

Adsorption from Aqueous Solution Based on the Synergism between Hydrogen Bonding and Hydrophobic Interactions

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ABSTRACT: The adsorption of aniline, *N*-methyl aniline, and *N,N*-dimethyl aniline on carboxyl resin(D152) in different media, water, ethanol, and hexane have been studied. In water the adsorption affinity of three sorbates on D152 increased with an increasing number of methyl groups on N atoms, which indicated that the adsorption of the three sorbates on D152 was driven by a hydrophobic interaction. But the adsorption enthalpy of the three sorbates exceeded the van der Waals force and was in the range of hydrogen bonding interactions, which indicated that the hydrogen bonding also played an important role. In hexane the adsorption affinity decreased with the increasing number of methyl groups on the N atom, presenting the reverse order to that in water. This fact revealed that the hydrogen bonding played a predominant role for the adsorption in hexane.

In ethanol, there was no adsorption of three sorbates on D152 resin, because both the van der Waals force and the hydrogen bonding interaction between the resin and sorbate were depressed. The hydrogen bonding between resin and sorbates in water was also depressed, but the hydrogen bonding adsorption remained. This result suggested that there might be a synergetic effect between the van der Waals and hydrogen bonding interactions in the adsorption of sorbate on D152 resin in water. The synergetic effect was explained thermodynamically. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 841–845, 2005

Key words: resin; adsorption; adsorption enthalpy; aniline; selectivity

INTRODUCTION

The adsorption resins have been widely used in the separation and purification of mixtures in chemical, food, pharmaceutical, and environment industries.^{1–3} Up to present, almost all of the adsorption applications were carried out in aqueous medium, and the adsorption was mainly driven by the hydrophobic interaction.⁴ The disadvantage of hydrophobic adsorption is its low selectivity, which limits its application. To improve the adsorption selectivity, the adsorption should be based on a single or a small number of highly specific mechanisms. Gregory et al.^{5–8} have studied the hydrogen bonding adsorption and concluded that the hydrogen bonding adsorption possessed high selectivity. However, their studies were all performed in nonaqueous systems (mainly in *n*-hexane), the simple reason for which is that the hydrogen bonding adsorption is fully exhibited in the nonpolar media, while it is strongly depressed in polar media, such as water and ethanol. Although the adsorption in water is mainly driven by the hydrophobic interac-

tion, some researchers have presumed that much of the adsorption in the aqueous medium is due to the formation of hydrogen bonding between the surface of the polymeric sorbent and hydrogen binding group of the sorbates.^{9–12} An example of such studies was the purification of extracts from *Ginkgo biloba* leaves with polymeric sorbents. The authors believed that the adsorption of the ginkgo flavonol glycosides on the polymeric adsorbents was based on the formation of hydrogen bonding between the carbonyl group of the resin and the ginkgo flavonol glycosides. Another example is the adsorption of phenols adsorption on poly(4-vinyl pyridine) resin(PVP) in aqueous solution, and they assumed that the adsorption contributed to the formation of the hydrogen bonding between the sorbent and the sorbate. However, all of them didn't provide evidence for the hydrogen bonding adsorption in aqueous solution. Hydrogen bonding adsorption in aqueous solution had not been studied yet.

In this article, the adsorption of the model compounds aniline, *N*-methyl aniline, and *N,N*-dimethyl aniline in water, ethanol, and hexane have been studied. Here, we confirm that hydrogen bonding was formed between the polymeric sorbent and the sorbates in aqueous solution and explained this fact thermodynamically.

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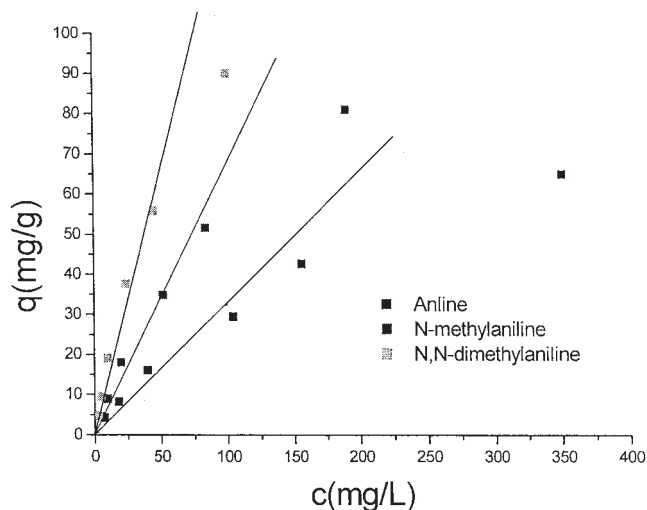


Figure 1 The adsorption isotherms of three anilines on carboxyl resin in water.

EXPERIMENTAL PROCEDURES

Resin

Carboxyl resin(D152) was purchased from Nankai University Chemical Factory (Tianjin, Peoples Republic of China). The properties of D152 resin were as follows: exchange capacity 6.8 mEq/g dry resin; surface area 41.6 m²/g; skeletal density 1.31 g/cm³. Prior to use, the resin was extracted with acetone for 8 h and was columned. The column was washed with 1N NaOH, water, and 1N HCl and, after this, washed with a large amount of water. Finally, the resin was washed with ethanol and *n*-hexane and was air dried for use.

Reagents

Aniline, *N*-methyl aniline, and *N,N*-dimethyl aniline were analytical grade and were purified by distillation before use. Ethanol and *n*-hexane were analytical grade.

Adsorption

In all the adsorption equilibrium studies for individual solutes, a certain amount of the D152 resin was vigorously shaken with a certain volume of sorbate solutions in tightly stoppered flasks for at least 10 h. A range of concentrations was employed for each sorbate. The concentrations of initial and residual sorbates were measured with a UV spectrophotometer (Shanghai No.3 Analytical Apparatus Factory, Shanghai, China) The sorbates adsorbed on the resins were calculated from following equation:

$$q = (C_0 - C)V/M$$

where q is the adsorption capacity(mg/g dry adsorbent), C_0 and C are the initial and final solute concentrations(mg/L), V is the volume of sorbate solution(L), and M is the mass of the dry adsorbent(g). All the equilibrium adsorption studies were confined to low solute concentration regions so that the adsorbed amounts varied as linearly as possible with the equilibrium solute concentrations. The adsorption affinity of the solute (q/C) was determined as the ratio of the adsorbed to the dissolved solute concentrations and was identical to the slopes of the adsorption isotherms.

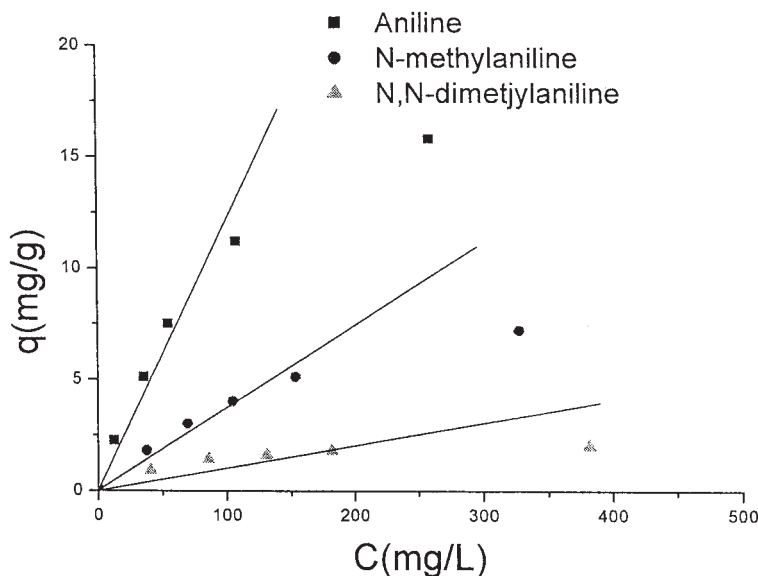


Figure 2 The adsorption isotherms of three anilines on carboxyl resin in hexane.

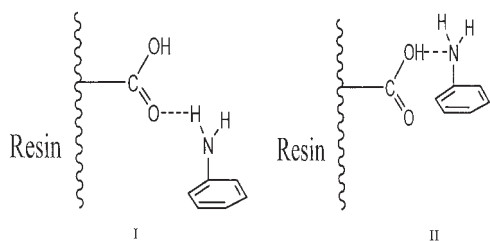


Figure 3 The possible ways of hydrogen bonding to occur between the D152 resin and aniline in hexane.

Adsorption enthalpy

The adsorption enthalpies for three compounds were measured using the van't Hoff method. In this method the temperature dependence of the adsorption equilibrium can be related to the adsorption enthalpy. The thermodynamic relationship for the calculation of adsorption enthalpy is:¹³⁻¹⁵

$$\ln(q/c) = -\Delta H^{\circ}/RT + [\Delta S^{\circ}/R - \ln \Psi]$$

where R is the universal gas constant, T is the absolute temperature (K), ΔH° and ΔS° are the standard enthalpy and entropy, and ψ is the proportionality constant. By confining our studies to low solute concentrations, ΔH° , ΔS° , and ψ remain constant. The plot of $\ln(q/c)$ versus $1/T$ should yield a straight line with a slope of $-\Delta H^{\circ}/RT$, and ΔH° thus was obtained.

RESULTS AND DISCUSSION

The adsorption isotherm is obtained by plotting the adsorption capacity (q) versus the equilibrium sorbate

concentration (c). The adsorption isotherms of aniline, *N*-methyl aniline, and *N,N*-dimethyl aniline on carboxyl resin in water and *n*-hexane are shown in Figures 1 and 2. It can be seen from Figure 1 that the adsorption affinity of aniline, which has no nitrogen-bonded methyl group, was the lowest; the *N*-methyl aniline, which has one nitrogen-bonded methyl group, was intermediate; while the *N,N*-dimethyl aniline, which contains two methyl groups, was the highest. On the contrary, the adsorption affinities in hexane for the three aromatics were in the reverse order (Fig. 2). These reflected the different adsorption mechanisms in different media. The adsorption of the three aromatics in water may be attributed mainly to hydrophobic interaction between them and the resin, because their adsorption affinities in water increased with the increasing numbers of hydrophobic methyl groups. The adsorption in hexane may be dealt with hydrogen bonding adsorption. Because the hydrophobic adsorption in hexane was thoroughly suppressed, while the hydrogen binding adsorption was fully strengthened.

The formation of hydrogen bondings between the resin and the aromatics in hexane have two possible routes, as shown in Figure 3. The first is the oxygen atoms (proton acceptor) of the carboxyl groups bond to the hydrogen atoms (proton donor) of the amine groups on the sorbates. The second is the hydrogen atom of the carboxyl group on resin hydrogen bonds the nitrogen atom of the sorbates. Aniline, which contains two hydrogen donors on the amino group, was adsorbed with the highest capacity, and *N,N*-dimethyl aniline, which has no hydrogen donor on the amino group, was adsorbed with the lowest capacity. These

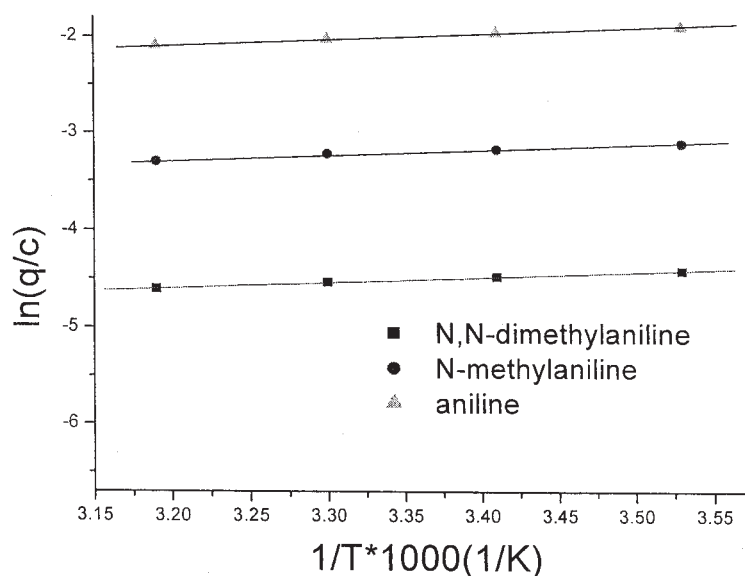


Figure 4 van't Hoff plot for adsorption of three aromatic amines in hexane.

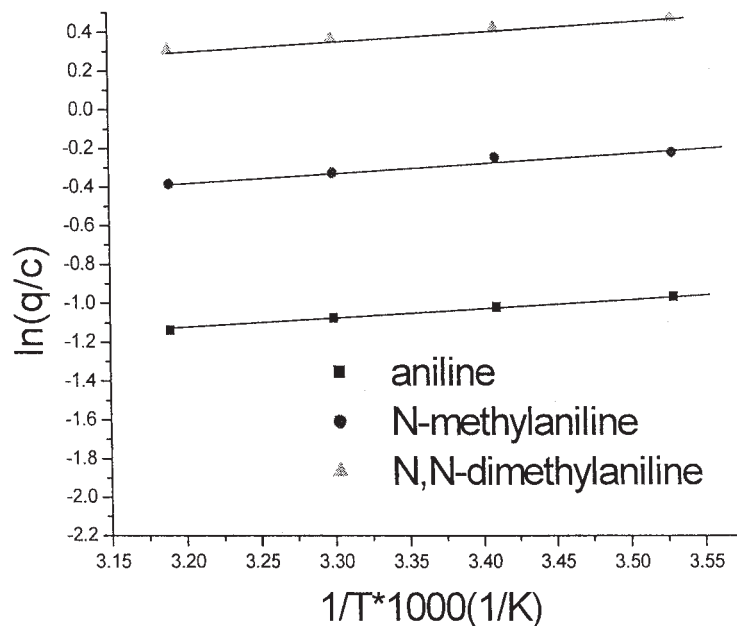


Figure 5 van't Hoff plot for adsorption of three aromatic amines in water.

indicated that the hydrogen bonding between the resin and the sorbates in hexane will be formed as the first route. This was supported by Gregory studies.^{5,7} But if this were the only way for the hydrogen adsorption between the resin and the sorbates in hexane to occur, the *N,N*-dimethyl aniline would have no adsorption in hexane because of the lack of the donor hydrogen. The fact that the *N,N*-dimethyl aniline also had some adsorption implies that the second way equally exists in the adsorption in hexane.

The adsorption capacities of the three aromatic amines in ethanol were nearly zero (data not shown), because both the hydrophobic and hydrogen bonding interactions between the resin and the sorbate are strongly suppressed.

To examine the adsorptions more intensively, the adsorption enthalpies of the model sorbates in water and hexane were evaluated. The adsorption enthalpies have been investigated by researchers to identify the hydrogen bonding adsorption mechanism in nonpolar media,¹³⁻¹⁵ but they have never been reported on an adsorption mechanism study in aqueous solution. Figures 4 and 5 show the plot of $\ln(q/c)$ versus $1/T$ for the adsorption of the three sorbates in water and hexane, respectively. From these plots, we can calculate the adsorption enthalpies (listed in Table I). From the data one can see that the adsorption enthalpies of the three anilines in hexane was in the range of the hydrogen bonding force.^{16,17} This supported the hydrogen bonding adsorption mechanism in hexane. But the adsorption enthalpies in aqueous solution were also in the range of the hydrogen bonding force, which demonstrated that the hydrogen bonding also played an

important role in the adsorption of the three aromatic amines in aqueous solution.

As mentioned above, the adsorption affinity of the three aromatic amines in ethanol were near zero, because both the hydrophobic and the hydrogen bonding interaction between the polymeric sorbent and the sorbates were strongly suppressed in ethanol. But the water also was a hydrogen bonding suppressing agent. Why did the hydrogen bonding adsorption exist, in water but not in ethanol? This question can be easily answered with the synergism between the hydrophobic and hydrogen bonding interactions, as shown in Figure 6. In ethanol because both the hydrophobic and hydrogen bonding interaction were suppressed, it is difficult for the hydrogen bond to form between the resin and the anilines. But, in water, because of the driving force of hydrophobic interaction, the aromatic amines were near the surface of the resin and close to the sites of hydrogen bonding on the resin. This facilitated the formation of hydrogen bonding between the sorbate and the resin. In fact, the formation of the hydrogen bonding between the resin and the anilines in water was similar to the intramo-

TABLE I
Adsorption Enthalpies ΔH° (kJ/mol) for Three Anilines in Water and Hexane

	Aniline	<i>N</i> -methylaniline	<i>N,N</i> -dimethyl aniline
In water	-18.01	-17.68	-16.97
In hexane	-20.40	-18.98	-17.43

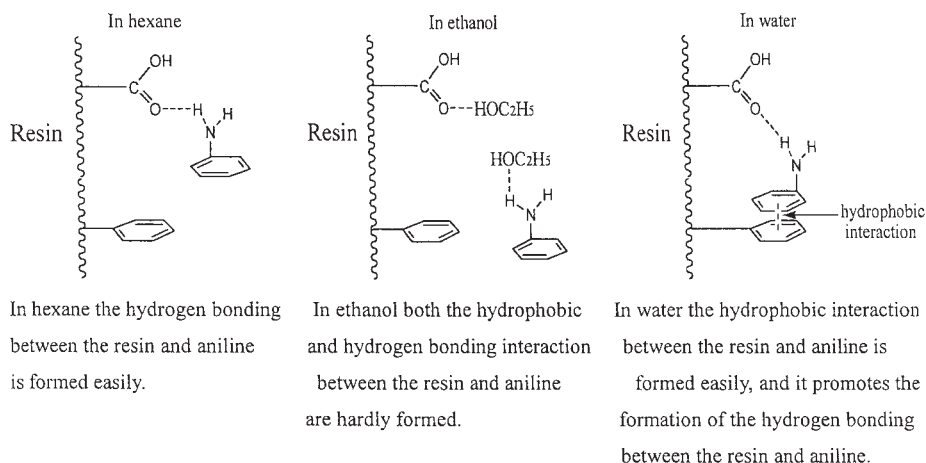


Figure 6 The interaction between the resin and aniline in different media: hexane, ethanol, and water.

lecular reaction, while, in ethanol, it was similar to the intermolecular reaction. The hydrophobic interaction promoted the formation of the hydrogen bonding between the resin and the sorbates.

Thermodynamically, the entropy loss for the formation of hydrogen bonding between the resin and anilines in water was much lower because the anilines were near the surface of the resin. Meanwhile the entropy loss in ethanol was much higher. So it is obvious that the formation of hydrogen bonding between the resin and the sorbates in water will occur more readily than that in ethanol.

CONCLUSION

The hydrophobic interaction between the polymeric adsorbent and the sorbate is the main driving force in water, and the hydrogen bonding is also able to become an important adsorption mechanism in water, because the hydrophobic interaction facilitates the formation of hydrogen bonding between the resin and the sorbate, although it is depressed by water. This facilitation is a synergism. It is obvious that the synergism between the adsorbent and sorbate will improve the capacity and enhance the adsorption selectivity.

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