

## BINARY COMPETITIVE AND COOPERATIVE ADSORPTION OF AROMATIC COMPOUNDS ON POLYMERIC RESINS\*

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**Abstract** The adsorption behaviors of 2-naphthalenesulfonic acid and aniline on a conventional macroporous resin Amberlite XAD4 and the other two newly-developed hypercrosslinked resins NDA101 and NDA100 were investigated in a single or binary batch system at 293 K and 313 K, respectively. All the adsorption isotherms of 2-naphthalenesulfonic acid and aniline on the test resins in both systems can fit well with the Langmuir equation, indicating that the adsorption is a favorable process. At the identical equilibrium concentration, the amount of aniline adsorbed on polymeric resins in the single system is higher than that in the binary system because of the competitive adsorption between 2-naphthalenesulfonic acid and aniline on the resin surface. However, the uptake amount of 2-naphthalenesulfonic acid in the binary system is markedly larger than that in the single system, which is presumably due to the cooperative effect arisen from the electrostatic interaction between 2-naphthalenesulfonic acid and aniline adsorbed on the resin surface. The simultaneous adsorption system was proven to be helpful for the selective adsorption toward 2-naphthalenesulfonic acid due to its larger selective index.

**Keywords:** Polymeric resin; 2-Naphthalenesulfonic acid; Aniline; Competitive adsorption; Cooperative adsorption.

### INTRODUCTION

Contamination of surface water and groundwater by aromatic compounds is one of the most serious environmental problems today. Among them 2-naphthalenesulfonic acid and aniline are the frequently encountered contaminants and the important substructures of potentially carcinogenic pollutants discharged from pharmaceutical, dyestuff, photographic, agrochemical, and metal plating industries. How to remove 2-naphthalenesulfonic acid and aniline from waste streams has increasingly become a significant environmental concern<sup>[1, 2]</sup>. Among lots of available techniques, adsorption on activated carbon has been extensively employed for the removal of trace organic contaminants from waste streams. In the past two decades, polymeric resins have been used as an alternative to activated carbon in industrial applications for the efficient removal of aromatic pollutants from wastewater<sup>[3–10]</sup>. Generally, contaminated water contains more than one organic compound species. It is thus of industrial interest and significance to study the adsorption behaviors of multiple organic compounds on polymeric resins. Due to the repulsive or attractive action between the adsorbates and the surface of resins or among the loaded adsorbates, adsorption of the binary components is expected to be competitive or cooperative. Now the competitive adsorption of organic pollutants onto the polymeric resin has been reported by many scientists<sup>[11–14]</sup>, but the cooperative adsorption of them can hardly be found<sup>[15, 16]</sup>. Also, the competitive and cooperative adsorption mechanism of aromatic compounds is still unclear. In the current study batch adsorption runs of 2-naphthalenesulfonic acid and aniline were carried out on Amberlite XAD4 and the other two newly

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developed resins NDA101, NDA100 in the single or binary batch systems. The purpose of the study is to achieve a better understanding on the interactions between 2-naphthalenesulfonic acid and aniline species and then to explain the competitive or cooperative adsorption more clearly.

## MATERIALS AND METHODS

### Materials

The spherical Amberlite XAD-4 resin was purchased from Rohm & Haas Company (Philadelphia, USA). NDA101 and NDA100 were supplied by Jiangsu N & G Environmental Technology Co. Ltd. (Jiangsu, China). The aqueous solutions of adsorbates were prepared by dissolving 2-naphthalenesulfonic acid or aniline into deionized water without further pH adjustment. Some physical properties of 2-naphthalenesulfonic acid and aniline are presented in Table 1.

**Table 1.** Physical properties of adsorbates at 298 K

| Adsorbate                  | Cross-sectional distance <sup>a</sup> (m) | Volume <sup>a</sup> (m <sup>3</sup> /mol) | Saturated concentration in water (mol/m <sup>3</sup> ) | pK <sub>a</sub> <sup>b</sup> |
|----------------------------|-------------------------------------------|-------------------------------------------|--------------------------------------------------------|------------------------------|
| 2-Naphthalenesulfonic acid | $8.78 \times 10^{-10}$                    | $146.3 \times 10^{-6}$                    | 490 <sup>c</sup>                                       | 0.57                         |
| Aniline                    | $5.15 \times 10^{-10}$                    | $91.7 \times 10^{-6}$                     | 376 <sup>b</sup>                                       | 4.6                          |

<sup>a</sup> Taken from software "ChemSketch" of Advanced Chemistry Development Inc.

<sup>b</sup> Taken from Lange's "Handbook of Chemistry"

<sup>c</sup> Measured in the present study

### Characterization of NDA101 and NDA100

The hypercrosslinked polymeric resins NDA100 was prepared by controlling the post-crosslinking reaction, while NDA101 was obtained by amination of NDA100 with dimethylamine in the postcrosslinking process<sup>[2]</sup>. The specific surface area and the pore distribution of both resins were determined with an ASAP 2010 M (Micromeritics Instrument, Norcross, USA) surface area measurement instrument. Infrared spectra were obtained from a Nexus 870 SX IR spectrometer (USA) with KBr pelleted samples. The basic exchange capacity was measured by acidimetric method.

The characteristics of the polymeric resins employed in the present study are listed in Table 2. It can be seen that the specific surface area of NDA100 is much higher than that of XAD4 and NDA101 by about 310 and 380 m<sup>2</sup>/g, respectively. The obvious difference is that the two NDA resins have higher micropore area, while XAD4 has only 74 m<sup>2</sup>/g of micropore area, about one tenth of NDA100. Additionally, XAD4 has the largest pore diameter of 5.8 nm, while NDA101 has the smallest one of 2.4 nm.

**Table 2.** Characteristic properties of the test resins

| Property                             | Amberlite XAD4 | NDA101                                | NDA100                       |
|--------------------------------------|----------------|---------------------------------------|------------------------------|
| Structure                            | Polystyrene    | Aminated hypercrosslinked polystyrene | Hypercrosslinked polystyrene |
| Polarity                             | Nonpolar       | Moderately polar                      | Nonpolar                     |
| BET surface area (m <sup>2</sup> /g) | 914            | 845                                   | 1225                         |
| Micropore area (m <sup>2</sup> /g)   | 74             | 561                                   | 740                          |
| Average pore diameter (nm)           | 5.8            | 2.4                                   | 3                            |
| Particle size (mm)                   | 0.4–0.6        | 0.2–0.4                               | 0.4–0.6                      |
| Tertiary amino group (mmol/g)        | 0              | 0.14                                  | 0                            |
| Color                                | White          | Deep brown                            | Deep brown                   |

### Adsorption Isotherms

Single component adsorption isotherms were performed using the conventional bottle-point technique at two temperatures (293 K and 313 K). Batch adsorption runs were carried out in 100 mL glass flasks. Prior to use, all the resins were extracted with ethanol for 8 h in a Soxhlet apparatus and desiccated under vacuum at 325 K for 24 h. A definite amount of 0.050 g resins were directly introduced into a 100 mL glass flask. Owing to their non-polarity, XAD4 and NDA100 were necessarily wetted with 0.5 mL of methanol and then rinsed three times with deionized water before use. Subsequently, 50 mL of an aqueous solution of 2-naphthalenesulfonic acid or aniline with an initial concentration ranging from 0.15 to 2 mmol/L was added into each flask. The batch factor (mL/g) was maintained at 1000 throughout this study.

Adsorption of binary components system were conducted by following the above procedures except that the initial individual concentrations of aqueous solutions were varied from 0.15 to 2 mmol/L with a 1:1 molar ratio of 2-naphthalenesulfonic acid and aniline.

The flasks were then transferred into a G 25 model incubator shaker with thermostat (New Brunswick Scientific Co. Inc.) and shaken under 150 r/min for 24 h. Note that the adsorption equilibrium is readily attained according to preliminary kinetics studies at the given temperature. The amount of 2-naphthalenesulfonic acid and aniline adsorbed can be calculated by the following equation:

$$Q_e = V_l (c_0 - c_e) / 1000W \quad (1)$$

where  $c_0$  and  $c_e$  denote the initial concentration (mmol/L) and the residual concentration at equilibrium (mmol/L) respectively,  $Q_e$  refers to the amount of 2-naphthalenesulfonic acid or aniline adsorbed on the resins (mmol/g),  $V_l$  is the volume of the aqueous solution (mL), and  $W$  is the mass of dry resins (g).

The solution concentrations were determined using HPLC, which was connected to a Waters 600 controller, Waters 600 pump and Waters 2487 dual absorbance UV detector at 274 nm (Waters, USA). The mobile phase used was 0.1%  $\text{KH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ :methanol = 70:30 (V/V) and corresponding flow rate was determined as 1 mL/min.

## RESULTS AND DISCUSSION

### Single Component Adsorption

The adsorption isotherms of 2-naphthalenesulfonic acid or aniline in the single system on XAD4, NDA100 as well as NDA101 at 293 K (a) and 313 K (b) are shown in Fig. 1.

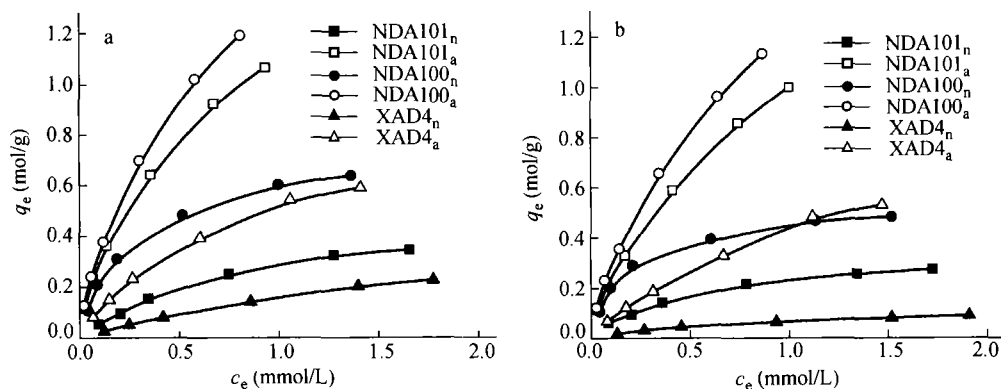


**Fig. 1** Equilibrium adsorption isotherms of 2-naphthalenesulfonic acid (solid symbols) and aniline (blank symbols) on XAD4, NDA100 and NDA101 in single component system at (a) 293 K and (b) 313 K. NDA101<sub>n</sub>, NDA100<sub>n</sub> or XAD4<sub>n</sub> means 2-naphthalenesulfonic acid adsorbed on the corresponding resins, while NDA101<sub>a</sub>, NDA100<sub>a</sub> or XAD4<sub>a</sub> means aniline, respectively.

Adsorption of aromatic compounds on polymeric resins has been successfully described qualitatively and quantitatively by adopting several models, one of which is the Langmuir<sup>[17, 18]</sup> approach based on several

assumptions, including the energetically homogeneous surface of resins, no interaction between the adsorbed molecules, the identical mechanisms for adsorption and a complete monolayer adsorption on the surface. Although the assumptions are not all met by aromatic compounds adsorption, the Langmuir model has been demonstrated to provide an accurate description of the relevant process. Langmuir model is represented by the Eq. (2):

$$Q_e = \frac{K_l Q_m C_e}{1 + K_l C_e} \quad (2)$$

where  $Q_m$  is the maximum adsorption capacity (mmol/g), namely complete coverage of available adsorption sites, and  $K_l$  is the affinity constant<sup>[19]</sup>. The results of the nonlinear least-squares regression analyses with the Langmuir equation were presented in Table 3. It can be seen that Langmuir isotherm models fit the adsorption data well since all the correlative factors  $R^2$  are larger than 0.99<sup>[20]</sup>.

**Table 3.** Langmuir isotherm parameters for 2-naphthalenesulfonic acid and aniline adsorption in single and binary components system

| Adsorbent | Adsorbate                  | Adsorption system | Temp. (K) | $K_l$ | $Q_m$ (mmol/g) | $R^2$ |
|-----------|----------------------------|-------------------|-----------|-------|----------------|-------|
| XAD4      | 2-Naphthalenesulfonic acid | Single            | 293       | 0.447 | 0.517          | 0.999 |
|           |                            |                   | 313       | 1.197 | 0.128          | 0.998 |
|           | Aniline                    |                   | 293       | 1.270 | 0.927          | 0.999 |
|           |                            |                   | 313       | 0.723 | 1.042          | 0.997 |
| NDA100    | 2-Naphthalenesulfonic acid | Single            | 293       | 3.841 | 0.753          | 0.997 |
|           |                            |                   | 313       | 5.754 | 0.531          | 0.995 |
|           | Aniline                    |                   | 293       | 2.374 | 1.738          | 0.993 |
|           |                            |                   | 313       | 1.874 | 1.740          | 0.992 |
| NDA101    | 2-Naphthalenesulfonic acid | Single            | 293       | 1.182 | 0.530          | 0.998 |
|           |                            |                   | 313       | 1.915 | 0.356          | 0.995 |
|           | Aniline                    |                   | 293       | 2.096 | 1.586          | 0.994 |
|           |                            |                   | 313       | 1.451 | 1.661          | 0.993 |
| XAD4      | 2-Naphthalenesulfonic acid | Binary            | 293       | 0.706 | 0.757          | 0.999 |
|           |                            |                   | 313       | 0.747 | 0.621          | 0.998 |
|           | Aniline                    |                   | 293       | 2.735 | 0.478          | 0.994 |
|           |                            |                   | 313       | 3.147 | 0.425          | 0.997 |
| NDA100    | 2-Naphthalenesulfonic acid | Binary            | 293       | 3.302 | 0.974          | 0.984 |
|           |                            |                   | 313       | 3.244 | 0.932          | 0.988 |
|           | Aniline                    |                   | 293       | 2.678 | 0.921          | 0.987 |
|           |                            |                   | 313       | 4.489 | 0.668          | 0.992 |
| NDA101    | 2-Naphthalenesulfonic acid | Binary            | 293       | 1.009 | 0.904          | 0.996 |
|           |                            |                   | 313       | 1.437 | 0.775          | 0.996 |
|           | Aniline                    |                   | 293       | 1.990 | 0.763          | 0.989 |
|           |                            |                   | 313       | 2.125 | 0.648          | 0.993 |

Moreover, the distribution coefficient  $K_d$  (L/g) is defined as<sup>[20]</sup>:

$$K_d = \frac{(c_0 - c_e)}{c_e} \cdot \frac{V_L}{1000W} \quad (3)$$

where  $K_d$  can be an indicative of the adsorption affinity, which is actually the slope of the isotherms. The  $K_d$  of 2-naphthalenesulfonic acid or aniline in the single component system on XAD4, NDA100 and NDA101 are shown in Table 4.

**Table 4.** Distribution coefficient of 2-naphthalenesulfonic acid and aniline adsorption in single and binary components system

| Adsorbent | Adsorbate                  | Adsorption system | Temp. (K) | $K_d$ (L/g) |       |       |       |       |       |
|-----------|----------------------------|-------------------|-----------|-------------|-------|-------|-------|-------|-------|
|           |                            |                   |           | 0.15*       | 0.30* | 0.50* | 1.00* | 1.60* | 2.00* |
| XAD4      | 2-Naphthalenesulfonic acid | Single            | 293       | 0.217       | 0.207 | 0.193 | 0.166 | 0.145 | 0.127 |
|           |                            |                   | 313       | 0.137       | 0.121 | 0.099 | 0.070 | 0.054 | 0.047 |
|           | Aniline                    |                   | 293       | 1.204       | 1.009 | 0.872 | 0.649 | 0.514 | 0.419 |
|           |                            |                   | 313       | 0.839       | 0.701 | 0.594 | 0.491 | 0.431 | 0.360 |
| NDA100    | 2-Naphthalenesulfonic acid |                   | 293       | 2.579       | 2.335 | 1.646 | 0.934 | 0.604 | 0.468 |
|           |                            |                   | 313       | 2.452       | 2.046 | 1.370 | 0.650 | 0.412 | 0.318 |
|           | Aniline                    |                   | 293       | 5.858       | 4.134 | 3.110 | 2.310 | 1.762 | 1.477 |
|           |                            |                   | 313       | 4.601       | 3.355 | 2.474 | 1.905 | 1.507 | 1.307 |
| NDA101    | 2-Naphthalenesulfonic acid |                   | 293       | 0.581       | 0.472 | 0.448 | 0.335 | 0.255 | 0.208 |
|           |                            |                   | 313       | 0.726       | 0.467 | 0.391 | 0.275 | 0.191 | 0.158 |
|           | Aniline                    |                   | 293       | 4.353       | 3.394 | 2.633 | 1.792 | 1.368 | 1.145 |
|           |                            |                   | 313       | 3.244       | 2.678 | 1.920 | 1.426 | 1.153 | 0.999 |
| XAD4      | 2-Naphthalenesulfonic acid | Binary            | 293       | 0.575       | 0.489 | 0.421 | 0.344 | 0.285 | 0.252 |
|           |                            |                   | 313       | 0.378       | 0.406 | 0.354 | 0.297 | 0.243 | 0.203 |
|           | Aniline                    |                   | 293       | 1.378       | 0.851 | 0.748 | 0.439 | 0.300 | 0.246 |
|           |                            |                   | 313       | 0.962       | 0.921 | 0.691 | 0.420 | 0.275 | 0.211 |
| NDA100    | 2-Naphthalenesulfonic acid |                   | 293       | 3.436       | 2.674 | 2.114 | 1.293 | 0.988 | 0.800 |
|           |                            |                   | 313       | 3.417       | 2.656 | 1.938 | 1.103 | 0.719 | 0.585 |
|           | Aniline                    |                   | 293       | 3.042       | 2.170 | 1.689 | 0.940 | 0.711 | 0.575 |
|           |                            |                   | 313       | 3.166       | 2.255 | 1.551 | 0.829 | 0.519 | 0.425 |
| NDA101    | 2-Naphthalenesulfonic acid |                   | 293       | 1.090       | 0.862 | 0.670 | 0.542 | 0.421 | 0.375 |
|           |                            |                   | 313       | 1.168       | 0.989 | 0.801 | 0.553 | 0.422 | 0.366 |
|           | Aniline                    |                   | 293       | 1.750       | 1.403 | 0.986 | 0.645 | 0.476 | 0.410 |
|           |                            |                   | 313       | 1.487       | 1.107 | 0.883 | 0.543 | 0.409 | 0.333 |

\* The original concentration of solution (mmol/L)

As shown in Fig. 1 and Tables 3 and 4, the affinity of adsorbates towards the polymeric resins is lowered as the equilibrium concentrations increase. This is probably due to the reduction of adsorption sites and the augment of electrostatic repulsion caused by the increase in the negative or positive charge of the adsorbed 2-naphthalenesulfonic acid or aniline.

For adsorption of aromatic compounds onto polymeric resin from aqueous solution, there are many factors that influence the adsorption capacity, including specific surface area, pore structure, hydrophobicity of adsorbates, as well as  $\pi$ - $\pi$  dispersion interaction of aromatic rings and the compatibility between resin and adsorbate. The adsorption capacity is generally correlated to its specific surface area; however other

characteristics of the resin in nature may sometimes play important roles in adsorption behaviors<sup>[6, 10, 21]</sup>. According to Tables 3 and 4, the order of both  $K_d$  and  $Q_m$  values for the adsorption of 2-naphthalenesulfonic acid or aniline is NDA100 > NDA101 > XAD4, showing that the adsorption property of NDA100 and NDA101 is superior to XAD4. This may be attributed to their much larger micropore area. Another factor is the existence of amino groups on the polymeric matrix of NDA101, which ensure the realization of electrostatic interaction and a good compatibility between the polymer matrix and 2-naphthalenesulfonic acid, leading to the expected higher adsorption affinity of 2-naphthalenesulfonic acid to NDA101 than to XAD4.

It can also be seen that, owing to its better hydrophobic property (see Table 1), aniline exhibits higher adsorption affinity and adsorption capacity on the test resins in comparison with 2-naphthalenesulfonic acid. Moreover, the electronic density of the aromatic ring of adsorbates results in the differences in their adsorption behaviours. The amino group of aniline molecule enhances the electronic density of its aromatic ring, whereas the sulfonic group of 2-naphthalenesulfonic acid molecule does not. It is reasonable that the higher electron density in the ring supplies more  $\pi$ -electrons to interact with the resin and accordingly increases the affinity of aniline to resins<sup>[22]</sup>. Additionally, a part of amino groups on the structure of NDA101 helps to enhance the adsorption affinity of 2-naphthalenesulfonic acid through electrostatic interaction. By taking the smaller size of aniline molecule and the higher electronic density of its aromatic ring into consideration, aniline also exhibits higher adsorption affinity towards NDA101 in comparison with 2-naphthalenesulfonic acid.

With respect to the effect of temperature, it is shown in Table 4 that the affinity constant ( $K_d$ ) of both 2-naphthalenesulfonic acid and aniline toward NDA101, NDA100 and XAD4 is decreased with the increase in temperature, indicating the adsorption is in exothermic nature, but the greater water affinity of 2-naphthalenesulfonic acid and aniline at higher temperature cannot be ruled out.

### **Binary Components Adsorption**

Figure 2 depicts the adsorption isotherms of binary aqueous species in the mixtures of 2-naphthalenesulfonic acid/aniline on XAD4, NDA100 and NDA101 at the initial molar concentration ratio of 1. Their adsorption isotherms also show a good fit with the Langmuir model with a correlative factor  $R^2 > 0.98$ , and the results are summarized in Table 3. The  $K_d$  values of 2-naphthalenesulfonic acid or aniline in the binary components system on XAD4, NDA100 and NDA101 are also shown in Table 4.

As shown in Fig. 2 and Tables 3 and 4,  $q_e$  and  $K_d$  of aniline in the binary system on the corresponding resins are much lower than those in the single system, indicating that 2-naphthalenesulfonic acid molecules have a competitive effect on the aniline adsorption. As for the same kind of the dominant adsorption driving force by  $\pi$ - $\pi$  dispersion interaction discussed in previous sections, the competition for the adsorption sites should be involved in the predominant mechanism because the sizes of 2-naphthalenesulfonic acid and aniline molecules (around 0.9 nm and 0.5 nm respectively) are small enough to pass through the pore of XAD4, NDA100 and NDA101 (around 5.8 nm, 3.0 nm and 2.4 nm, respectively). Additionally, due to its larger molecule size and more water clusters around the strong electron-withdrawing sulfonic group, the surface area occupied by one molecule of 2-naphthalenesulfonic acid on resin surface is much larger than that of aniline. Then, it is reasonable that the amount of 2-naphthalenesulfonic acid molecules adsorbed causes the larger amount of aniline molecules to be desorbed.

On the contrary, the amount adsorbed ( $q_e$ ) and the adsorption affinity ( $K_d$ ) of 2-naphthalenesulfonic acid in the binary system on the corresponding resins are obviously higher than those in the single system, indicating that aniline molecules have a cooperative effect on the 2-naphthalenesulfonic acid adsorption. In other words, the aniline molecules adsorbed enhance the adsorption of 2-naphthalenesulfonic acid molecules. In the viewpoint of the interaction, the additional electrostatic interaction occurs between the sulfonic and amino groups on the loaded adsorbates (2-naphthalene sulfonic acid and aniline, respectively). Furthermore, the electrostatic repulsion among the 2-naphthalenesulfonic acid molecules adsorbed could be partly shielded by the loaded aniline molecules, allowing a closer packing on the hydrophobic surface.

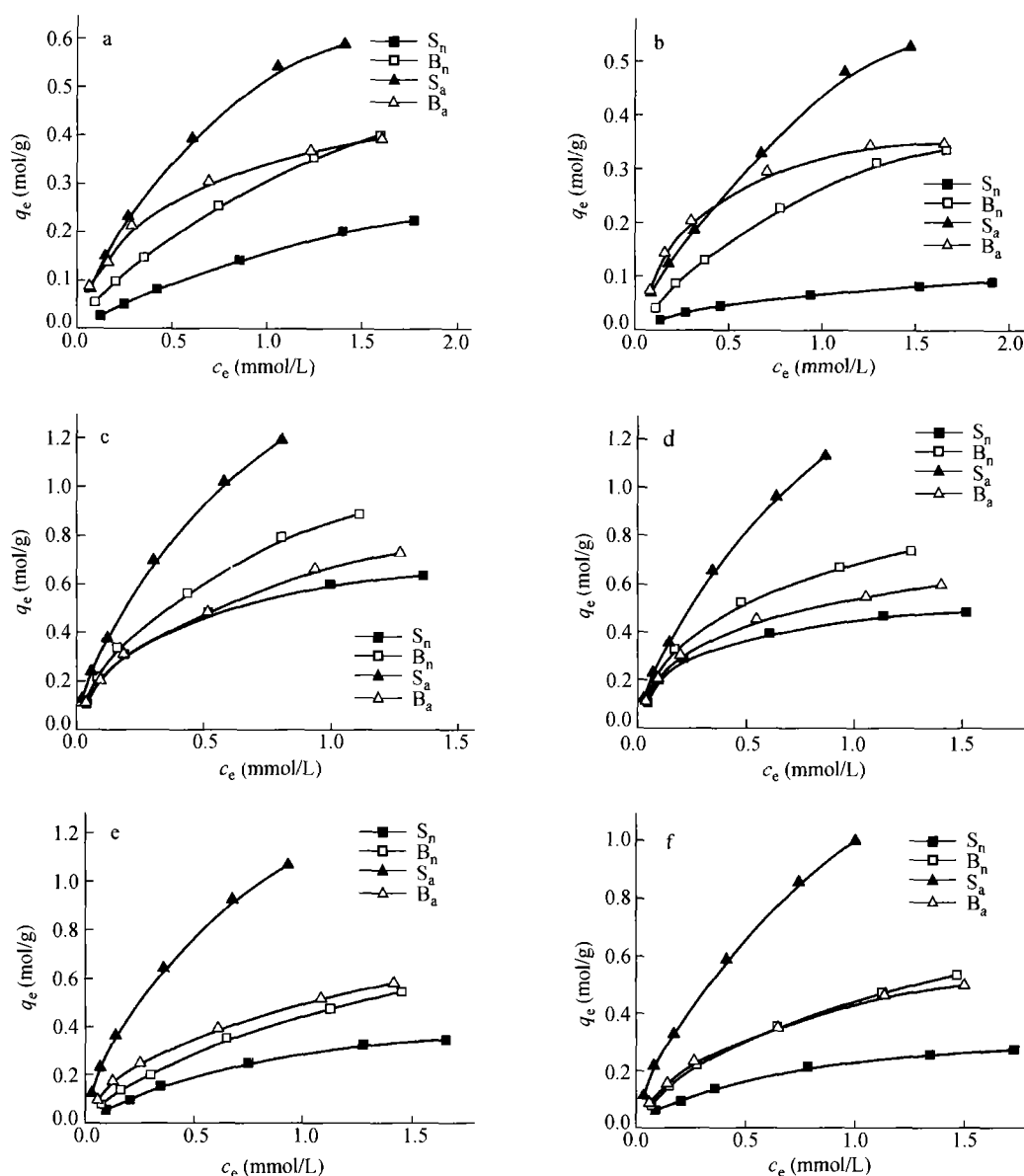


**Fig. 2** Equilibrium adsorption isotherms of 2-naphthalenesulfonic acid and aniline on XAD4 ((a) 293 K, (b) 313 K), NDA100 ((c) 293 K, (d) 313 K) and NDA101 ((e) 293 K, (f) 313K) in the single (solid symbols) and in the binary system (blank symbols)

$S_n$  or  $B_n$  means 2-naphthalenesulfonic acid absorbed in the single or the binary system,  $S_a$  or  $B_a$  means aniline absorbed in the single or the binary system, respectively.

### Selectivity Index

Selectivity index is often used to evaluate the adsorption affinity of two different adsorbates on resins. The selectivity index of one component to the other is defined as:

$$S_{1/2} = K_{d1}/K_{d2} \quad (4)$$

where  $K_{d1}$  and  $K_{d2}$  represent the distribution coefficient (L/g) of the two adsorbates, respectively. The selectivity indexes of 2-naphthalenesulfonic acid to aniline on XAD4, NDA100 and NDA101 in the binary system at 293 K and 313 K are given in Table 5. Also, the  $K_{d1}/K_{d2}$  values from the single system are listed as reference. The

selectivity index of 2-naphthalenesulfonic acid in the binary system is much higher than the reference value in the single system, indicating that aniline molecules adsorbed on the resin surface help 2-naphthalenesulfonic acid molecules to leave from the bulk to the solid phase by the electrostatic interaction. It can also be seen that the adsorption selectivity of 2-naphthalenesulfonic acid increases expectedly with initial concentrations in the experimental concentration range. Additionally, the adsorption selectivity of 2-naphthalenesulfonic acid on XAD4 and NDA100 decreases as the temperature increases, but the adsorption selectivity on NDA101 does not. This is probably due to the fact that the increase in the solubility of 2-naphthalenesulfonic acid is greater than that of aniline as the temperature increases. On the other hand, the adsorption affinity of 2-naphthalenesulfonic acid toward NDA101 increases as the temperature rises, which is attributed to the enhancement of electrostatic interactions between sulfonic groups of 2-naphthalenesulfonic acid molecules and amino groups on the polymeric matrix of NDA101.

**Table 5.** Selectivity index of 2-naphthalenesulfonic acid to aniline adsorption in single and binary components system

| Adsorbent | Adsorption system | Temp. (K) | $S_{1/2}$ |       |       |       |       |       |
|-----------|-------------------|-----------|-----------|-------|-------|-------|-------|-------|
|           |                   |           | 0.15*     | 0.30* | 0.50* | 1.00* | 1.60* | 2.00* |
| XAD4      | Single            | 293       | 0.180     | 0.205 | 0.221 | 0.256 | 0.283 | 0.305 |
|           |                   | 313       | 0.163     | 0.173 | 0.167 | 0.142 | 0.125 | 0.131 |
| NDA100    |                   | 293       | 0.440     | 0.565 | 0.529 | 0.404 | 0.343 | 0.317 |
|           |                   | 313       | 0.533     | 0.610 | 0.554 | 0.341 | 0.274 | 0.243 |
| NDA101    |                   | 293       | 0.133     | 0.139 | 0.170 | 0.187 | 0.186 | 0.182 |
|           |                   | 313       | 0.224     | 0.174 | 0.204 | 0.193 | 0.166 | 0.158 |
| XAD4      | Binary            | 293       | 0.417     | 0.574 | 0.563 | 0.783 | 0.951 | 1.025 |
|           |                   | 313       | 0.392     | 0.441 | 0.512 | 0.707 | 0.885 | 0.961 |
| NDA100    |                   | 293       | 1.129     | 1.232 | 1.251 | 1.375 | 1.390 | 1.391 |
|           |                   | 313       | 1.079     | 1.178 | 1.249 | 1.330 | 1.386 | 1.374 |
| NDA101    |                   | 293       | 0.623     | 0.614 | 0.680 | 0.841 | 0.884 | 0.914 |
|           |                   | 313       | 0.785     | 0.893 | 0.908 | 1.018 | 1.032 | 1.100 |

\* The original concentration of solution (mmol/L)

## CONCLUSION

Two hypercrosslinked polymeric resins (NDA100 and NDA101) were used for the removal of 2-naphthalenesulfonic acid and aniline from their aqueous solutions, and their adsorption capacities for adsorbates were found to be higher than XAD-4, which can be attributed to their high specific surface area and high micropore area.

Competitive and cooperative adsorption behaviors were observed in the binary components system. 2-Naphthalenesulfonic acid molecules have a competitive effect on the aniline adsorption onto XAD4, NDA100 and NDA101. The competition for the adsorption sites is considered to be a predominant factor in the competitive adsorption mechanism. On the contrary, aniline molecules have a cooperative influence on the adsorption for 2-naphthalenesulfonic acid onto the corresponding resins. Electrostatic interaction between 2-naphthalenesulfonic acid and aniline molecules adsorbed on resin surface is considered to be the predominant cooperative adsorption mechanism. In comparison with aniline, the binary adsorption system helps to adsorb 2-naphthalenesulfonic acid due to its larger selective index.

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