

ADSORPTION OF LATERALLY INTERACTING 1-NAPHTHOL/1-NAPHTHYL-AMINE MIXTURES ON NONPOLAR SURFACES FROM AQUEOUS SOLUTIONS*

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Abstract The binary adsorption behavior of 1-naphthol/1-naphthylamine mixtures in water on nonpolar adsorbent Amberlite XAD4 was investigated at 293 K, 303 K and 313 K, respectively. The experimental uptakes of 1-naphthol and 1-naphthylamine in all binary-component systems of different molar ratios were obviously higher than the corresponding uptakes predicted by the extended Langmuir model, assuming no interaction between the adsorbed molecules of the two components. This phenomenon was attributed to the cooperative adsorption effect arising from the hydrogen bonding interaction between 1-naphthol and 1-naphthylamine molecules. A modified extended Langmuir model was proposed to describe the binary adsorption behavior by means of introducing a fitting parameter related with the cooperative adsorption effect of the adsorbates.

Keywords: Modified model; 1-Naphthol; 1-Naphthylamine; Adsorbate-adsorbate interaction; Cooperative effect.

INTRODUCTION

Different kinds of organic compounds are commonly found in contaminated water. Among them, aromatic compounds are regarded frequently as contaminants. Owing to their acute toxicity and poor biodegradability, 1-naphthol and 1-naphthylamine, representatives of naphthalene compounds, are the most crucially concerned contaminants and also the most important substructures of potentially carcinogenic pollutants discharged from pharmaceutical, dyestuff, photographic, and agrochemical industries. Therefore, efficient removal of aromatic compounds from waste streams has increasingly become a significant environmental concern^[1–3]. Adsorption is still a major pollution treatment method used for the elimination of organic compounds from water. In the past two decades, polymeric adsorbents, which possess wider variations on surface chemistry, surface area, and porosity than activated carbons, have been used as an alternative in industrial applications for efficiently removing and recovering the valuable aromatic compounds from wastewater. In order to increase the efficiency of polymeric adsorbents through a better knowledge of the interactions which take place between the adsorbent surface and the organic pollutant (single system or forming part of a multi-component system), various aspects such as the effect of polymer matrix and/or chemical surface characteristics, the contribution of dispersive-electrostatic forces on the adsorbate–adsorbent interaction, *etc.* are still under discussion^[4–11].

* This study was funded by the National Natural Science Foundation of China (No. 20274017) and the Natural Science Foundation of Jiangsu Province (No. BK2004415).

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Received January 24, 2005; Revised March 25, 2005; Accepted April 13, 2005

To study the involved interactions during the adsorption process, a single adsorbate is normally chosen. However, it is unrealistic to find only a single pollutant in wastewater. The multi-component nature of the mixture introduces additional complications, which require many new factors to be taken into account. Depending on the repulsive or attractive interactions between the adsorbates and the surface of adsorbents or among the adsorbates, the adsorption process of binary components tested is expected to be either competitive or cooperative. Though a few works have been published on the competitive adsorption of organic pollutants^[12–15] and even less works focused on the cooperative adsorption of organic, particularly aromatic compounds on polymeric adsorbents^[16, 17], the mechanisms worked behind the cooperative properties of aromatic compounds are not clear.

Therefore, through the adsorption behaviors of 1-naphthol and 1-naphthylamine on XAD4 in single or binary batch systems, the objective of the present work is to demonstrate the potential of a new modified model for correlating binary adsorption equilibria using a single binary fitting parameter, and to achieve a better qualitatively and quantitatively understanding on the interactions between the adsorbates and the surface of adsorbent or among the adsorbates.

EXPERIMENTAL

Materials

The aqueous solutions of adsorbates (containing 0.2% ethanol) were prepared by dissolving 1-naphthol and 1-naphthylamine (Shanghai Chemical Reagent Station, China) in ethanol and diluting by deionized water without further pH adjustment. The nonpolar adsorbent Amberlite XAD4 was supplied by Rohm & Haas (Philadelphia, PA, USA). Their specific surface area and pore size distribution were measured on an ASAP-2010C Micromeritics Instrument (USA) using nitrogen adsorption.

Characterization of Polymeric Beads

BET surface area and average pore diameter of the commercial adsorbent XAD4 are 714 m²/g and 5.8 nm, respectively. Its chemical structure of nonpolar polystyrene is believed to be favourable for the adsorption of aromatic compounds due to π - π dispersion interaction between the aromatic ring of the compounds and the phenyl ring of the polymer matrix^[18].

Adsorption Isotherms

Single component adsorption isotherms were determined using the conventional bottle-point technique at three temperatures (293 K, 303 K and 313 K). Batch adsorption runs were carried out in 100 mL glass flasks. Prior to use, XAD4 adsorbents were extracted with ethanol for 8 h in a Soxhlet apparatus and vacuum desiccated at 325 K for 24 h. Fixed adsorbent dosages of 0.050 g were directly introduced into a 100 mL glass flask. Subsequently 50 mL of an aqueous solution of 1-naphthol or 1-naphthylamine with an initial concentration ranging from 0.6 to 8 mmol/L was added into each flask.

The adsorption isotherms for binary-component system were conducted by following the above procedures except that the initial total mixtures concentrations of aqueous solutions were varied from 0.6 to 8 mmol/L with 75/25, 50/50 and 25/75 molar ratios of 1-naphthol/1-naphthylamine respectively. As an example, the isotherms of the mixtures of 75% of 1-naphthol and 25% of 1-naphthylamine are named as the molar fraction (y) of naphthol/naphthylamine mixtures 75/25.

The flasks were then transferred into a G25 model incubator shaker with thermostat (New Brunswick Scientific Co. Inc.) and shaken under 150 r/min for 24 h. Within this period the adsorption is sufficient to attain equilibrium according to preliminary kinetics studies at the given temperature. Because the values of pH at adsorption equilibrium in the tested single or binary-component systems are kept at 5 to 8, it is assumed that the different values of pH would not significantly influence the adsorption behavior of adsorbates. The amount adsorbed for 1-naphthol and 1-naphthylamine can be calculated by the following equation:

$$Q_e = V_1(c_0 - c_e) / 1000W \quad (1)$$

where c_0 and c_e denote the initial concentration (mmol/L) and the residual concentration at equilibrium (mmol/L) respectively, Q_e is the amount of adsorbed 1-naphthol or 1-naphthylamine on the adsorbents (mmol/g), V_l is the volume of the aqueous solution (mL), and W is the mass of the dry adsorbents (g).

The solution concentrations were determined using a Waters high performance liquid chromatography (HPLC), which was connected to Waters 600 controller, Waters 600 pump and Waters 2487 Dual Absorbance UV detector at 274 nm (Waters, USA). The mobile phase was 0.1% KH_2PO_4 - H_2O :methanol = 70:30 (V/V) and its flow rate was controlled at 1 mL/min.

THEORETICAL MODEL

Correlation of Single-component Isotherms

The adsorption of aromatic compounds on polymeric adsorbents in single-component system has been successfully described qualitatively and quantitatively by adopting several models^[19, 20], one of which is the Langmuir approach based on some assumptions, including the energetically homogeneous surface of adsorbents, no interaction between the adsorbed molecules, the identical mechanisms for adsorption, and a complete monolayer adsorption on the surface. Although all the assumptions are not typically met by aromatic compounds adsorption, the Langmuir model has been demonstrated to provide an accurate description of adsorption processes.

For single-component cases the Langmuir model (LM) is represented by Eq. (2):

$$\text{LM equation} \quad Q_e = \frac{K_l Q_m c_e}{1 + K_l c_e} \quad (2)$$

Moreover, the semi-exponential Freundlich model (FM) is also usually adopted:

$$\text{FM equation} \quad Q_e = K_f c_e^{1/n} \quad (3)$$

where Q_e is the amount adsorbed at equilibrium (mmol/g), c_e is the equilibrium concentration in bulk fluid phase (mmol/L), Q_m is the maximum adsorption capacity (mmol/g), namely complete coverage of available adsorption sites, K_l is the affinity constant; K_f is an indicator of adsorption capacity, and $1/n$ is related to the magnitude of the adsorption driving force and to the adsorbent site energy distribution^[11, 21].

Correlation of Binary-component Isotherms with ELM and MLM

For binary-component cases Extended Langmuir model (ELM) is the simplest and most widely used model, which is represented by Eq. (4):

$$\text{ELM Equation} \quad Q_{ei} = \frac{K_{li} Q_{mi} C_{ei}}{1 + K_{l1} C_{e1} + K_{l2} C_{e2}} \quad (i=1 \text{ or } 2) \quad (4)$$

where Q_{mi} and K_{li} are the model parameters (the subscripts 1 and 2 represents the two kinds of adsorbates, respectively), which can be derived from measurements made with single, pure compounds by using Eq. (2). It is particularly useful for multi-component systems composed of adsorbates which individually followed LM isotherms and gave reasonable estimates when the single adsorbate values Q_m agreed closely. However, the basic assumptions are not reasonable when $Q_{m1} \neq Q_{m2}$. An ELM isotherm derived from the parameters of single-component LM isotherms would not satisfy the Gibbs-Duhem relationship and would not be compatible with thermodynamics. In practice, poor results are obtained in such cases^[22].

Thus, for 1-naphthol/1-naphthylamine mixture adsorption systems the hydrogen bonding interaction between 1-naphthol and 1-naphthylamine was considered, and a Modified Extended Langmuir model (MLM) was developed by introducing a parameter, the cooperative efficiency (θ_i) of adsorbates, into Eq. (4):

$$\text{MLM equation} \quad Q_{ei} = \frac{K_{li} Q_{mi} c_{ei}}{1 + K_{l1} C_{e1} + K_{l2} C_{e2}} (1 + \theta_i) \quad (i=1 \text{ or } 2) \quad (5)$$

Assume that the cooperative efficiency (θ) arising from the adsorbate-adsorbate lateral interaction is linearly related with the amount adsorbed at equilibrium (Q_e) of the other adsorbate:

$$\begin{aligned}\theta_1(Q_{e2}) &= a_1 Q_{e2} + b_1 \\ \theta_2(Q_{e1}) &= a_2 Q_{e1} + b_2\end{aligned}\quad (6)$$

where a and b are constant parameters of cooperative efficiency (the subscripts 1 and 2 also represents the two kinds of adsorbates, respectively). By combining Eqs. (1), (5) and (6), the calculated amount adsorbed by 1-naphthol (Q_{ea}^{cal}) and 1-naphthylamine (Q_{eb}^{cal}) at equilibrium can be obtained:

$$\begin{aligned}Q_{ea}^{cal} &= \frac{K_{la} Q_{ma} c_{ea}}{1 + K_{la} c_{ea} + K_{lb} c_{eb}} (1 + a_a (c_{0b} - c_{eb}) V_1 / 1000W + b_a) \\ Q_{eb}^{cal} &= \frac{K_{lb} Q_{mb} c_{eb}}{1 + K_{la} c_{ea} + K_{lb} c_{eb}} (1 + a_b (c_{0a} - c_{ea}) V_1 / 1000W + b_b)\end{aligned}\quad (7)$$

where the subscripts a and b represents 1-naphthol and 1-naphthylamine, respectively; the superscripts cal and exp indicate calculated and experimental amounts adsorbed, respectively. Finally, correlation of binary-component adsorption isotherms of 1-naphthol/1-naphthylamine on nonpolar adsorbent is evaluated by the Chi-Square (χ^2) in the amount adsorbed, where Q_{ei}^{exp} and Q_{ei}^{cal} are obtained from experimental results and Eq. (7), respectively and n is the total number of experimental points:

$$\chi^2 = \frac{\sum_{i=1}^n (Q_{ei}^{exp} - Q_{ei}^{cal})^2 / Q_{ei}^{exp}}{n - 1}\quad (8)$$

RESULTS AND DISCUSSION

Correlation of Single-Component Adsorption Isotherms

The fitting parameters in each of these models were optimized to the experimental data simultaneously at all temperatures using the nonlinear regression method with Levenberg-Marquardt algorithm in the amount adsorbed. The experimental data and the optimized correlations for LM and FM models are plotted in Fig. 1. The regression parameters are given in Table 1, along with the corresponding χ^2 in the amount adsorbed. LM model gives the better results in correlating the single component adsorption equilibriums; therefore, it is expected to be strong competitor for the new model in correlating binary adsorption equilibriums. The single-component parameters from LM model are used below for the correlation (MLM) or prediction (ELM) of complex binary adsorption equilibriums.

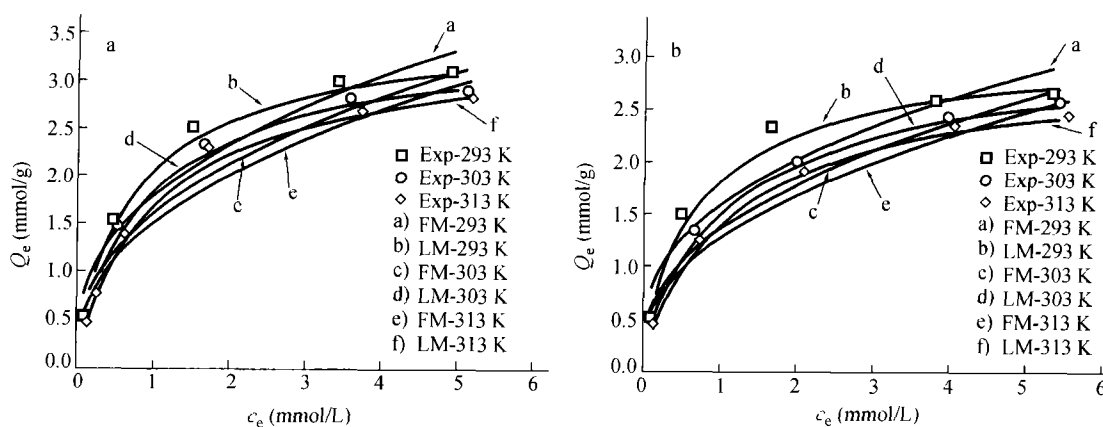


Fig. 1 Correlated (lines) and experimental (symbol) single-component adsorption isotherms of (a) 1-naphthol and (b) 1-naphthylamine on XAD4

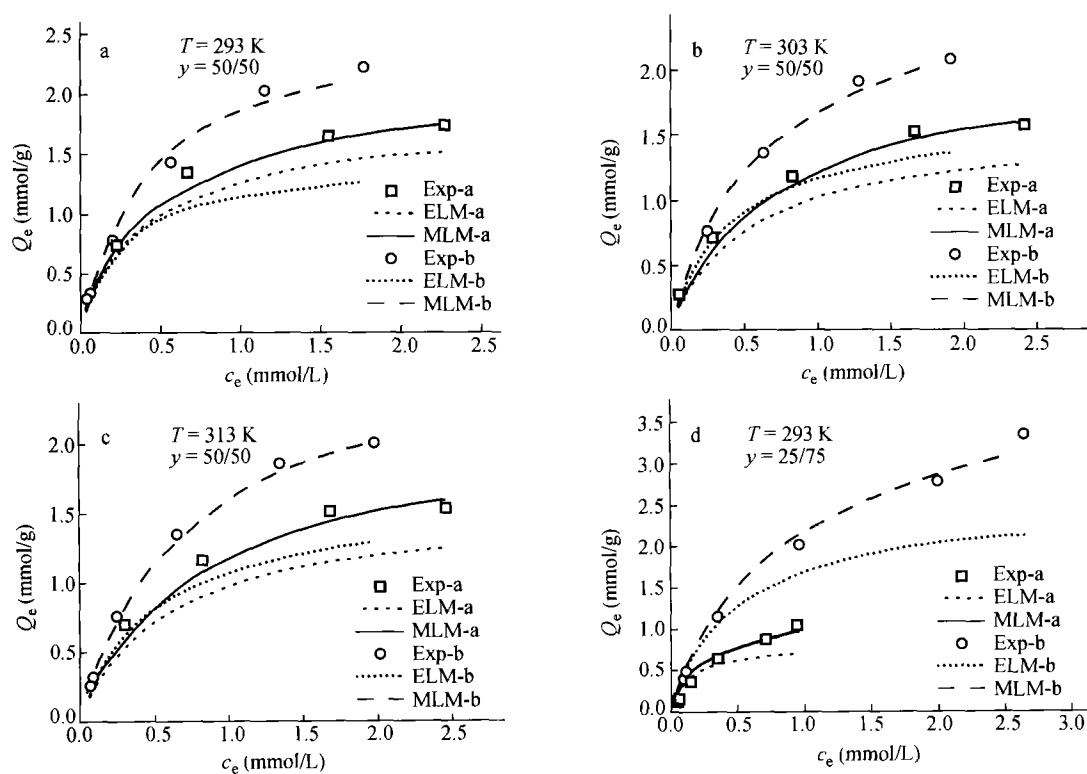
Table 1. The single-component adsorption isotherm parameters for FM and LM

Adsorbent	Adsorbate	Temp. (K)	LM			FM		
			K_1	Q_m (mmol/g)	χ^2	K_f	n	χ^2
XAD4	Naphthol	293	2.057	2.941	0.002	1.661	3.040	0.067
		303	1.285	2.887	0.003	1.402	2.589	0.023
		313	1.152	2.804	0.004	1.315	2.537	0.017
	Naphthylamine	293	1.922	3.391	0.003	1.877	2.836	0.055
		303	1.530	3.286	0.003	1.690	2.668	0.053
		313	1.275	3.246	0.001	1.573	2.549	0.043

As shown in Fig. 1 and Table 1, the adsorption capacity and affinity of 1-naphthylamine to XAD4 are much higher than those of 1-naphthol at 303 K and 313 K^[11]. This is probably due to the greater electronic density of its aromatic ring enhanced by the amino group of 1-naphthylamine molecule, whereas the hydroxyl group of 1-naphthol molecule reduces it. Because the nonpolar adsorbent absorbs the both compounds by π - π dispersion interaction between the aromatic ring of 1-naphthol or 1-naphthylamine and the phenyl ring of the adsorbent, the greater electron density in the ring supplies more π -electrons to interact with the adsorbent and accordingly increase the affinity of 1-naphthylamine to the adsorbent^[23]. In addition, the different water affinities of 1-naphthol or 1-naphthylamine cannot be ruled out.

Correlation of Binary-component Adsorption Isotherms

Figure 2 shows correlations with MLM and predictions with ELM for binary adsorption equilibria of 1-naphthol/1-naphthylamine on XAD4, the goodness of which was estimated using the χ^2 of Eq. (8) in the amount adsorbed. The optimum a values and the corresponding χ^2 for ELM and MLM are shown for each binary system in Table 2.



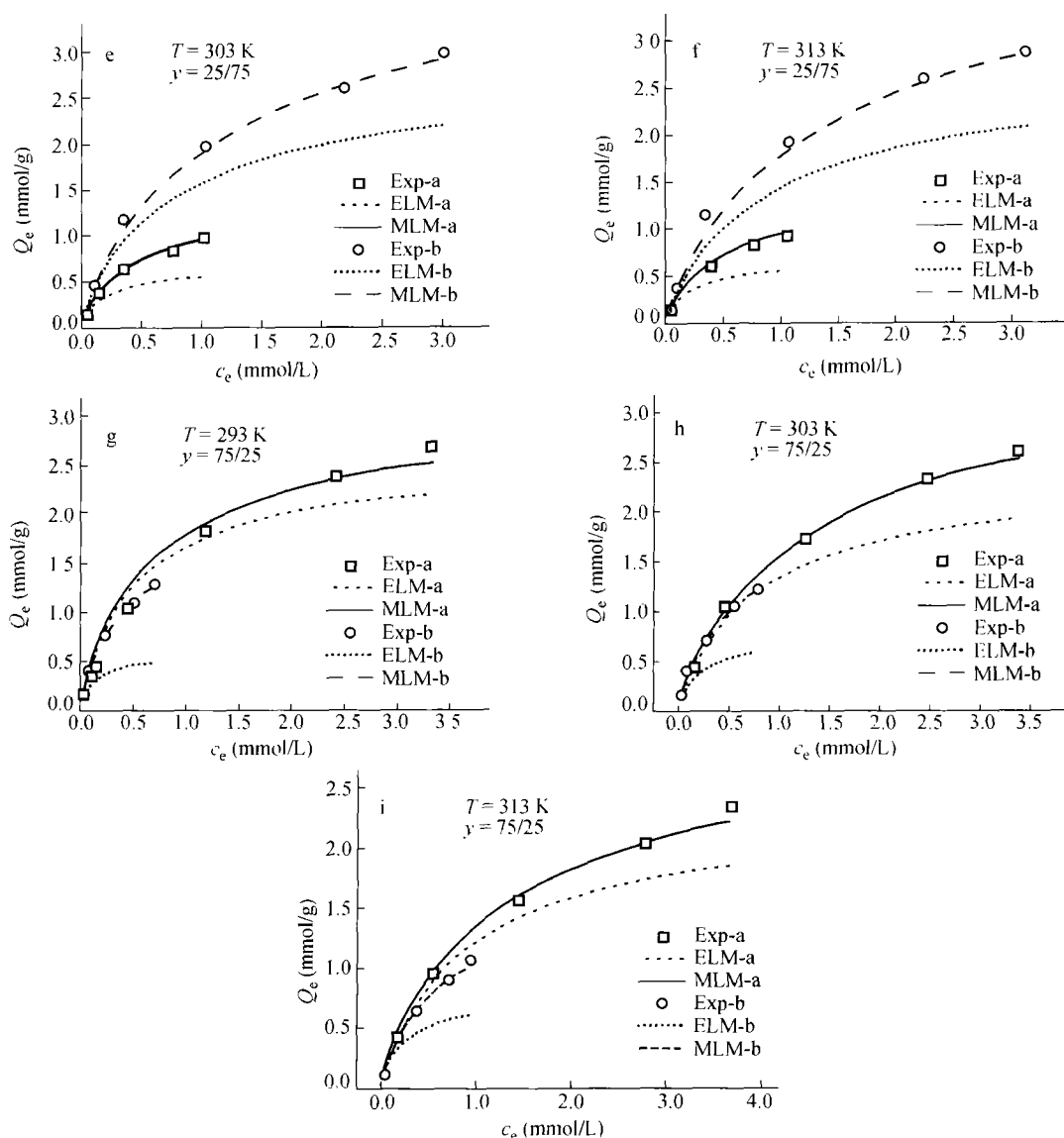


Fig. 2 Correlated MLM and predicted ELM versus experimental binary-component amounts adsorbed on XAD4

The subscripts a and b represents 1-naphthol and 1-naphthylamine, respectively; y means the molar fraction of 1-naphthol/1-naphthylamine in original solutions.

Considering that 1-naphthol and 1-naphthylamine have similar adsorption driving by π - π dispersion interaction on nonpolar surfaces when plotted alone as mentioned in the previous section, the parameter b of Eq. (7) can be assumed as zero, but it is most important that there is competitive adsorption between 1-naphthol and 1-naphthylamine for the similar adsorption sites^[12, 14]. While, as shown in Fig. 2, the experimental uptakes of 1-naphthol and 1-naphthylamine in all binary-component systems are obviously higher than the corresponding uptakes predicted from ELM, Eq. (4), using single component parameters, indicating the existence of the expected cooperative effect. Furthermore, the ability of MLM, which is referred to as ELM to correlate such complex binary adsorption equilibria, because of the remarkable flexibility introduced by the binary fitting parameter, a , is demonstrated here by fitting sample binary systems. The much less χ^2 values for MLM in Table 2 confirm that MLM is more suitable to describe the adsorption behaviors of 1-naphthol/1-naphthylamine mixtures

with adsorbate-adsorbate interactions. It also can be seen that the positive values of the cooperative efficiency (θ), given by the positive parameter a , quantitatively attest the expected cooperative effect on the 1-naphthol/1-naphthylamine mixtures adsorption in aqueous solutions. Moreover, the cooperative efficiency (θ) is mostly linearly related with the adsorbed amount of the other adsorbate.

Table 2. The optimized a and b values for ELM and MLM at XAD-4

Molar fraction (y)		Naphthol			Naphthylamine		
Naphthol/ Naphthylamine	Temp. (K)	a_a	χ^2		a_b	χ^2	
		MLM	ELM	MLM	MLM	ELM	MLM
75/25	293	0.114	0.091	0.050	0.436	0.245	0.001
	303	0.260	0.151	0.007	0.340	0.147	0.001
	313	0.189	0.061	0.008	0.405	0.071	0.002
50/50	293	0.069	0.024	0.002	0.584	0.368	0.016
	303	0.127	0.051	0.004	0.392	0.212	0.003
	313	0.142	0.056	0.004	0.296	0.227	0.000
25/75	293	0.109	0.036	0.010	0.400	0.414	0.035
	303	0.247	0.060	0.002	0.320	0.207	0.005
	313	0.254	0.047	0.003	0.360	0.240	0.004

The cooperative adsorption mechanism in the tested binary-component systems may be mainly attributed to the hydrogen-bonding interaction. It occurs between the lone pair of electrons on nitrogen of tertiary amino group of 1-naphthylamine and the hydrogen of hydroxyl group of 1-naphthol and can be treated as a Lewis acid-base interaction, which can decrease the free energy for adsorption, and the electrostatic repulsion between loaded 1-naphthol molecules or between loaded 1-naphthylamine molecules could be shielded and neutralized by each other, allowing a closer packing on the hydrophobic surface^[17]. Additionally, the outward amino group of 1-naphthylamine molecule or hydroxyl group of 1-naphthol molecule absorbed may form some new “hydrogen-bonding adsorption sites”.

CONCLUSIONS

The adsorption behaviors of 1-naphthol, 1-naphthylamine and 1-naphthol/1-naphthylamine mixtures in water on XAD4 were compared in single or binary batch systems at 293 K, 303 K and 313 K. The larger uptakes of 1-naphthylamine on XAD4 may be attributed to its greater electron density in the aromatic ring than that of 1-naphthol, which provides a stronger π - π dispersion interaction between the adsorbate and the adsorbent. The extra uptakes of 1-naphthol and 1-naphthylamine can be notably observed in binary adsorption systems and are attributed to the cooperative effect arising from the hydrogen-bonding association between adsorbates on the adsorbent surface.

A new modified Langmuir model developed to investigate the cooperative adsorption was correlated successfully with binary adsorption equilibria using only single component isotherm parameters and one binary fitting parameter. A remarkable accuracy was achieved for different molar ratio binary mixtures. The χ^2 values in the component amounts adsorbed were in all cases substantially lower than those obtained from the popular ELM. Moreover, this new model is easy to use, as it requires very little iteration to solve the implicit set of coupled algebraic equations. It should thus find considerable use in correlating binary adsorption equilibria from correlated single component and binary data.

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