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Sorption of BTEX mixtures to organobenonites

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Abstract: Organobentonites synthesized by replacing the metal ions in bentonite with cetyltrimethylammonium (CTMA) or tetramethylammonium cation(TMA) were investigated for their behaviors to sorb benzene, toluene, *p*-xylene from water. The results served to distinguish the sorption mechanisms(adsorption or partition) of the two types of organobentonites. Bentonites modified with short-chain alkyl functional groups(e.g., TMA) sorb organic contaminants primarily by an adsorption process, in which the sorbed amount decreases with increasing steric hindrance of the organic compound and the process exhibits a competitive effect because of steric hindrance in multi-solute systems. In contrast, the sorption of contaminants to organobentonites modified with long-chain alkyl groups (e.g., CTMA) occurs by partition process without exhibiting a competitive effect, and the additional organic compounds may induce a cosorptive effect. In the latter case, the measured distribution coefficients of organic compounds between organobentonites and water($\log K_d$) are positively correlated with the octanol-water partition coefficients of the compounds($\log K_{ow}$) and the sorption process exhibits no competitive effect in multi-solute systems.

Keywords: organobentonite; organic compounds; adsorption; partition

Introduction

Organobentonites, which may be obtained by substituting the inorganic cations with the quaternary ammonium cations at exchangeable sites of natural bentonites, could act as effective sorbents for organic contaminants due to their organophilic properties (Smith, 1990; Zhu, 1997). Recent studies (Smith, 1991; Zhu, 1998) have shown that this sorption is affected by several important factors, such as the contaminant(solute) properties and the molecular structure of exchanged organic cations. Sorption of organic compounds from water by organobentonites consists of either partition or adsorption (Boyd, 1988; Lee, 1990). The sorption mechanism for organobentonites having short-chain alkyl or aryl substituted groups is mainly by adsorption, while that for organobentonites exchanged with long-chain alkyl functional groups is essentially by partition (Smith, 1995). However, earlier studies focused on the behavior of single organic contaminants; there were few investigations on the sorption of solutes in multi-solute systems.

According to traditional surface-coverage or space-filling adsorption theory, the amount adsorbed for a given solute in multi-solute systems would be less than that in single-solute systems because of the adsorptive competition. Rytwo (Rytwo, 2001) suggested that the molecular structure of a sorbed organic compound affects the sorption behavior of organobentonites; for example, acriflavin can sorb more easily than can diquat. However, an earlier study (Sheng, 1996) indicated that the sorption of organic compounds to the organic fraction of an organically could improve the clay's organic-phase sorption capacity, implyingthat the sorption of an organic compound can be enhanced by the presorption of another organic compound. The above studies indicated that the sorption of mixed organic compounds by organobentonites is generally different from that by surface adsorption, which exhibits a competitive effect between the compounds. We could deduce from the sorption data which uptake mechanism is involved for an organobentonite, as an adsorption process would be competitive and affected by molecular structure of organic contaminants, e.g., by the steric hindrance in the multi-solutes. By contrast the sorption by organobentonite involving partition would not exhibit competitive in multi-solute systems, and the presence of other organic compounds could lead to a cosorptive effect. Therefore, investigating the sorption of multiple solutes to organobentonites could help expound the sorption process of an organobentonite, which offers a new method for distinguishing the two-sorption mechanisms. In order to understand the multi-solute sorption by organobentonites, we used 100TMAB-bentonites and 100CTMAB-bentonites as our model organoclays to investigate the sorption of multi-solutes.

1 Materials and methods

Bentonite used was prepared from primarily Na^+-montmorillonite as the starting material by first drying and grinding the sample into powder (100-mesh). Its cation-exchange capacity (CEC) was determined with the $BaCl_2$-triethanolamine method to be 90 mmol/100 g. The reagents and chemicals were purchased from Shanghai Chemical Reagent Co. Ltd. Cetyltrimethylammonium bromide (CTMAB) and tetramethylammonium bromide(TMAB) were of analytical grade. Benzene, toluene and *p*-xylene were of chromatogram grade.

1.1 Analytical methods

The concentration of benzene, toluene and *p*-xylene in aqueous solution were determined by GC, the detection limits being 0.9, 2.9, and 3.8 mg/L respectively. Gas chromatography was carried out on a model 9790-WLFX gas chromatograph equipped with a flame ionization detector. The column used was packed with DNP and Bentane. Carrier gas was high-purity nitrogen at a flow of 50 ml/min. The oven temperature was 80℃. Operating temperatures for the injection port and detector were 200℃. All sorption measurements were carried out in duplicate.

1.2 Preparations of organobentonite

Organobentonites were synthesized from bentonite by

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reacting with aqueous solutions containing a given type of quaternary ammonium cation. First, a total of 20 g previously dried bentonite was mixed with 200 ml aqueous solution that contains different amounts of a quaternary ammonium cation. The mixtures were then subject to mechanically stirring for 2 h in a 60—70℃ water bath. The resultant bentonites were separated from aqueous solution by vacuum filtration and rinsed twice with distilled water. Finally, the obtained organobentonites were dried at 80—90℃, activated for 1 h at 105℃, and mechanically ground with a mortar and pestle to less than 100 mesh.

The resulting organobentonites are identified by a prefix that indicates the percent of the bentonite's CEC satisfied by the organic cation followed by the abbreviation for the specific type of organic cation. Thus, for example, 100TMAB refers to an organobentonite that has 100% of its CEC satisfied by tetramethylammonium cations.

1.3 Procedures for water treatment

A batch equilibration method was used to quantify BTEX sorption to the organobentonites. Eight initial concentrations were prepared in the range 20 to 200 mg/L for benzene, 10 to 100 mg/L for toluene and *p*-xylene. A total of 0.20 g organobentonite was first mixed with 10 ml solution containing the organic contaminants in a 25 ml glass centrifuge tubes with caps. The isotherms of binary mixtures were obtained as follows: aqueous solutions (10 ml) at eight initial concentrations of benzene in the range of 20 to 200 mg/L and of toluene or *p*-xylene in range of 10 to 100 mg/L, toluene in the range of 10 to 100 mg/L and of *p*-xylene in range of 10 to 100 mg/L were added simultaneously to the glass centrifuge tubes. The added amounts of benzene and toluene, or benzene and *p*-xylene, or toluene and *p*-xylene corresponded to about the same relative concentrations for each solute. The suspension was then shaken for 1 h at 25℃ on a gyratory shaker(THZ-C) at a speed of 150 r/min. Preliminary kinetic investigations indicated that sorption equilibrium was reached in less than 45 min. After centrifugation, the concentration of an organic compound in the aqueous phase was determined by GC. To obtain the amount sorbed by the organobentonite, a control experiment without organobentonite was carried out in parallel, with which the losses of a sorbate(contaminant) by vaporization and adsorption to glass centrifuge tube were measured. In all cases, the losses of benzene, toluene and *p*-xylene were found to be 14.8%, 8.7%, and 16.7%, respectively. The above experiments were repeated three times and the results were relatively reproducible.

2 Results and discussion

2.1 Sorption of single solute

Capacities of 100TMAB-bentonite and 100CTMAB-bentonite to sorb benzene, toluene and *p*-xylene from water are shown by the isotherms shown in Fig.1 and Fig.2. The sorption data are fitted with a linear equation over the range of experimental concentrations as:

$$Q = KC_e + A, \qquad (1)$$

where Q is the sorbed amount of organic compounds to the organobentonite(mg/g), C_e is the equilibrium concentration of the solute(mg/L) in aqueous phase; K and A are two fitted parameters. As could be seen from the figures, the experimental data are well represented by the linear regression. The linear constants K and A obtained are presented in Table 1.

Table 1 Formulas and properties of organic compounds

Organic compound	Molecular weight	S, mg/L	$\lg K_{ow}$
Benzene	78.12	1755	2.13
Toluene	92.14	542	2.73
p-xylene	106.17	202	3.15

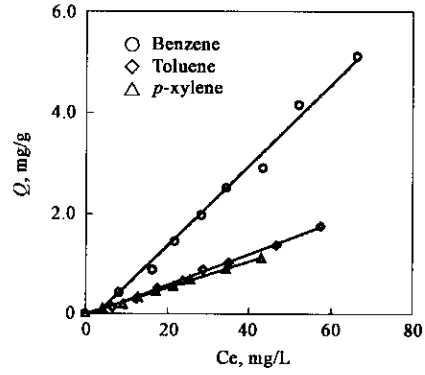

Fig.1 Sorption isotherms of benzene, toluene and *p*-xylene on 100TMAB-bentonites

As shown in Table 1, Table 2 and Fig.1 and Fig.2, the sorption capabilities of BTEX to 100TMAB-organobentonite, which contains short-chain alkyl functional groups, are related to the molecular structures of contaminants, in which the sorption amount Q decreases with an increase in the steric hindrance of the compound, viz. benzene > toluene > *p*-xylene. It suggested that the uptake mechanism is adsorption. However, the uptake mechanism of 100CTMAB-organobentonite, which contains long-chain alkyl functional groups, is by partition. Fig. 3 shows that the distribution coefficient($\log K_d$) of organic compound between organobentonites and water is positively correlated with the corresponding $\log K_{ow}$ (K_{ow} is octanol-water partition

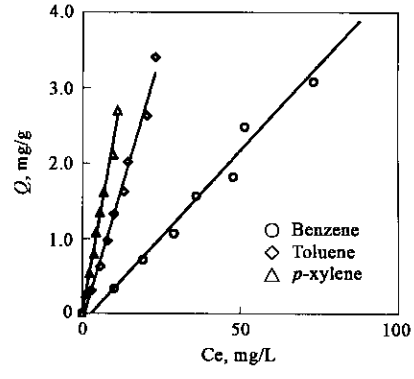

Fig.2 Sorption isotherms of benzene, toluene and *p*-xylene on 100CTMAB-bentonites

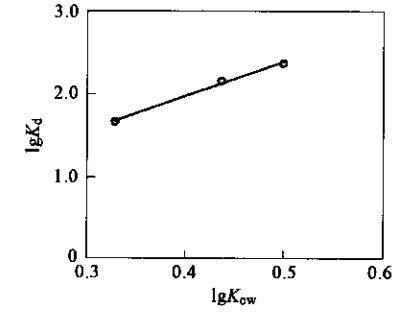

Fig.3 Relationships between $\lg K_{ow}$ and $\lg K_d$

coefficients of the organic compound). Compared to benzene, toluene and *p*-xylene, with a larger ring size would have a higher hydrophobicity and organophilicity, and thus have an increased partition affinity.

Table 2 Regression data for sorption isotherms and partition coefficients(K_d)

Organobentonite	Target compound	Solution	Regression equation (Q: mg/g, C_e: mg/L)	Correlation coeffient	K_d
100TMAB	Benzene	Single solute	$Q = 0.0797C_e - 0.2370$	0.994	79.7
	Toluene		$Q = 0.0309C_e - 0.0458$	0.999	30.9
	p-xylene		$Q = 0.0263C_e - 0.0088$	0.999	26.3
100CTMAB	Benzene		$Q = 0.0460C_e - 0.1352$	0.993	46.0
	Toluene		$Q = 0.1437C_e - 0.1236$	0.994	144
	p-xylene		$Q = 0.2356C_e - 0.0018$	0.996	236
100TMAB	Benzene	Benzene, toluene	$Q = 0.0877C_e - 0.4962$	0.987	87.7
	Toluene		$Q = 0.0251C_e - 0.0397$	0.998	25.1
	Benzene	Benzene, *p*-xylene	$Q = 0.0908C_e - 0.4160$	0.991	90.8
	p-xylene		$Q = 0.0221C_e - 0.0342$	0.997	22.1
100CTMAB	Benzene	Benzene, toluene	$Q = 0.0557C_e - 0.1935$	0.995	55.7
	Toluene		$Q = 0.1666C_e - 0.1663$	0.994	167
	Benzene	Benzene, *p*-xylene	$Q = 0.0502C_e - 0.1815$	0.997	50.2
	p-xylene		$Q = 0.2722C_e - 0.0272$	0.990	272

2.2 Sorption of solutes to organobentonites by adsorption

With benzene, toluene and *p*-xylene as sorbates, the sorption of single solutes and of two series of binary solutes, i.e., benzene/*p*-xylene and benzene/toluene by 100TMAB-organobentonites were examined. The sorption isotherms are shown in Fig. 4—6, and regression constants from experimental data are shown in Table 2. We could see from Fig.4—6 that the sorption capacity of benzene in the binary-solute(benzene + xylene) solution was greater than in single-solute solution, but the sorption capacity of toluene or *p*-xylene in binary-solute(toluene or *p*-xylene) solution is less than in single-solute solution (toluene or *p*-xylen). The reason might be that toluene or *p*-xylene is subject to a greater steric hindrance than benzene in multi-solute sorption; it is a weaker solute compared to benzene due to its weaker tendency to occupy adsorption sites(Lee, 1990). So the sorption of *p*-xylene or toluene does not effectively occupy sites on the surface of organobentonites. Because of the large steric hindrance for toluene or *p*-xylene due to its large molecular structure, the solute sorption would be reduced by the presence of other solutes as a result of competition between multiple solutes for available adsorption sites. This was corresponding to organobentonite, which modified by short-chain alkyl functional groups that remove organic contaminants from solution primarily by an adsorption process. That is, in the binary-solute system(i.e. benzene/toluene, benzene/*p*-xylene), the sorption of molecules with weaker steric hindrance(i.e. benzene) to organobentonites is primarily by an adsorption process, which is influenced little by solutes with stronger steric hindrance(i.e. toluene, *p*-xylene). On the other hand, the sorption capacity of molecules with a greater steric effect (i.e. toluene, *p*-xylene) will be reduced by co-existing molecules with weaker steric hindrance(i.e. benzene).

2.3 Sorption of solutes to organobentonites by partition

With benzene, toluene and *p*-xylene as model sorbates, the sorption of single solutes and of two series of multi-solutes, i.e., benzene/toluene and benzene/*p*-xylene, by 100CTMAB-organo-bentonites were examined. The sorption isotherms are shown in Fig.7—9, and the parameters from linear regression are presented in Table 2. From the sorption isotherms we could see that the sorption capacity of benzene,

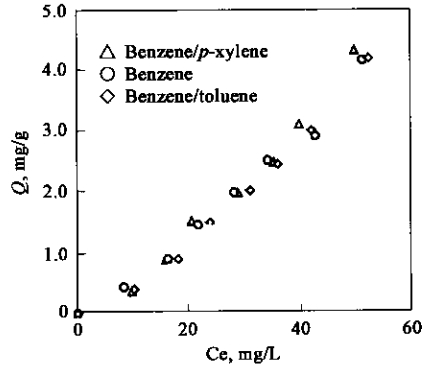

Fig.4 Sorption isotherms of benzene on 100TMAB-bentonites

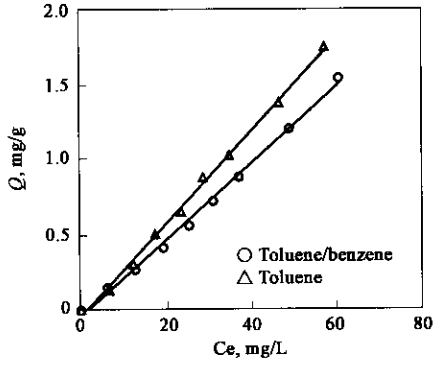

Fig.5 Sorption isotherms of toluene on 100TMAB-bentonites

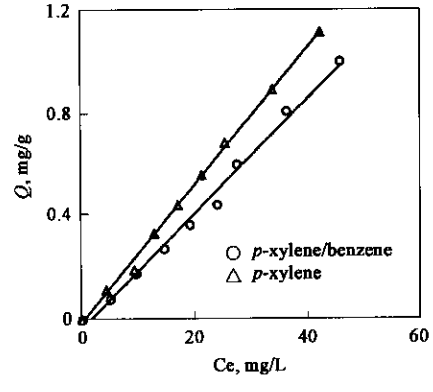

Fig.6 Sorption isotherms of *p*-xylene on 100TMAB-bentonites

toluene or *p*-xylene is larger in binary-solute solution than in single-solute solution. This suggests that the sorption mechanism of organic compound to 100CTMAB-organobentonites does not occupy adsorption sites. Thus we might conclude that the sorption of organic compounds enhances the organic matter content of 100CTMAB-organobentonite, which induces an enhanced partitioning of other organic compounds, i.e., the sorption of two organic compounds could result in a cooperative effect. This effect could be related to the molecular structures of the solutes. The Π bond in aromatic compounds produces a dipole, which could interact with the dipole between cation and bentonite. This interaction between the dipoles increases the distance between layers in bentonites, which makes it easier for molecules to enter the bentonite, thus enhancing the partition capacity. This effect applies to organobentonites that contain long-chain alkyl functional groups that sorb contaminants primarily by a partition process. That is, in the binary-solute system (i.e. benzene/toluene or benzene/*p*-xylene), the 100CTMAB-organobentonite sorbs contaminants by a partition process without exhibiting a competitive effect, and the additional organic compounds may induce a cosorptive effect.

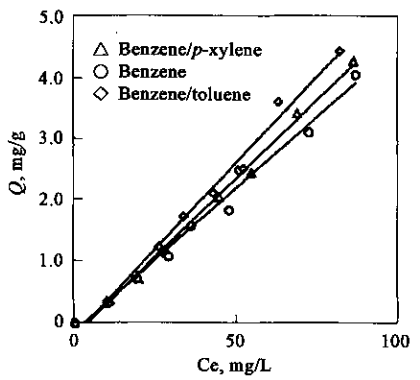

Fig.7 Sorption isotherms of benzene on 100CTMAB-bentonites

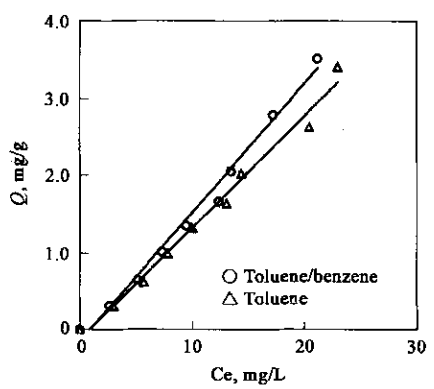

Fig.8 Sorption isotherms of toluene on 100CTMAB-bentonites

3 Conclusions

Single-solute and multi-solute sorption by organobentonites is presented in this study. The observed sorption

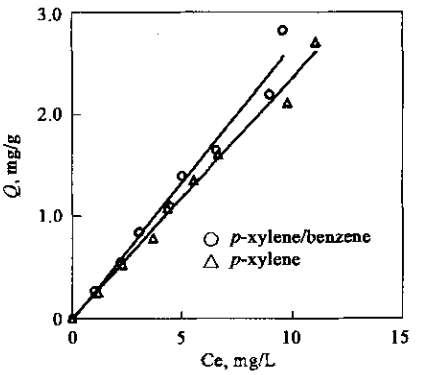

Fig.9 Sorption isotherms of *p*-xylene on 100CTMAB-bentonites

data are characteristic of the uptake mechanisms of organic contaminants with two types of organobentonites (100TMAB and 100CTMAB). Over the range of experimental concentrations, 100TMAB with short-chain alkyl functional groups removes organic contaminants from solution primarily by an adsorption process, in which the sorbed amount Q decreases with the increasing steric hindrance of the organic compound and the sorption exhibits a competitive effect. In contrast, the contaminant uptake by 100CTMAB, which possesses long-chain alkyl groups, is via partition. In the latter system, the distribution coefficients ($\log K_d$) of organic compounds between organobentonite and water are positively correlated to $\log K_{ow}$, and no competitive sorption between the solutes is observed.

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