amine should be given by

$$(q/C)_{PRI} = 2\kappa e^{-\Delta H'/RT} \quad (11)$$

where the κ in the above equation is identical to that in Eq. (9). Also, if the enthalpy change for the formation of a single hydrogen bond is only slightly dependent on contributions made by the *N*-methyl group, then the enthalpy change for the adsorption of *N*-methylaniline should be similar to that for the adsorption of aniline. This follows from the first assumption that only a single hydrogen bond is responsible for the adsorption of both aniline and *N*-methylaniline.

Selective Adsorption from Mixtures

The previous thermodynamic treatment, which was used to explain the adsorption of the individual solutes, was applied directly to explain the selectivity of solute adsorption from solute mixtures. It is assumed that the adsorption of individual solutes is unaffected by the presence of other solutes in either the solid or liquid phases. This latter assumption is most reasonable under conditions in which the solute concentration in both phases is very small. With these assumptions, the separation factor (α) for

the selective adsorption of aniline from a mixture containing both aniline and *N*-methylaniline can be predicted from Eq. (11) and (9) to be

$$\alpha = \frac{(q/C)_{PRI}}{(q/C)_{SEC}} = 2 \tag{12}$$

Since *N,N*-dimethylaniline should be unable to adsorb onto the polycarboxylic ester sorbent, then separation factors for the selective adsorption of either aniline or *N*-methylaniline from a mixture containing *N,N*-dimethylaniline should be infinite.

RESULTS AND DISCUSSION

Adsorption of Individual Solutes

Initial adsorption studies were conducted by adding the polycarboxylic ester sorbent to hexane solutions containing a single solute (either *N,N*-dimethylaniline, *N*-methylaniline, or aniline). The adsorption isotherms for these studies are shown in Fig. 2. As expected, aniline adsorbed better than *N*-methylaniline, while no adsorption of *N,N*-dimethylaniline was observed.

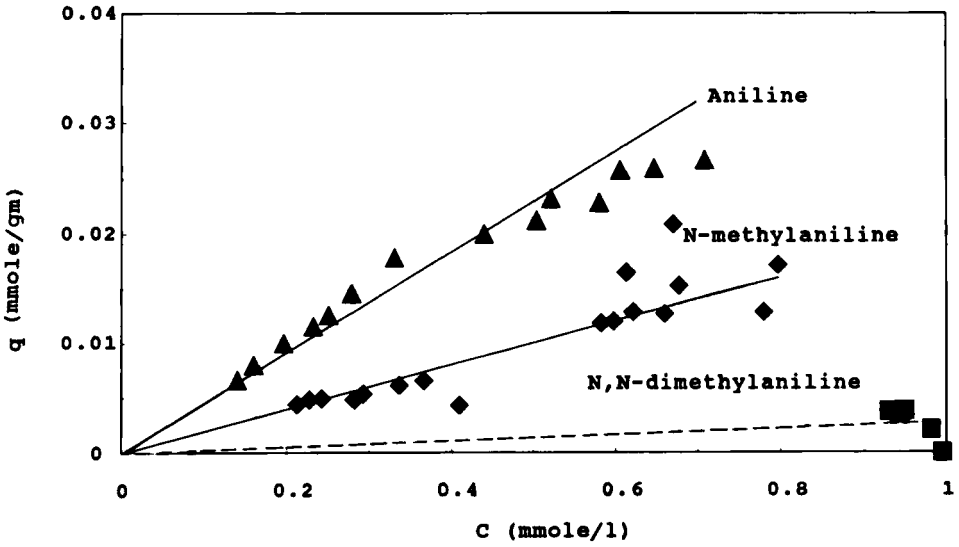

FIG. 2. Adsorption isotherms for individual solutes from hexane solutions.

The average values of q/C for the adsorption of aniline and *N*-methylaniline were 0.046 and 0.020 (mmol adsorbed/g)/(mmol dissolved/L), respectively. If our thermodynamic description of adsorption is correct, then Eqs. (9) and (11) predict that the ratio q/C for aniline adsorption would be 2.0 times that for the adsorption of *N*-methylaniline. This compares to the observed value of 2.3. Despite the quantitative similarity, it is important to recognize that there are two terms (κ and $\Delta H°$) in Eqs. (9) and (11) which are assumed to be the same for the adsorption of aniline and *N*-methylaniline. Before concluding that our thermodynamic description is consistent with experimental observations, we attempted to independently determine the similarity of one of these constants for the adsorption of each of the solutes.

Temperature Dependence of Adsorption

By examining the temperature dependence of the adsorption equilibria, it is possible to estimate the adsorption enthalpy ($\Delta H°$). If κ in Eq. (9) remains constant over a given temperature range, then a semilogarithmic plot of q/C vs $1/T$ should yield a straight line with the slope proportional to the enthalphy change for adsorption. Figure 3 shows such van't Hoff plots for the adsorption of aniline and *N*-methylaniline. From the slopes in Fig. 3, it can be seen that adsorption is exothermic with an enthalpy change calculated to be -4.8 and -4.3 kcal/mol for the adsorption of

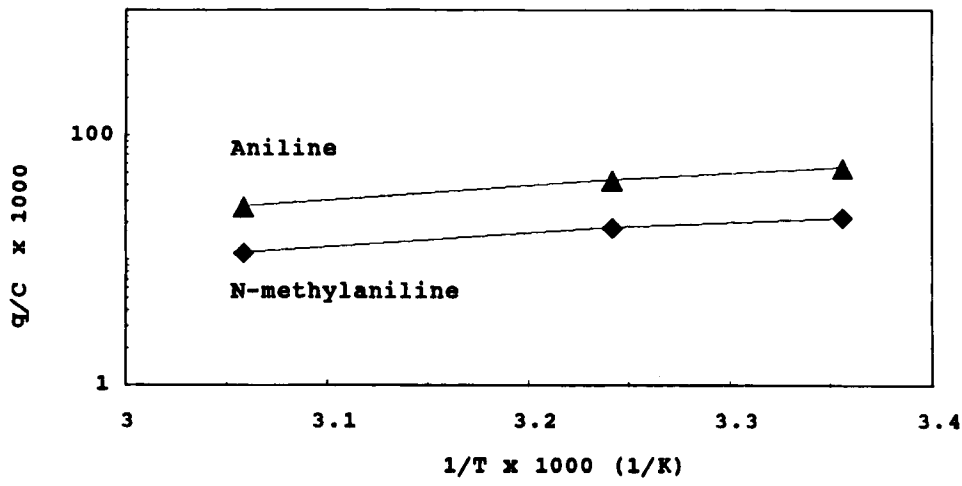

FIG. 3. Van't Hoff plots for the temperature dependence of adsorption equilibria.

aniline and *N*-methylaniline, respectively. The magnitude of these enthalpy changes is consistent with those reported for hydrogen bonding (*15*, *16*). Further, the similarity of the enthalpy changes strongly suggest that the adsorption of *N*-methylaniline and aniline involve the same number of hydrogen bonds. This result supports our assumption that aniline adsorption involves only a single hydrogen bond as illustrated in Fig. 1. Finally, as can be seen from the data in Table 1, the ratio of q/C for aniline adsorption is calculated to be between 2.2 and 2.5 times greater than that for the adsorption of *N*-methylaniline. Again these values compare to the predicted value of 2.0. In summary, these results support our assumptions that ΔH° for the adsorption of *N*-methylaniline and aniline are similar; and that differences in the adsorption of these amines reflect differences in the number of nitrogen-bonded hydrogen atoms available for binding.

Selective Adsorption from Mixtures

From the previous results it appears that the polycarboxylic ester sorbent could be used to selectively adsorb solutes from multicomponent mixtures. To study the selectivity of adsorption, we examine three separate mixtures, each containing two solutes in hexane. In the first case we tested mixtures containing one solute which can hydrogen bond and another solute which cannot hydrogen bond. Figure 4(a) and 4(b) show these results for mixtures containing either aniline and *N,N*-dimethylaniline, or *N*-methylaniline and *N,N*-dimethylaniline. As expected, those solutes which were capable of hydrogen bonding (i.e., aniline and *N*-methylaniline) adsorbed while *N,N*-dimethylaniline did not adsorb. Due to the limited sensitivity of our analytical techniques, no attempt was made to estimate the large separation factors observed in these studies.

We also examined the selective adsorption from a mixture containing two solutes which were both capable of hydrogen bonding, but with dif-

TABLE 1

Comparison of the Adsorption of Aniline and *N*-Methylaniline from Hexane onto the Polycarboxylic Ester Sorbent (XAD-7)

	q/C [(mmol/g)/(mmol/L)]	
T (°C)	Aniline	*N*-Methylaniline
25	0.055	0.022
35	0.044	0.018
54	0.027	0.012

fering affinities. This experiment was conducted with a mixture containing aniline and *N*-methylaniline, and the results are shown in Fig. 4(c). As expected, both solutes were adsorbed but aniline was preferentially adsorbed onto the sorbent. An average separation factor for these experiments was determined to be 2.6, which compares to a value 2.0 predicted from Eq. (12).

Comparison of Observed and Predicted Adsorption Equilibrium

The similarity between the observed and predicted separation factors suggests that the thermodynamic description developed in this work is consistent with the actual adsorption process. However, there were small differences between predicted and observed adsorption equilibria. For instance, in all cases studied (e.g., in single solute or multicomponent studies) it was observed that aniline adsorbed 2.1 to 2.6 times more than *N*-methylaniline. These observed values are slightly more than the predicted value of 2.0. It is possible that this discrepancy is due to a small difference in the enthalpy of adsorption between aniline and *N*-methylaniline. In our thermodynamic treatment we have assumed that the enthalpy changes for aniline and *N*-methylaniline adsorption are identical. To account for a 30% discrepancy in the separation factor between the theoretical and observed

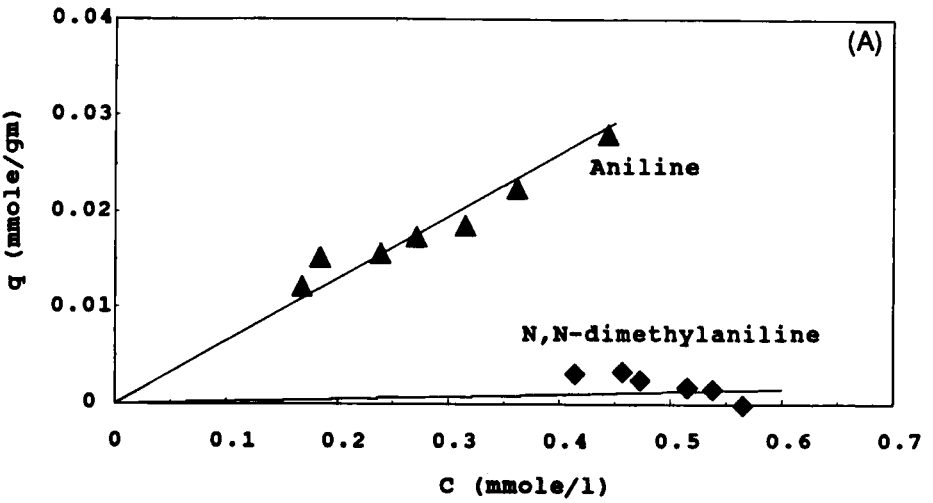

FIG. 4. Selective adsorption of solutes from hexane solutions containing a mixture of two solutes. Solute mixtures studied were (a) aniline and *N,N*-dimethylaniline, (b) *N*-methylaniline and *N,N*-dimethylaniline, and (c) aniline and *N*-methylaniline.

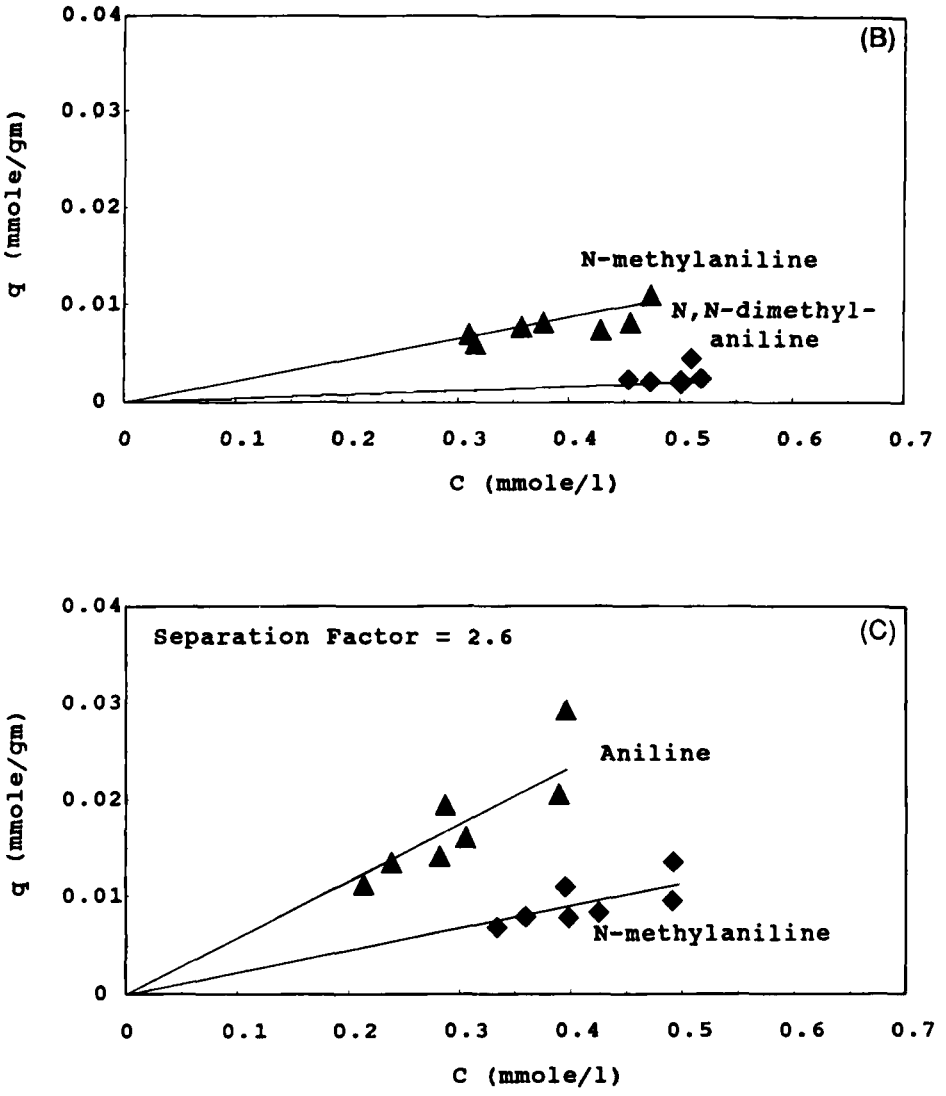

FIG. 4 (*continued*).

values, the adsorption of aniline would only need to be about 0.16 kcal/mol more exothermic than the adsorption of *N*-methylaniline. Clearly the van't Hoff method which was used to estimate ΔH° is unable to detect such small differences. On the other hand, the sensitivity of the separation factor to such small differences in ΔH° suggests that the enthalpy change

for the adsorption of aniline must be very similar to that for *N*-methylaniline adsorption. Such a similarity in the enthalpies would support our assumption that aniline is adsorbed through the formation of a single (and not two) hydrogen bond.

It is also possible that the small discrepancies in the predicted and observed adsorption equilibria could be due to differences in the value of κ between Eqs. (9) and (11). Clearly the assumptions that the standard entrophy change for adsorption and both liquid- and solid-phase activity coefficients are identical for aniline and *N*-methylaniline are rather large assumptions which have not been experimentally verified.

CONCLUSIONS

In this work we observed that solutes could be selectively adsorbed onto a neutral polycarboxylic ester sorbent based on their ability to form a hydrogen bond. This result is significant because hydrogen bonding is one of the few low energy, yet highly specific mechanisms which can be exploited for separations. By exploiting this mechanism it is possible to obtain very high separation factors for selectively adsorbing a solute which can hydrogen bond from a mixture of solutes which are unable to hydrogen bond. When a mixture contains several solutes which are capable of hydrogen bonding, our results indicate that the separation factor for selective adsorption depends on the hydrogen bonding abilities of the individual solutes. It should be noted, however, that to exploit the specificity of the hydrogen bonding mechanism, it is essential that the sorbent be capable of binding solutes only through this single mechanism. Neutral polymers with well-defined chemical properties have provided such sorbents. It should also be noted that we have not yet considered solvent effects. By using hexane as the solvent, we have avoided complications associated with the formation of hydrogen bonds between the solvent and either the sorbent or the solutes.

The second important result from this work is that because adsorption appears to be based solely on hydrogen bonding, our physical understanding of this adsorption could be readily translated into a quantitative thermodynamic description. This thermodynamic model adequately explained the results for the adsorption of individual solutes. In addition, information on the adsorption of individual solutes could be extrapolated to predict the selective adsorption of solutes from mixtures. Such predictive abilities are invaluable if the knowledge gained in this work is to be applied to other systems.

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