Adsorption of Aromatic Sulphonic Acids onto Macroporous Exchangers: Effect of the Chemical Structure of the Adsorbent on the Adsorption Capacity

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ABSTRACT: The adsorption of 2-naphthalene sulphonic acid from aqueous solution was studied using macroporous weak base exchangers with different matrices. This study reports the results of the favourable adsorption behaviour of 2-naphthalene sulphonic acid onto polymeric anion exchangers. The difference in adsorption affinity, together with the enthalpic and entropic changes associated with the adsorption process, was interpreted in terms of the chemical structure of the exchangers and appropriate interaction between the non-polar moiety of the aromatic anion and the exchanger matrices. The exchanger matrix had a distinct influence on the adsorption capacity of the aromatic sulphonic acid.

INTRODUCTION

Aromatic sulphonic acids are important intermediates in the production of a variety of synthetic dyes, optical brighteners, fluorescent whitening agents and pharmaceuticals. As a result, a wide variety of benzene and naphthalene sulphonates and their substitutes are produced on a large scale in the chemical industry. The effluent from manufacturing processes is known to contain significantly high concentrations of these compounds due to their good water solubility and strong hydrophilicity. Although, in contrast to linear alkylbenzene sulphonates, they have a low acute toxicity and show no genotoxic and carcinogenic effects (Greim et al. 1994), most aromatic sulphonates which do not possess a hydrophobic alkyl chain are biologically persistent compounds (Alonso and Barcello 1999). Furthermore, they possess a high mobility within the aquatic environment and cause pollution of surface waters because of their low octanol/water partition coefficients (log $K_{ow}$ < 2.2) (Loos and Niessner 1998). For these various reasons, the removal of aromatic sulphonates from wastewaters is of great importance for the protection of natural waters.

Adsorption is a prominent method for the treatment of aqueous effluents containing organic substances because of the high concentrating ability of typical adsorbents (Tiyurupa et al. 1995, Xu et al. 2003). With this technology, it is possible not only to effectively treat the effluents, but also to recover significant quantities of reusable chemicals for possible recycling to the manufacturing process. Aromatic sulphonic acids tend to exist as ions in aqueous solution and are usually considered as hydrophobic ionisable organic compounds (HIOCs) (Jafvert et al. 1990). In contrast to unionised hydrophobic aromatic compounds, aromatic sulphonic acids are not amenable to efficient removal by conventional hydrophobic sorbents such as activated carbon and non-ionic macroreticular polymeric resins (Gustafson et al. 1968). The removal of HIOCs from aqueous
solution, e.g. various carboxylic acids and phenols that exist as anions in water over a wide range of pH values, using macroporous weak base anion exchanger has received increasing attention in recent years (Takatsuji and Yoshida 1998; Cloete and Marais 1995; Anasthas and Gaikar 1999; Li and Sengupta 1999).

In the present work, 2-naphthalene sulphonic acid (2-NSA) was employed as a representative aromatic sulphonic acid with its adsorption equilibrium onto two polymeric weak base exchangers, i.e. poly(divinylbenzene-co-ethylvinylbenzene) [poly(DVB-co-EVB)] and a poly(aliphatic carboxylic ester), being studied. The specific goal of the work reported here was to examine how the chemistry of the adsorbent surface affects both the adsorption affinity and the binding energy. It is believed that such a study could be useful in designing an appropriate adsorbent for a specific task.

EXPERIMENTAL

Materials

2-Naphthalene sulphonic acid (2-NSA) was purchased from the Shanghai Chemical Reagent Station (Shanghai, P. R. China). This was dissolved in deionised water for batch adsorption experiments. The two macroporous weak base exchangers employed, viz. poly(divinylbenzene-co-ethylvinylbenzene) [poly(DVB-co-EVB)], NGI-301 and a poly(aliphatic carboxylic ester) (NGI-311), were available commercially and purchased from the Jiangsu Nange Environmental Technology Company (Jiangsu Province, P. R. China). Their physical properties and structures are listed in Table 1. Prior to initial use, the adsorbents were extracted with acetone for at least 8 h and then

| Adsorbent | Structure | Matrix type | Functional group | Saturation capacity of HCl, Q<sub>0</sub> (mmol/g dried resin) |
|-----------|-----------|-------------|------------------|---------------------------------------------------------------|
| NGI-301   | H<sub>2</sub>C—CH—CH<sub>2</sub>—CH<sub>2</sub>—CH<sub>2</sub>—H<sub>3</sub>N<sub>n</sub> | polystyrene, macroporous | tertiary amine | 4.8                                                          |
| NGI-311   | H<sub>2</sub>C—CH—CH<sub>2</sub>—CH<sub>2</sub>—CH<sub>2</sub>—H<sub>3</sub>N<sub>n</sub> | polyacrylic, macroporous | tertiary amine, secondary amine | 6.0 |
washed repeatedly with deionised water, aqueous hydrochloric acid, deionised water and aqueous sodium hydroxide, respectively, in sequence and finally dried under vacuum at 333 K for 2 h.

**Batch adsorption studies of aromatic sulphonic acids**

Batch adsorption experiments of 2-NSA onto the two adsorbents at three different temperatures (301 K, 311 K and 321 K) were performed as follows. A known amount of adsorbent (0.100–0.250 g) was introduced directly into a flask and then an aqueous solution of 2-NSA of known concentration was added to each flask. The flask was placed in a G25 model incubator shaker (New Brunswick Scientific Co. Inc., NJ, USA) at a pre-determined temperature and shaken for 24 h at 150 rpm to ensure that the adsorption process had attained equilibrium. When this stage had been reached, the concentration of 2-NSA remaining in the aqueous solution (C_e) was determined. The initial concentration of the solutions studied (C_0) was 1000 mg/l in each case. The concentration of adsorbate in the adsorbent phase, q_e (mmol/g), was calculated from the relationship:

\[
q_e = \frac{V_1(C_0 - C_e)}{W \times M}
\]

where \(V_1\) is the volume of solution (ml), \(W\) is the weight of dry adsorbent (g) and \(M\) is the molecular weight of 2-NSA (208.25 g/mol).

The concentrations of 2-NSA in the aqueous solution were measured at a wavelength of 230 nm using a high-performance liquid chromatogram (Waters Associates, Milford, MA, USA).

**RESULTS AND DISCUSSION**

**Adsorption characteristics: effect of the polymer matrix**

Equilibrium data concerning the adsorption of 2-NSA from aqueous solution onto the two adsorbents NGI-301 and NGI-311 under the same conditions are presented in Figure 1. In order to understand how the chemical structures of the adsorbents influence the adsorption process, the adsorbed amounts were divided by the exchange capacity of the adsorbent, \(Q_0\), in each case. As can be seen from the data depicted in Figure 1, the poly(DVB-co-EVB) adsorbent NGI-301 exhibited a higher adsorptive capacity than the poly(aliphatic carboxylic ester) adsorbent NGI-311, despite the latter having a more polar matrix.

Several studies have demonstrated that, in general, the adsorption of inorganic acids and organic acids onto weak base exchangers follows a two-step mechanism (Bhandari et al. 1992a,b, 2000). In the first step, the amino groups of the exchanger (denoted as R) are protonated by H+ ions derived from the acid, resulting in the formation of a positively charged surface on the pore walls of the exchanger. The second step, i.e. acid anion association, arises from electrostatic or coulombic interaction between the positively charged RH+ groups and the negatively charged acid anions. This means that the adsorption of inorganic acids and organic acids onto weak base exchangers occurs mainly as a result of electrostatic interaction. Hence, according to this adsorption mechanism, strictly from an electrostatic or coulombic interaction viewpoint, the two polymeric anion exchangers examined in this study, viz. NGI-301 and NGI-311, should have a similar adsorption affinity towards 2-NSA.
Figure 1. Comparison of adsorption capacities of 2-NSA onto (a) NGI-301 and (b) NGI-311 at (a) 301 K, (b) 311 K and (c) 321 K. All other variables were maintained constant in each case.
However, as shown in Figure 1, at the same equilibrium concentration of the two adsorbates, NGI-301 exhibited a higher adsorption ability than NGI-311. Such a distinct discrepancy could suggest that the matrix of the polymeric exchanger played a significant role in influencing the adsorption capacity. The matrix corresponds to the skeletal organic component in the polymeric ion exchanger in addition to the charged functional groups. Since NGI-301 possesses a macroporous polystyrene matrix with divinylbenzene crosslinking, 2-NSA adsorption would be expected to be enhanced by hydrophobic interactions between the poly(DVB-co-EVB) matrix and the non-polar 2-NSA$^-$ moiety. However, for NGI-311 with a more polar polyacrylic matrix, the adsorption capacity was significantly lower due to weaker hydrophobic interactions. Furthermore, it is likely that specific solute–adsorbent interactions involving $\pi$-electrons were also responsible for 2-NSA adsorption onto the adsorbents. The delocalised $\pi$-electrons of the poly(DVB-co-EVB) exchanger NGI-301 would enhance the adsorption ability by interacting with the $\pi$-electrons of the aromatic rings of 2-NSA$^-$. Since the poly(alkylated carboxylic ester) exchanger NGI-311 lacks $\pi$-electrons, it was not capable of enhancing its ability to interact with 2-NSA$^-$ through $\pi$-interactions.

In summary, therefore, it is not unreasonable to expect that the effect of the adsorbent matrix in 2-NSA adsorption would be significant. This contention is discussed further below in terms of the adsorption thermodynamics.

### Adsorption isotherms

The adsorption isotherms for 2-NSA onto the adsorbents NGI-301 and NGI-311 at different temperatures are shown in Figure 2. Favourable adsorption isotherms of 2-NSA were obtained for the two adsorbents, the adsorption capacities increasing with the increase in the equilibrium concentration of adsorbate in the aqueous solution. The adsorption equilibrium data were interpreted using the Langmuir and Freundlich isotherms. Table 2 shows the values of the isotherm parameters estimated by non-linear regression analysis. Although both the Langmuir and Freundlich models provided a satisfactory representation of the data and yielded similar correlation coefficients $R^2$, it was more convenient to evaluate thermodynamic parameters using the Freundlich equation. Consequently, the Freundlich equation was chosen for predicting $q_e$ and $C_e$ values in the present work.

### Thermodynamic considerations: adsorption enthalpy versus entropic contribution

Estimations of the isosteric enthalpy of adsorption, as well as of the free energy and entropy of adsorption, were interpolated from the data using the Freundlich isotherm equation. The isosteric enthalpy of adsorption was calculated through the use of the derivative Van’t Hoff equation (Garcia-Delgado et al. 1992), i.e.

$$\ln \left( \frac{1}{C_e} \right) = -\frac{\Delta H}{RT} + \ln K_a$$

(2)

where $\Delta H$ is the isosteric enthalpy of adsorption, $R$ is the gas constant and $C_e$ is the equilibrium concentration of solute (mmol/l) at the absolute temperature $T$. The Freundlich isotherm was used to obtain the values of $C_e$ at different temperatures (301 K, 311 K and 321 K), while $\Delta H$ was calculated from the slope of the linear plot of $\log(1/C_e)$ versus $1/T$. 


Values of the free energy and the entropy of adsorption were obtained from equations (3) and (4), respectively (Bell and Tsezos 1987):

\[ \Delta G = -RT \int q_e \frac{dx}{x} \]  

(3)

and

Figure 2. Adsorption isotherms for 2-NSA onto (a) NGL-301 and (b) NGL-311 at \( J = 301 \) K, \( 311 \) K, and \( 321 \) K, respectively.
where $x$ represents the molar fraction of adsorbate in solution. Subsequently, $q_e$ was replaced by the Freundlich isotherm equation whose use demonstrated the apparent free-energy independence of $q_e$ (Bell and Tsezos 1987). This led to the relationship:

$$\Delta G = -nRT$$

Table 3 provides a summary of the estimated values of the three thermodynamic parameters for 2-NSA adsorption onto the adsorbents studied. These results allow the following observations to be made:

1. The adsorption of 2-NSA onto weak base exchangers occurred via an exothermic process (i.e., $\Delta H$ was negative). However, the adsorption of 2-NSA onto NGI-301 was much less exothermic ($\Delta H \approx 0$) compared to that onto NGI-311. This result is in agreement with the effect of temperature on the adsorption isotherms of 2-NSA. As shown in Figure 2, the adsorption capacity of NGI-311 decreased strongly with increasing temperature whereas that for NGI-301 only decreased slightly, despite NGI-301 possessing a higher adsorption affinity.

### Table 2. Parameter Values for the Adsorption Isotherms of 2-NSA

| Adsorbent | Temp. (K) | $K_L$ | $a$ | $R^2$ | $K_F$ | $n$ | $R^2$ |
|-----------|-----------|-------|-----|-------|-------|-----|-------|
| NGI-301   | 301       | 66.060| 4.174 | 0.992 | 5.148 | 4.950 | 0.924 |
|           | 311       | 57.411| 4.234 | 0.974 | 5.091 | 5.001 | 0.957 |
|           | 321       | 49.017| 4.343 | 0.949 | 5.119 | 4.933 | 0.987 |
| NGI-311   | 301       | 3.328 | 4.368 | 0.955 | 3.328 | 2.871 | 0.982 |
|           | 311       | 2.524 | 4.202 | 0.974 | 2.949 | 2.677 | 0.966 |
|           | 321       | 2.108 | 4.346 | 0.979 | 2.884 | 2.502 | 0.972 |

### Table 3. Estimated Thermodynamic Parameters for the System

| Adsorbent | $q_e$ (mmol/g) | $\Delta H$ (kJ/mol) | $\Delta G$ (kJ/mol) | $\Delta S$ (kJ/mol) |
|-----------|----------------|---------------------|---------------------|---------------------|
|           |                | (at 301 K)          | (at 301 K)          |                     |
| NGI-301   | 2.0            | -1.752              | -12.387             | 10.635              |
|           | 2.5            | -1.611              | -12.387             | 10.776              |
|           | 3.0            | -1.496              | -12.387             | 10.891              |
| NGI-311   | 2.0            | -22.058             | -7.185              | -14.873             |
|           | 2.5            | -18.751             | -7.185              | -11.566             |
|           | 3.0            | -16.048             | -7.185              | -8.863              |
2. The value of $\Delta G$ was negative for both systems, thereby confirming that the adsorption of 2-NSA onto macroporous weak base anion exchangers was spontaneous and favourable thermodynamically. The free energy change for NGI-301 was lower than for NGI-311, suggesting that 2-NSA would adsorb selectively onto NGI-301.

The free energy change $\Delta G$ is given by the relationship:

$$\Delta G = \Delta H - T \Delta S$$  \hspace{1cm} (6)

Hence, both enthalpic and entropic changes help to decide the overall selectivity of the adsorption process. Note that the negative value of $\Delta G$ for NGI-301 resulted from positive entropic contributions, i.e., the favourable adsorption of 2-NSA was an entropy-driven process. In contrast, the negative free energy change for NGI-311 indicates an enthalpy-driven process. Expressed in another way, this indicates that the entropy contribution (i.e. $T \Delta S$) for NGI-301 with the non-polar polystyrene matrix was significantly larger than that for NGI-311 possessing a relatively polar matrix.

Our observations coupled with the results reported by other workers suggest that the matrix structures of the polymeric exchangers determined the difference in enthalpy and entropy for the adsorption of 2-NSA. In examining this suggestion, it was useful to consider the theory developed by Frank and Wen (1957) and by Nemethy and Scheraga (1962) which suggests that water molecules tend to turn away from a non-polar moiety and reorganise themselves into clusters through hydrogen bonding, thereby becoming highly ordered (i.e. 'icebergs') when organic solutes are introduced. According to this theory, the water molecules surrounding the matrix of NGI-301 would be more ordered relative to those surrounding NGI-311, which was more polar (i.e. less hydrophobic) due to its open-chain aliphatic structure that contained carbonyl groups. As discussed above, in the adsorption of 2-NSA onto NGI-301, once a 2-NSA$^-$ ion entered the exchanger phase and was bound to the protonated functional group, its non-polar part tended to be in direct contact with the non-polar matrix of the exchanger through hydrophobic and $\pi$-interactions. Consequently, an entropy increase contribution to the overall adsorption process occurred because the 'icebergs' surrounding the adsorbent matrix were broken down causing disordering of the water molecules. In addition, thermal energy is required for breaking the hydrogen-bonding network of the 'icebergs' within the exchanger, resulting in a positive enthalpy contribution to the overall adsorption process. In contrast, for the adsorption of 2-NSA adsorption onto NGI-311, because of the weaker hydrophobic interaction between the non-polar part of the 2-NSA and the polar matrix of the adsorbent, the entropy and enthalpy changes of the process could be neglected. Hence, the entropy and enthalpy changes of the overall adsorption process were more positive, resulting in a more negative free energy change for NGI-301 relative to NGI-311.

CONCLUSIONS

This study demonstrated that the two polymeric weak base exchangers NGI-301 and NGI-311 exhibited favourable adsorption behaviours towards 2-NSA. The high adsorption capacity of 2-NSA onto NGI-301 relative to NGI-311 was attributed mainly to the hydrophobic and $\pi$-electron interaction between the matrix of NGI-301 and the non-polar part of the 2-NSA$^-$ ion. The thermodynamic results also demonstrated that the hydrophobic matrix of the exchanger played a significant role in influencing the adsorption affinity. The entropy contribution (i.e. $T \Delta S$) towards
the adsorption process for NGI-301 that possessed a non-polar polystyrene matrix was significantly larger than that for NGI-311 with a relatively polar matrix. The negative $\Delta G$ values for NGI-301 resulted from positive entropy contributions, i.e., favourable 2-NSA sorption was an entropy-driven process. In contrast, the negative free energy change for NGI-311 was associated with an enthalpy-driven process.

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