

THERMODYNAMIC STUDY ON ADSORPTION OF AROMATIC SULFONIC ACIDS ONTO MACROPOROUS WEAK BASE ANION EXCHANGER FROM AQUEOUS SOLUTIONS

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Abstract The adsorption equilibrium isotherms of three aromatic sulfonic acid compounds, 2-naphthalenesulfonic acid, *p*-toluenesulfonic acid and *p*-chlorobenzenesulfonic acid, from aqueous solutions by macroporous weak base anion exchanger within the temperature range of 293 K–313 K were obtained. Several isotherm equations were correlated with the equilibrium data, and the experimental data was found to fit the three-parameter Redlich-Peterson equation best within the entire range of concentrations. The study showed that the hydrophobicity of solute has distinct influence on adsorption capacity of the anion exchanger for the aromatic sulfonic acid. Moreover, estimations of the isosteric enthalpy, free energy, and entropy change of adsorption were also reported. The positive isosteric enthalpy and entropy change for adsorption indicate an endothermic and entropy driven process in the present study.

Keywords Aromatic sulfonic acids, Macroporous weak base anion exchanger, Adsorption thermodynamics

INTRODUCTION

Aromatic sulfonic acids are important intermediates in the production of a variety of synthetic dyes, optical brighteners, fluorescent whitening agents and pharmaceuticals. A variety of substituted benzene and naphthalene sulfonates are thus produced on a large scale in the chemical industry. Generally, aromatic sulfonic acids are prepared by sulphonation of simple aromatic hydrocarbons or their derivatives. Due to the good solubility and strong hydrophilicity of aromatic sulfonic acids, the effluent from the manufacturing processes is known to contain significantly high concentrations of these compounds. Contrary to linear alkylbenzene sulfonates, most of the aromatic sulfonates without a hydrophobic alkyl chain are biologically resistant^[1], resulting in ineffective biodegradation of these substances. On the other hand, the treatment efficiency of general chemical and physical methods for the aromatic sulfonic acids is unsatisfactory because of their high solubility in water. As a result, they can easily pass through the wastewater treatment process into the receiving water body. Because of their low octanol-water partition coefficients ($\lg K_{ow} < 2.2$)^[2], they possess a high mobility within the aquatic environment and cause contamination of surface waters. Although they have a low acute toxicity and exhibit no carcinogenic effects^[3], some of the aromatic sulfonates may still result in ecotoxicological risk. Therefore, effective removal of aromatic sulfonates from wastewaters has been of great importance for protecting the water environment.

Adsorption is a prominent method for the treatment of effluents containing organic substances in dilute aqueous solution because of the high concentrating ability of a typical adsorbent^[4, 5]. With this technology, not only the waste streams could be effectively treated, but also enormous amounts of some useful chemicals could be recovered for reuse in the manufacturing process. Usually, aromatic sulfonic acids tend to exist in the form of ions in aqueous solutions and are considered as hydrophobic ionizable organics (HIOCs)^[6]. Contrary to

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Received July 29, 2003; Revised November 20, 2003; Accepted November 27, 2003

nonionized hydrophobic aromatic compounds, aromatic sulfonic acids are not easy to remove by conventional hydrophobic sorbents such as activated carbon and non-ionic macroreticular polymeric resins^[7]. In recent years, removal of organic acidic compounds such as some carboxylic acids and phenols from aqueous solutions by using macroporous weak base anion exchanger has received increasing attention^[8–11]. Up to the present, however, systematic study on the adsorption properties of aromatic sulfonic acids has not been reported.

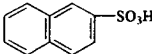
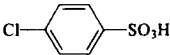
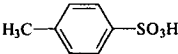
Thermodynamics is a fundamental approach for describing equilibrium, and for better understanding of the thermodynamic aspects of adsorption reactions and can help us to evaluate the adsorption process. In the present work, the batch adsorption of aromatic sulfonic acids (*p*-toluenesulfonic acid (*p*-TSA), *p*-chlorobenzenesulfonic acid (*p*-CBSA), and 2-naphthalenesulfonic acid (2-NSA)) on the macroporous weak base anion exchanger D301 in the free base form was observed. The effect of hydrophobicity of solute on adsorption capacity was analyzed, and particular emphasis was laid on the analysis of the adsorption isotherm of aromatic sulfonic acids on D301. In addition, values for enthalpy, free energy, and entropy change of adsorption have also been estimated, with the aid of which the results and adsorption mechanism of the present study were thermodynamically interpreted.

EXPERIMENTAL

Materials

2-Naphthalenesulfonic acid (2-NSA), *p*-toluenesulfonic acid (*p*-TSA), and *p*-chlorobenzenesulfonic acid (*p*-CBSA), were purchased from Shanghai Chemical Reagent Station (Shanghai, China). In the batch adsorption experiments, they were all dissolved in deionized water. Their physical properties are listed in Table 1.

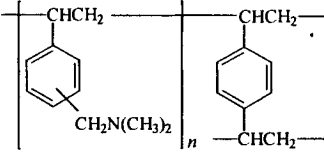
Table 1. Physical properties of aromatic sulfonic acids

Substance	Molecular structure	Molecular weight	lgK _{ow} [*]
2-NSA		208.25	1.98
<i>p</i> -CBSA		190.62	0.78
<i>p</i> -TSA		170.20	0.73

^{*}Calculated according to Ref. [12].

The macroporous weak base anion exchange resin (D301) was provided by Langfang Electrical Resin Co. Ltd. (Hebei province, China). Some characteristics of D301 are listed in Table 2. Prior to their use, the resins were extracted with acetone for at least 8 h, and were consecutively washed with deionized water, aqueous hydrochloric acid, deionized water and aqueous sodium hydroxide respectively, and finally dried under vacuum for 2 h at 333 K.

Table 2. Characteristics of polymeric anion exchanger D301

Structure	Matrix	Functional group	Capacity (mmol/g, dried resin)
	Polystyrene, macroporous	Tertiary amine	4.8

Batch Adsorption of Aromatic Sulfonic Acids

Experiments on batch adsorption of aromatic sulfonic acids on D301 at three different temperatures (293 K, 303 K and 313 K) were performed as follows: A certain amount of D301 resin (0.100–0.450 g) was introduced into the flasks directly, and an aqueous solution of different aromatic sulfonic acids with known concentration was then added. The flasks were finally placed in a G25 model incubator shaker (New Brunswick Scientific Co. Inc., New Jersey, USA) at a preset temperature and shaken at 150 rpm for 24 h to ensure the attainment of

adsorption equilibrium. Then, the remaining concentrations of aromatic sulfonic acids (c_e) in the aqueous solutions were determined. The initial concentrations (c_0) of the solutions were all 1000 mg/L. The adsorbent-phase concentration of adsorbates Q_e (mmol/g) was thus calculated according to

$$Q_e = V_1(c_0 - c_e)/MW \quad (1)$$

where V_1 is the volume of solution (mL), W is the weight of dry resin (g), and M is the molecular weight of corresponding aromatic sulfonic acids.

The concentrations of the aromatic sulfonic acids in the aqueous solutions were analyzed at different wavelengths using a high performance liquid chromatograph (Waters Assoc., Milford, MA, USA) with a C_{18} column, the mobile phase was 0.02 M tetrabutylammonium chlorate in water-methanol (50:50, V/V).

RESULTS AND DISCUSSION

Adsorption Isotherms

Generally, adsorption isotherms are important for describing adsorption capacity and evaluating the feasibility of using an adsorbent for a particular separation system. Moreover, the isotherms may play an important role in modeling procedures for the design of adsorption process. In addition, adsorption isotherms can be potentially used for theoretical evaluation and interpretation of thermodynamic parameters. Equilibrium adsorption isotherms of *p*-TSA, *p*-CBSA, and 2-NSA on D301 resin at 293 K, 303 K and 313 K are shown in Figs. 1–3. For all the three aromatic sulfonic acids, favorable adsorption isotherms were obtained, and the adsorption capacities increase with increasing equilibrium concentration of adsorbate in the aqueous solution. In the present work, the adsorption data were further correlated with the following Langmuir, Freundlich and Redlich-Peterson isotherm equations, respectively.

(1) Langmuir Eq.

$$Q_e = aK_L c_e / (1 + K_L c_e) \quad (2)$$

(2) Freundlich Eq.

$$Q_e = K_F c_e^n \quad (3)$$

(3) Redlich-Peterson Eq. (R-P equation)^[13]

$$Q_e = K_R c_e / (1 + b c_e^m) \quad (4)$$

where a , b , m , n , K_L , K_F and K_R are the isotherm parameters to be determined.

The two parameters in the Langmuir and Freundlich equation can be graphically determined, while the three parameters in the R-P equation were obtained by using Origin 6.2 software to perform the nonlinear regression analysis. In order to compare the validity of the isotherm equations, a mean relative deviation, Δq , is defined and calculated as follows^[13]:

$$\Delta q(\%) = (100/N) \sum_{i=1}^N \{ |Q_{e,i}^{\text{expt}} - Q_{e,i}^{\text{calc}}| / Q_{e,i}^{\text{expt}} \} \quad (5)$$

where the superscripts “calc.” and “expt.” represent the calculated and experimental values respectively, and N is the number of measurements. The isotherm parameters and their correlation coefficient R^2 , together with Δq , are shown in Table 3, and the fitted curves of the modeling equations using values from Table 3, are presented in Figs. 1–3.

From the results above, it can be seen that the experimental data could not be satisfactorily correlated with the Freundlich isotherm with the lower correlation coefficients R^2 and the larger deviation of about 20% for *p*-

TSA. In contrast, Langmuir and R-P equations fitted well with the isothermal data of *p*-TSA, *p*-CBSA as well as 2-NSA. Although the Langmuir model has the similar correlation coefficients R^2 as the R-P model, as is shown in Figs. 1–3, the fitting curves of the Langmuir equation deviate considerably from the equilibrium isotherm data of aromatic sulfonic acids. However, R-P equation is more suitable to correlate the isotherm data over an entire range of concentrations for all the aromatic sulfonic acids as compared with Langmuir equation, the mean relative deviations were less than 4.5% in all cases. Consequently, the R-P equation was chosen for predicting Q_e and c_e values in the present work.

Table 3. Isotherm parameters, correlation coefficient R^2 and mean relative deviation Δq

Isotherms	Parameter	2-NSA			<i>p</i> -CBSA			<i>p</i> -TSA		
		293 K	303 K	313 K	293 K	303 K	313 K	293 K	303 K	313 K
Freundlich	K_f	6.783	7.313	8.017	6.340	6.687	6.575	5.415	6.013	6.06
	n	0.288	0.295	0.319	0.303	0.32	0.301	0.320	0.359	0.349
	R^2	0.967	0.953	0.929	0.949	0.958	0.94	0.958	0.958	0.932
Langmuir	Δq	6.24%	7.95%	11.07%	9.43%	8.35%	10.21%	7.9%	19.7%	10.44%
	K_L	243.74	215.79	140.73	84.94	87.75	95.59	31.80	24.52	21.92
	a	3.156	3.31	3.74	3.679	3.561	3.736	3.981	4.294	4.655
R-P	R^2	0.968	0.986	0.982	0.994	0.982	0.995	0.989	0.996	0.994
	Δq	9.99%	6.70%	5.36%	4.57%	6.95%	3.92%	5.87%	3.91%	2.77%
	K_R	2545.1	1384.3	778.3	462.8	455.4	463.6	166.8	132.8	123.6
	b	433.6	250.65	155.4	95.8	93.8	97.7	35.0	26.9	25.7
	m	0.772	0.815	0.875	0.862	0.823	0.888	0.863	0.883	0.931
	R^2	0.992	0.989	0.993	0.998	0.998	0.999	0.995	0.999	0.999
	Δq	4.37%	4.39%	4.29%	2.23%	1.71%	1.61%	2.45%	1.26%	2.97%

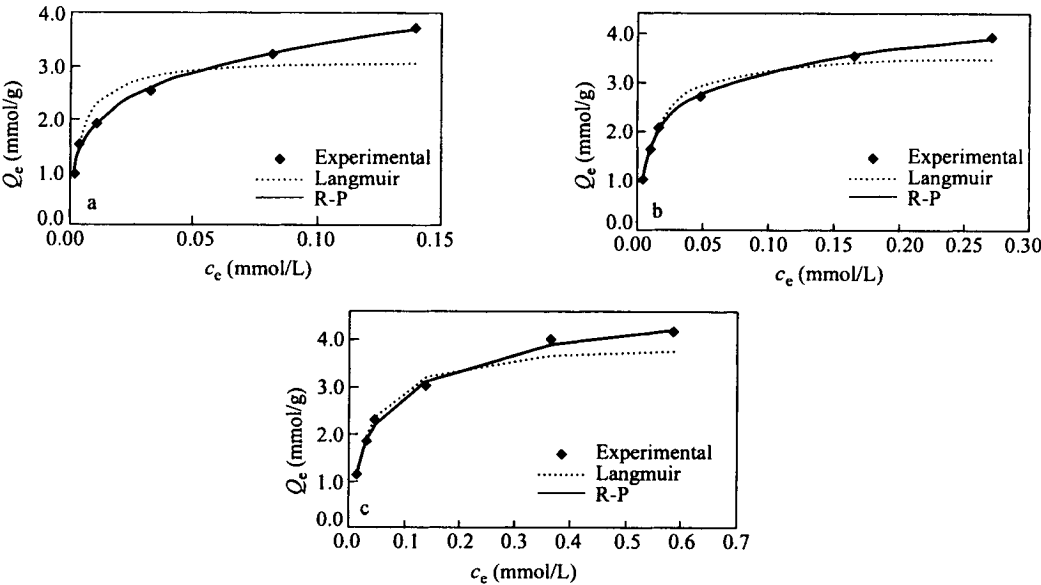


Fig. 1 Equilibrium adsorption data and fitting curves of adsorption of (a) 2-NSA, (b) *p*-CBSA, and (c) *p*-TSA with D301 at 293 K by different isotherm models

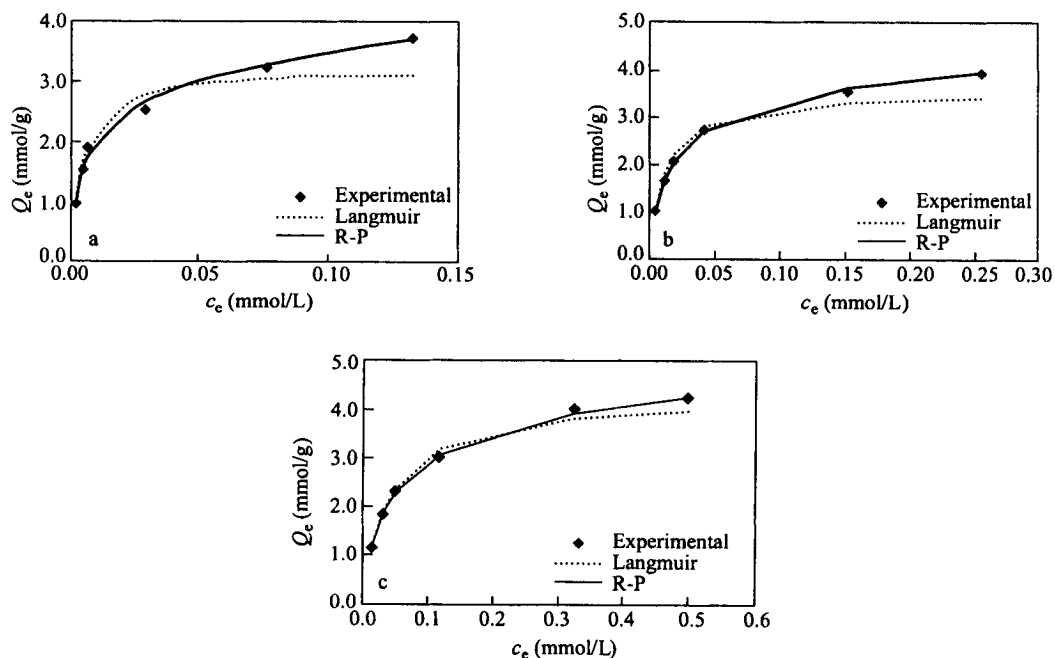


Fig. 2 Equilibrium adsorption data and fitting curves of adsorption of (a) 2-NSA, (b) *p*-CBSA and (c) *p*-TSA with D301 at 303 K by different isotherm models

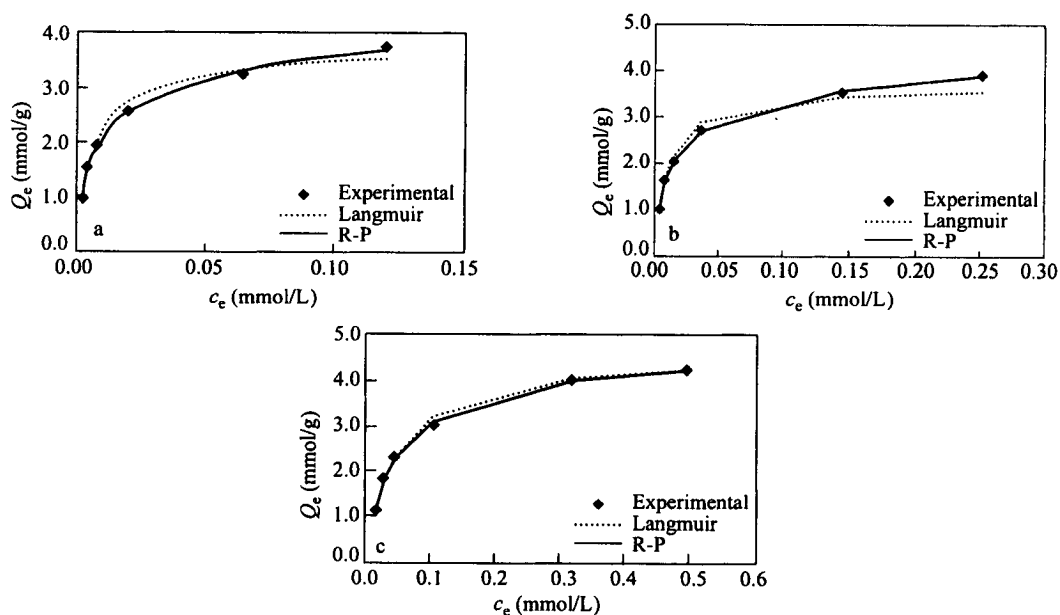


Fig. 3 Equilibrium adsorption data and fitting curves of adsorption of (a) 2-NSA, (b) *p*-CBSA, and (c) *p*-TSA with D301 at 313 K by different isotherm models

Adsorption Characteristics

Equilibrium data concerning adsorption of 2-NSA, *p*-CBSA and *p*-TSA from aqueous solutions, together with their corresponding fitting curves of R-P isotherm equations, are presented in Fig. 4.

Adsorption of aromatic sulfonic acids on a weak base resin follows a two-step mechanism^[14]. In the first

step, the amino groups of the resin (denoted by R) are protonated by H^+ ion of the acid, which results in the formation of a positively charged surface on the pore walls of the resin. In the second step, sulfonic anion association results from the electrostatic or Coulombic interaction between the positively charged RH^+ groups and the negatively charged anions of acids. Therefore, it is believed that the adsorption of aromatic sulfonic acids on D301 is mainly a result of electrostatic interaction, because 2-NSA, *p*-TSA and *p*-CSA acids are electrostatically identical and they both have one negative charge, and the adsorption capacities of 2-NSA, *p*-TSA or *p*-CBSA onto D301 resin should be identical from the electrostatic or Coulombic interaction viewpoint. However, the study shows obvious difference in adsorption capacities for 2-NSA, *p*-TSA and *p*-CBSA. As shown in Fig. 4, when the same equilibrium concentration of adsorbates is determined, the adsorption capacity has the following order: 2-NSA > *p*-CBSA > *p*-TSA. Such discrepancies, in general, may be attributed to hydrophobic interactions resulting from the nonpolar moiety (NPM) of the aromatic anions. The octanol-water partition coefficient (K_{ow}) of undissociated aromatic sulfonic acids may be a representative measure of the solute hydrophobicity. From Table 2, the K_{ow} of aromatic sulfonic acids was found to increase in the same order mentioned above. From the discussion above, it can be seen that the hydrophobic interaction between the matrix of polystyrene-divinylbenzene resin D301 and the NPM of aromatic anions plays a significant role in determining the adsorption capacity of a specific system. A similar hydrophobic interaction effect has also been observed for adsorption of various chlorophenols onto a polymeric anion exchanger^[15].

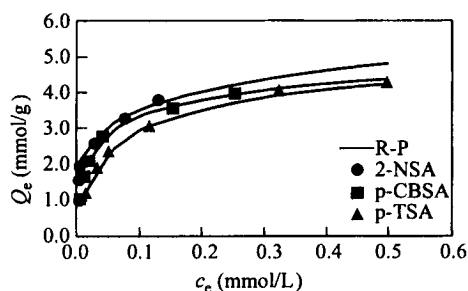


Fig. 4 Comparison of adsorption capacities of 2-NSA, *p*-TSA and *p*-CBSA onto D301 under identical conditions

Thermodynamic Parameters of Adsorption

Experiments on batch adsorption on D301 were carried out at 293 K, 303 K and 313 K, respectively. Estimations of the isosteric enthalpy changes of adsorption, as well as free energy and entropy changes of adsorption, were made from data interpolated using the best fitting isotherm, *i.e.*, the R-P isotherm equation.

The isosteric enthalpy changes of adsorption were calculated with a derivative Van't Hoff Eq.^[16]:

$$\ln\left(\frac{1}{c_e}\right) = -\frac{\Delta H}{RT} + \ln(K_0) \quad (6)$$

where ΔH is the isosteric enthalpy change of adsorption, R is the gas constant, and c_e is the equilibrium concentration of solute in mmol/L at the absolute temperature T . At different temperatures (293 K, 303 K and 313 K), the values of c_e were obtained from the well-fitted isotherms. ΔH was calculated from the slope of the line plotted as $\lg c_e$ versus $1/T$.

Values for the free energy change of adsorption can be obtained using an expression derived from the Gibbs adsorption isotherm^[16]:

$$\Delta G = -RT \int_0^X Q \frac{dx}{x} \quad (7)$$

where X represents the molar fraction of the adsorbate in solution, Q was then replaced by the R-P isotherm equation, and the final expression was integrated numerically using Romberg's algorithm.

Entropy variation values can be estimated using previously calculated ΔH and ΔG values and the Gibbs-Helmholtz equation^[16]:

$$\Delta S = (\Delta H - \Delta G) / T \quad (8)$$

Table 4 shows a summary of the estimated values for the three thermodynamic parameters of aromatic sulfonic acids. The following observations are noteworthy: (1) ΔG values are negative, confirming that the adsorption of the aromatic sulfonic acids onto the macroporous weak base anions exchanger is favorable. (2) When the aromatic sulfonic acids are dissolved in water, water molecules tend to form more structured clusters surrounding the hydrophobic NPM of the aromatic sulfonic acid anion^[17, 18]. Thereby, when the aromatic sulfonic acid anion is moved from water to the resin phase, the water clusters surrounding the NPM of the aromatic sulfonic acid anion break down and may lead to an increase of overall entropy. At the same time, the disruption of water–water hydrogen bonding in the more structured water clusters results in a positive enthalpy change. The positive ΔS and ΔH may verify occurrence of the predominantly hydrophobic interaction between the NPM of the aromatic sulfonic acid anion and the nonpolar matrix of D301 resin.

Table 4. Estimated thermodynamic parameters of the system

Adsorbate	Q_e (mmol $\cdot$ g ⁻¹)	ΔH (kJ $\cdot$ mol ⁻¹)	ΔG (kJ $\cdot$ mol ⁻¹)	ΔS (J $\cdot$ mol ⁻¹ $\cdot$ K ⁻¹)
2-NSA	3.5	11.58	-7.49	65.09
	2.5	17.84	-6.40	82.73
<i>p</i> -CBSA	3.5	8.03	-6.52	49.65
	2.5	8.22	-5.06	45.33
<i>p</i> -TSA	3.5	11.30	-5.86	58.58
	2.5	11.77	-2.90	59.92

CONCLUSIONS

The adsorption isotherm data for the three aromatic sulfonic acids on a macroporous weak base anion exchanger can satisfactorily fit with the Redlich-Peterson equation in the present study. The adsorption capacity follows the order: 2-NSA > *p*-CBSA > *p*-TSA. The discrepancy of adsorption capacity is mainly attributed to the hydrophobic matrix of aromatic sulfonic acids anions.

The negative values of free energy change show that the solute would be more concentrated on the adsorbent than in the bulk solution, and the adsorption is thus favorable. The adsorption of aromatic sulfonic acids onto macroporous weak base anion exchanger from aqueous solutions is an entropy-driven and endothermic process. The isosteric enthalpy (ΔH) and entropy change (ΔS) are both positive, implying a predominant hydrophobic interaction between the hydrophobic matrix of the ion exchanger and the NPM of the aromatic anions during the adsorption process. It was found that the equilibrium adsorption capacities (Q_e) increase with increasing octanol-water partition coefficient (K_{ow}), which is a representative measurement of the solute hydrophobicity.

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