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# Chemical behavior of organic compounds in the interface of water/dual-cation organobentonite

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**Abstract** The sorption behavior of polar or ionizable organic compounds, such as *p*-nitrophenol, phenol and aniline, in the water/organobentonite systems is investigated. Both adsorption and partition occur to the sorption of organic compounds to dual-cation organobentonites. The separate contributions of adsorption and partition to the total sorption of organic compounds to dual-cation organobentonites are analyzed mathematically in the first time. The factors to the contributions are also discussed. The results indicated that the contribution of adsorption and partition is related to the composition and ratio of dual-cation surfactants exchanging onto the bentonite. The sorption of organic compounds to dual-cation organobentonite is dominated by adsorption at low concentrations and by partition at high concentrations, making the organobentonites powerful sorbents for organic contaminants over wide range of concentrations.

**Keywords:** dual-cation organobentonite; *p*-nitrophenol; phenol; aniline; sorption behavior

## Introduction

Nonaqueous-phase (immiscible) organic liquids (NAPL) are known to be a serious groundwater pollution problem (Mercer, 1990; National Research Council, 1994). Typical NAPLs include spent solvents, fuels, pesticides, and coal tars. The widespread occurrence of hydrophobic organic compounds (HOCs) in soils and groundwaters has led to intensive studies of the mobility and fate of these contaminants in subsurface environments and of their remediation potential. Organobentonite has excellent potential to remediation of groundwater pollution and treatment of non-biodegraded organic pollutant (Xu, 1997). So far, studies and applications of organobentonite is mostly limited to single-cation organobentonites.

The sorption properties of organobentonites depend greatly on the characteristics of the exchanged organic cations (Smith, 1990; Boyd, 1988; Zhu, 1997; 1998). Smith *et al.* (Smith, 1990; 1995) demonstrated that tetrachloromethane sorption to bentonite modified by exchanged small organic cations was exhibited by nonlinear isotherms, strong solute uptake, and competitive sorption. In contrast, tetrachloromethane sorption to bentonites modified by relatively large organic cations ( $C > 10$ ) exhibited by essentially linear isotherms, lower solute uptake, and noncompetitive sorption. The differences between the two groups of organoclay sorbents were attributable to different sorption mechanisms: adsorption for bentonite modified with organic cations of small functional groups and partition for bentonite modified with organic cations of relatively large functional groups. So both partition and adsorption should occur to sorption of organic compounds to a hybrid organobentonite, or a dual-cation organobentonite, wherein some fraction of its cation-exchange capacity is satisfied by quaternary ammonium cations with short-chain functional groups and another fraction of the cation-exchange capacity is satisfied by quaternary ammonium cations with a long-chain hydrocarbon group. However few studies were conducted to the sorption characteristics of dual-cation organobentonite. Smith *et al.* (Smith, 1995) and Zhu (Zhu, 1999; 2000) discussed the sorption properties of organic contaminants to dual-cation organobentonites. The results indicated that dual-cation organobentonites function primarily as adsorbent at low solute concentrations and as a partition medium at high solute concentrations, and would be useful for contamination involving only a few contaminants or a wide range of contaminants. Sorption capacity and rate of organic compounds to

organobentonite is directly related to the sorption behavior at the interface of water/organobentonite.

In recent years there has been increasing scientific concern with the sorption behavior of organic pollutants in multi-medium environment. It will become one of hot point of environmental research not only nowadays but also 21st century. But now environmental scientists pay close attention to the sorption behavior of organic compounds in the water/sediments (suspended particles). It is significant to comprehensively understand the transfer, change, fate and bioecological effect of organic compounds in multi-medium environment, and to take measures for the prevention and cure of pollution.

Whether studies for sorption characteristics of organobentonite or sorption mechanisms of multi-medium environment, people believe that both adsorption and partition occur to the sorption of organic pollutants to organobentonite or sediments. But it stays in qualitative recognition.

This paper studied the sorption behavior of polar or ionizable organic compounds, such as phenol, *p*-nitrophenol, and aniline, in the interface of water/organobentonite (dual-cation organobentonite). The objective of this study is to describe quantitatively the contribution of adsorption and partition to the total sorption of organic contaminants from water using a mathematics-analogue method. Trying to perfect the theory of partition. Comprehensively understanding the transfer, change, fate, bioecological effect of organic compounds in multi-medium environment. Provide academic basis for exploited news-style and effective organobentonite, and applied to remedy soils and groundwater pollution.

## 1 Materials and methods

### 1.1 Materials

Bentonite used was primarily Na<sup>+</sup>-montmorillonite from Zhejiang, China. Its cation exchange capacity (CEC) is 60 meq/100g bentonite. Cetyltrimethylammonium bromide (CTMAB), tetramethylammonium bromide (TMAB), *p*-nitrophenol, phenol, and aniline used were of analytical grade. Dodecyltrimethylammonium bromide (DTMAB, 95%), tetradecylbenzyltrimethylammonium chloride (BDTDA, 90%), and octodecyltrimethylammonium bromide (OTMAB, 80%) used were of industrial grade; they were purified before used for synthesizing organobentonites. Organic cation's structures are presented in Fig.1.

### 1.2 Analytical methods

*p*-nitrophenol, phenol, and aniline concentrations in water were analyzed by ultraviolet spectrophotometry, the detection limits being 0.05, 0.1, and 0.12 μg/ml, respectively.

### 1.3 Preparations of dual-cation organobentonite

A series of single-cation and dual-cation organobentonites were synthesized by reacting bentonite with aqueous solutions containing either one or two kinds of quaternary ammonium cations. A total of 40g of previously dried bentonite were mixed with 400 ml aqueous solutions of various kinds and amounts of one or two quaternary ammonium cations. The mixtures were subjected to

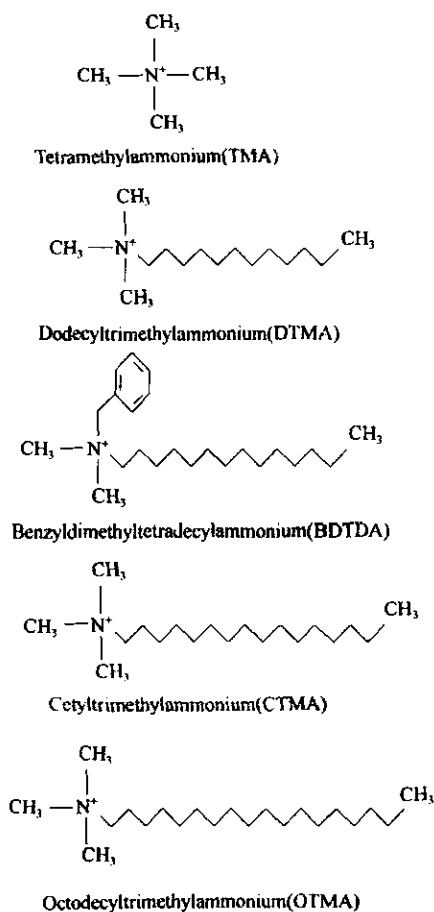


Fig.1 Chemical structure of quaternary ammonium cations used to prepare organoclays

mechanical stirring for 2h in a 60 – 70°C water bath. The treated bentonites were separated from water by vacuum filtration and washed twice by distilled water. The organobentonites were dried at 80 – 90°C, activated for 1h at 105°C, and mechanically ground with a mortar and pestle to less than 100 mesh.

The resulting organobentonites are identified by a prefix that states the percent of the bentonite's cation-exchange capacity satisfied by the organic cation followed by the abbreviation for the specific type of organic cation. For example, 40 TMAB identifies an organobentonite that has 40% of its cation-exchange capacity satisfied by tetramethylammonium cations. In cases where dual types of cations were exchanged onto the bentonite, two abbreviations of the specific types of organic cations are used to identify the resulting organobentonite. For example, 40TMAB/40DTMAB identifies an organobentonite that has 40% of its cation-exchange capacity satisfied by tetramethylammonium cations and an additional 40% satisfied by dodecyltrimethylammonium cations.

#### 1.4 Procedures for water treatment

A total of 0.50g of single-, or dual-cation organobentonite was combined with 25 ml of solution with an appropriate concentration of organic contaminant in 150 ml Erlenmeyer flasks with glass caps. The flasks were shaken for 1h at 25°C on a gyratory shaker at 150 r/min. After being centrifuged, the organic compound concentration in the aqueous phase was determined by ultraviolet spectrophotometry. The removal rates and sorption amounts for single-, or dual-cation organobentonites to treat the organic compounds in water were calculated. The losses of the compounds by both photochemical decomposition and sorption to the Erlenmeyer flask were found to be negligible. The volatilization losses of organic compounds were analyzed by contrasting to the blank with no shaking and centrifugation. The results showed insignificant volatilization losses of phenol, *p*-nitrophenol, and aniline by shaking and centrifuging.

## 2 Results and discussion

### 2.1 Organic carbon contents analysis

The properties of natural bentonite and a series of single-, or dual-cation organobentonites were characterized by organic-carbon-content analysis using LECO CS-344 type Carbon-Sulphate analyzer at the condition of 50% relative humidity and 25°C. The results are shown in Table 1.

### 2.2 Properties of organic compounds

Properties of organic pollutants, such as octanol-water partition coefficient ( $K_{ow}$ ), aqueous solubility, and partition coefficient ( $K_{oc}$ ) on bentonite normalized by the organic carbon content ( $K_{oc} = K_d/f_{oc}$ ), affected sorption of them to the same single-, or dual-cation organobentonite from water. Octanol-water partition coefficients ( $K_{ow}$ ), aqueous solubility(S) and partition coefficients ( $K_{oc}$ ) of organic compounds are presented in Table 2.

**Table 2** Octanol-water partition coefficients ( $K_{ow}$ ), aqueous solubility(S) and partition coefficients ( $K_{oc}$ ) of organic compounds

Organic compounds	<i>p</i> -nitrophenol	Phenol	Aniline
Octanol-water partition coefficient, $K_{ow}$	93	30	7.9
Aqueous solubility, $\mu\text{g/ml}$	$1.6 \times 10^4$	$9.3 \times 10^4$	$3.6 \times 10^4$
Partition coefficient, $K_{oc}$	35	14.2	4.90

**Table 1** The organic carbon contents of natural bentonite and dual-cation organobentonites

Clay type	Organic carbon contents, %	Clay type	Organic carbon contents, %
Natural bentonite	0.057	40TMA/60DTMA	12.335
40TMA	2.234	40TMA/20BDTDA	8.285
40DTMA	9.605	40TMA/20CTMA	8.784
40TMA/20DTMA	6.408	40TMA/20OTMA	9.225
40TMA/40DTMA	9.685		

### 2.3 Optimal conditions for dual-cation organobentonite to remove organic compounds from water

The removal rates for dual-cation organobentonite to treat aqueous solution containing phenol,

or *p*-nitrophenol, or aniline were not much different over the pH range 2 – 12. The *pK*<sub>a</sub> values of phenol, and *p*-nitrophenol are 9.96 and 7.16, respectively. At pH < *pK*<sub>a</sub>, the removal rates of dual-cation organobentonites for phenol and *p*-nitrophenol remained unchanged. At pH > *pK*<sub>a</sub>, the removal rates were greatly increased. The aqueous solutions of organic compounds and organobentonites were adjusted to pH 7 in consideration of their applications for wastewater treatment.

The removal percentages of organic compounds by dual-cation organobentonite varied with time at pH 7 and 150 *r*/min in shaking. However, the removal rates of organic compounds from aqueous solution were basically invariant after the flasks were shaken for 30 min. Thus, the shaking time was setup to be 1h in the following experiments. In addition, the effects of the amounts of dual-cation organobentonites used in water treatment were also investigated. The removal rates increased gradually with the increasing amounts of the dual-cation organobentonite used in the water treatment. The amount of the dual-cation organobentonite was selected as 0.5g/25 ml aqueous solution in the following experiments in consideration of both the removal rates and treatment cost.

## 2.4 Contribution of adsorption and partition to total sorption

Isothermal sorption curves for single-, or dual-cation organobentonites to sorb *p*-phenol, phenol and aniline at pH 7 are plotted. Different initial concentration ranges of organic compounds were used because of their different solubilities. The initial concentration of *p*-nitrophenol, phenol, and aniline were less than 10000, 30000, and 20000 mg/ml, respectively. All experimental batch sorption data were fit to a sorption model using nonlinear least-squares regression. Table 3 presents the results of the nonlinear regression analyses with the logarithmic equations for the different solute-organobentonite combinations considered in this research.

Sorption of organic compounds to dual-cation organobentonites is affected by both adsorption and partition, and the contributions being a function of the types and amounts of incorporated quaternary ammonium cations (Campell, 1985). Thus, total sorption amount ( $Q_T$ ) of organic compounds to dual-cation organobentonites can be defined as follows:

$$Q_T = Q_A + Q_P. \quad (1)$$

The regression equations of organic compound sorption to dual-cation organobentonite conform to the model as follows:

$$Q_T = a \ln C_e + b. \quad (2)$$

**Table 3** Regression data for sorption isotherms of organic compounds on dual-cation organobentonites

Organic compounds	Clay type	Regression equations ( $Q$ : mg/g; $C_e$ : $\mu$ g/ml)	Correlation coefficients
<i>p</i> -nitrophenol	Natural bentonite	$Q = 3.3716 \ln C_e + 1.9355$	0.774
	40TMAB	$Q = 11.363 \ln C_e - 58.509$	0.984
	40DTMAB	$Q = 33.946 \ln C_e - 153.51$	0.976
	40TMAB/20DTMAB	$Q = 11.428 \ln C_e - 47.734$	0.978
	40TMAB/40DTMAB	$Q = 23.914 \ln C_e - 89.900$	0.984
	40TMAB/60DTMAB	$Q = 34.438 \ln C_e - 114.91$	0.971
	40TMAB/20BDTDAC	$Q = 13.709 \ln C_e - 51.282$	0.989
	40TMAB/20CTMAB	$Q = 16.638 \ln C_e - 68.993$	0.997
	40TMAB/20OTMAB	$Q = 16.251 \ln C_e - 58.450$	0.992
	Phenol	Natural bentonite	$Q = 5.1357 \ln C_e - 2.933$
40TMAB		$Q = 13.222 \ln C_e - 69.072$	0.987
40DTMAB		$Q = 28.763 \ln C_e - 161.34$	0.989
40TMAB/20DTMAB		$Q = 17.950 \ln C_e - 107.40$	0.974
40TMAB/40DTMAB		$Q = 22.721 \ln C_e - 120.07$	0.990
40TMAB/60DTMAB		$Q = 26.292 \ln C_e - 146.27$	0.985
40TMAB/20BDTDAC		$Q = 16.134 \ln C_e - 86.322$	0.983
40TMAB/20CTMAB		$Q = 18.172 \ln C_e - 95.958$	0.994
40TMAB/20OTMAB		$Q = 20.786 \ln C_e - 116.65$	0.966
Aniline		Natural bentonite	$Q = 8.3001 \ln C_e - 49.989$
	40TMAB	$Q = 13.799 \ln C_e - 78.403$	0.978
	40DTMAB	$Q = 40.317 \ln C_e - 238.62$	0.942
	40TMAB/20DTMAB	$Q = 19.856 \ln C_e - 116.39$	0.944
	40TMAB/40DTMAB	$Q = 35.121 \ln C_e - 198.93$	0.951
	40TMAB/60DTMAB	$Q = 40.121 \ln C_e - 233.60$	0.944
	40TMAB/20BDTDAC	$Q = 27.566 \ln C_e - 166.33$	0.939
	40TMAB/20CTMAB	$Q = 30.838 \ln C_e - 179.68$	0.950
40TMAB/20OTMAB	$Q = 22.692 \ln C_e - 128.85$	0.963	

According to theory of partition, it can be expressed as follows:

$$K_d = Q_p / C_e, \quad (3)$$

$$K_d = K_{oc} \cdot f_{oc}. \quad (4)$$

Where  $Q_T$  is the total sorption amount;  $Q_A$  is the sorption amount by adsorption;  $Q_P$  is the sorption amount by partition;  $C_e$  is the equilibrium aqueous concentrations of the solute (mg/L);  $K_d$  is the partition coefficients;  $K_{oc}$  is the organic-carbon normalized sorption coefficient ( $K_d$ );  $f_{oc}$  is the organic carbon fraction of the sorbent, which is equal to the percent organic carbon, and  $a$  and  $b$  are the fitted parameters. Thus, the separate contributions of partition and adsorption to the total amount of sorption can be calculated as follows:

$$Q_P = K_{oc} \cdot f_{oc} \cdot C_e; \quad (5)$$

$$Q_A = a \ln C_e + b - K_{oc} \cdot f_{oc} \cdot C_e. \quad (6)$$

When the data of organic carbon contents ( $f_{oc}$ ) in Table 1, partition coefficients normalized by the organic carbon in Table 2, and empirical constants  $a$  and  $b$  in Table 3 are substituted into Eqs. (4) and (5), the sorbet quantities caused by adsorption and partition, respectively, can be calculated. They are a function of with aqueous concentration (Table 4). Amount of adsorption is further simulated by Langmuir isotherm. The regression data is also presented in Table 4. Thus, the specific adsorption and partition contributions to the total sorption can be calculated at the given concentrations.

**Table 4** Equations for adsorption amount ( $Q_A$ ) and partition amount ( $Q_P$ ) with concentrations of organic compounds and analogue equation of  $Q_A$

Organic compound	Clay type	$Q_P$ , $\mu\text{g/g}$	$Q_A$ , $\mu\text{g/g}$	Langmuir equation for $Q_A$	Correlation coefficient
<i>p</i> -nitrophenol	Natural bentonite	$Q_P = 0.0199 C_e$	$Q_A = 3371.6 \ln C_e + 1935.5 - 0.0199 C_e$	$1/Q_A = 2.5664/C_e + 0.0136$	0.803
	40TMAB	$Q_P = 0.7819 C_e$	$Q_A = 11363 \ln C_e - 58509 - 0.7819 C_e$	$1/Q_A = 62.706/C_e + 0.0159$	0.836
	40DTMAB	$Q_P = 3.3618 C_e$	$Q_A = 33946 \ln C_e - 153510 - 3.3618 C_e$	$1/Q_A = 6.4887/C_e + 0.0072$	0.979
	40TMAB/20DTMAB	$Q_P = 2.2428 C_e$	$Q_A = 11428 \ln C_e - 47734 - 2.2428 C_e$	$1/Q_A = 13.594/C_e + 0.0265$	0.904
	40TMAB/40DTMAB	$Q_P = 3.3898 C_e$	$Q_A = 23914 \ln C_e - 89900 - 3.3898 C_e$	$1/Q_A = 3.7524/C_e + 0.0101$	0.988
	40TMAB/60DTMAB	$Q_P = 4.3172 C_e$	$Q_A = 34438 \ln C_e - 114910 - 4.3172 C_e$	$1/Q_A = 2.0791/C_e + 0.0061$	0.992
	40TMAB/20BDTDAC	$Q_P = 2.8998 C_e$	$Q_A = 13709 \ln C_e - 51282 - 2.8998 C_e$	$1/Q_A = 15.917/C_e + 0.0180$	0.889
	40TMAB/20CTMAB	$Q_P = 3.0744 C_e$	$Q_A = 16638 \ln C_e - 68993 - 3.0744 C_e$	$1/Q_A = 8.9350/C_e + 0.0174$	0.926
	40TMAB/20OTMAB	$Q_P = 3.2288 C_e$	$Q_A = 16250 \ln C_e - 58450 - 3.2288 C_e$	$1/Q_A = 7.4186/C_e + 0.0156$	0.933
	Phenol	Natural bentonite	$Q_P = 0.0081 C_e$	$Q_A = 5135.7 \ln C_e - 32933 - 0.0081 C_e$	$1/Q_A = 536.61/C_e + 0.0281$
40TMAB		$Q_P = 0.3172 C_e$	$Q_A = 13222 \ln C_e - 69072 - 0.3172 C_e$	$1/Q_A = 38.428/C_e + 0.0166$	0.952
40DTMAB		$Q_P = 1.3639 C_e$	$Q_A = 28763 \ln C_e - 161340 - 1.3639 C_e$	$1/Q_A = 23.259/C_e + 0.0089$	0.966
40TMAB/20DTMAB		$Q_P = 0.9099 C_e$	$Q_A = 17950 \ln C_e - 107400 - 0.9099 C_e$	$1/Q_A = 88.696/C_e + 0.0116$	0.800
40TMAB/40DTMAB		$Q_P = 1.3753 C_e$	$Q_A = 22721 \ln C_e - 120070 - 1.3753 C_e$	$1/Q_A = 17.501/C_e + 0.0119$	0.989
40TMAB/60DTMAB		$Q_P = 1.7516 C_e$	$Q_A = 26292 \ln C_e - 146270 - 1.7516 C_e$	$1/Q_A = 20.618/C_e + 0.0113$	0.971
40TMAB/20BDTDAC		$Q_P = 1.1765 C_e$	$Q_A = 16134 \ln C_e - 86322 - 1.1765 C_e$	$1/Q_A = 25.667/C_e + 0.0184$	0.970
40TMAB/20CTMAB		$Q_P = 1.2473 C_e$	$Q_A = 18172 \ln C_e - 95958 - 1.2473 C_e$	$1/Q_A = 21.133/C_e + 0.0157$	0.980
40TMAB/20OTMAB		$Q_P = 1.3099 C_e$	$Q_A = 20786 \ln C_e - 116650 - 1.3099 C_e$	$1/Q_A = 27.635/C_e + 0.0140$	0.972
Aniline		Natural bentonite	$Q_P = 0.0028 C_e$	$Q_A = 8300.1 \ln C_e - 49989 - 0.0028 C_e$	$1/Q_A = 124.96/C_e + 0.0240$
	40TMAB	$Q_P = 0.1095 C_e$	$Q_A = 13799 \ln C_e - 78403 - 0.1095 C_e$	$1/Q_A = 57.379/C_e + 0.0145$	0.964
	40DTMAB	$Q_P = 0.4706 C_e$	$Q_A = 40317 \ln C_e - 238620 - 0.4706 C_e$	$1/Q_A = 22.860/C_e + 0.0053$	0.979
	40TMAB/20DTMAB	$Q_P = 0.3140 C_e$	$Q_A = 19856 \ln C_e - 116390 - 0.3140 C_e$	$1/Q_A = 45.212/C_e + 0.0109$	0.972
	40TMAB/40DTMAB	$Q_P = 0.4746 C_e$	$Q_A = 35121 \ln C_e - 198930 - 0.4746 C_e$	$1/Q_A = 21.724/C_e + 0.0059$	0.967
	40TMAB/60DTMAB	$Q_P = 0.6044 C_e$	$Q_A = 40121 \ln C_e - 233600 - 0.6044 C_e$	$1/Q_A = 20.606/C_e + 0.0054$	0.980
	40TMAB/20BDTDAC	$Q_P = 0.4060 C_e$	$Q_A = 27566 \ln C_e - 166330 - 0.4060 C_e$	$1/Q_A = 38.149/C_e + 0.0080$	0.973
	40TMAB/20CTMAB	$Q_P = 0.4304 C_e$	$Q_A = 30838 \ln C_e - 179680 - 0.4304 C_e$	$1/Q_A = 27.396/C_e + 0.0070$	0.978
	40TMAB/20OTMAB	$Q_P = 0.4520 C_e$	$Q_A = 22692 \ln C_e - 128850 - 0.4520 C_e$	$1/Q_A = 31.151/C_e + 0.0098$	0.983

Fig.2 shows the relative relationship and changing amount of  $Q_T$ ,  $Q_A$ , and  $Q_P$  with equilibrium aqueous concentrations on the basis of analogue equations of phenol sorption to 40TMA/ 60DTMA (A) and

40TMA/200TMA (B). In the plots,  $C_0$  is equilibrium concentration when the contributions of adsorption and partition to sorption of organic compounds to dual-cation organobentonites are equal.

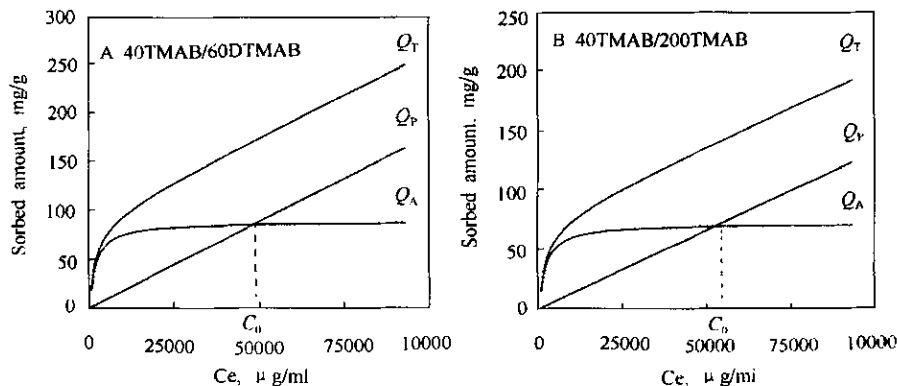


Fig.2 Phenol sorption amount ( $Q_A$ ,  $Q_P$ ,  $Q_T$ ) on 40 TMAB/60DTMAB(A) and 40CTMAB/200TMAB(B) from water at 25°C

Fig. 2 indicated that: (1) partition is increased linearly with the equilibrium concentration increasing; adsorption is increased nonlinearly with equilibrium concentration, and conforms to Langmuir isotherm. (2) The contribution of adsorption ( $Q_A$ ) to sorption of organic compounds to dual-cation organobentonites is larger than contribution of partition ( $Q_P$ ) at low relative concentrations; namely, when  $C_e < C_0$ ,  $Q_A > Q_P$ . The contribution of partition to sorption of organic compounds to dual-cation organobentonites is larger than contribution of adsorption at high relative concentrations; namely, when  $C_e > C_0$ ,  $Q_A < Q_P$ . (3)  $C_0$  is diagnostic parameter of sorption, and the value of it is related to the composition and ratio of dual-cation organobentonite, and properties of organic compounds. For example, the  $C_0$  of sorption of phenol to 40TMAB/60DTMAB(A) is less than one of sorption of phenol to 40TMAB/200TMAB(B), namely,  $C_0(A) < C_0(B)$ .

## 2.5 Effects of composition and ratio on contributions of adsorption and partition

The contributions of adsorption and partition is affected by composition and ratio of dual-cation surfactants exchanging into bentonite. Fig.3 and 4 show changing rule of contribution of partition ( $Q_P$ ) with ratio (Fig.3) and composition (Fig.4) of dual-cation organobentonite. Fig.5 and 6 show changing rule of contribution of adsorption ( $Q_A$ ) with ratio (Fig.5) and composition (Fig.6) of dual-cation organobentonite.

Fig.3 and 4 indicate that: (1) partition contribution to sorption of organic compounds to dual-cation organobentonites is increasing as the amounts of DTMA cations exchanged onto the bentonite increases from 0% to 60% of cation-exchange capacity. Namely, 40TMAB/60DTMAB > 40TMAB/40DTMAB > 40TMAB/20DTMAB > 40TMAB. (2) partition contribution to sorption of organic compounds to dual-cation organobentonites is increasing with increasing alkyl-chain of organic cations exchanged onto the bentonite. Namely, 40TMAB/20DTMAB > 40TMAB/20BDTDAC > 40TMAB/20CTMAB > 40TMAB/200TMAB.

Fig.5 and 6 indicate that: (1) adsorption contribution to sorption of organic compounds to dual-cation organobentonites is related to the alkyl-length and amount of long-cation quaternary exchanging onto the bentonite. (2) Adsorption contribution is also related to the properties and concentration of organic compounds.

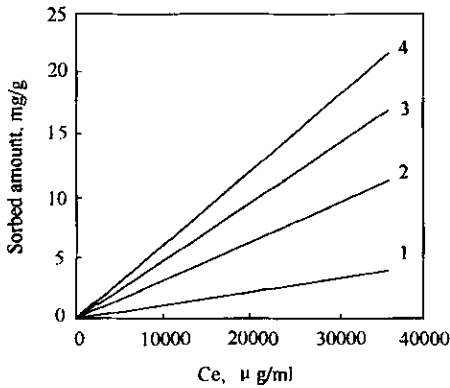


Fig. 3 Effects of ratio of dual-cation on partition contribution to sorption of aniline to dual-cation organobentonites

1. 40TMAB; 2. 40TMAB/20DTMAB; 3. 40TMAB/40DTMAB; 4. 40TMAB/60DTMAB

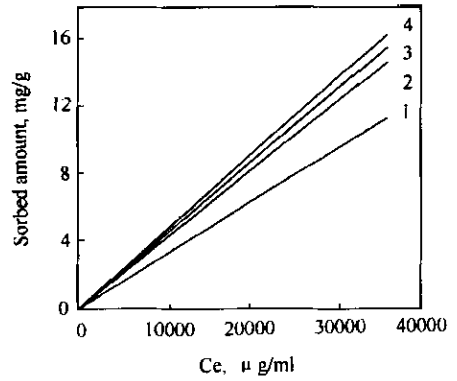


Fig. 4 Effects of composition of dual-cation on partition contribution to sorption of aniline to dual-cation organobentonites

1. 40TMAB/20DTMAB; 2. 40TMAB/20BDTDAC; 3. 40TMAB/20CTMAB; 4. 40TMAB/20OTMAB

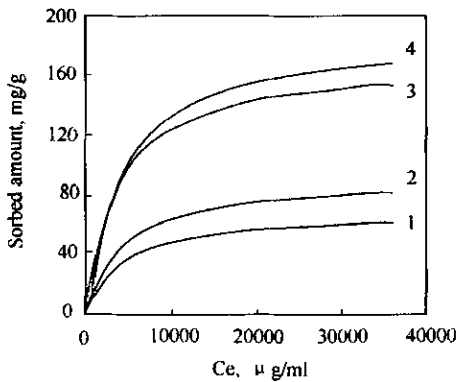


Fig. 5 Effects of ratio of dual-cation on adsorption contribution to sorption of aniline to dual-cation organobentonites

1. 40TMAB; 2. 40TMAB/20DTMAB; 3. 40TMAB/40DTMAB; 4. 40TMAB/60DTMAB

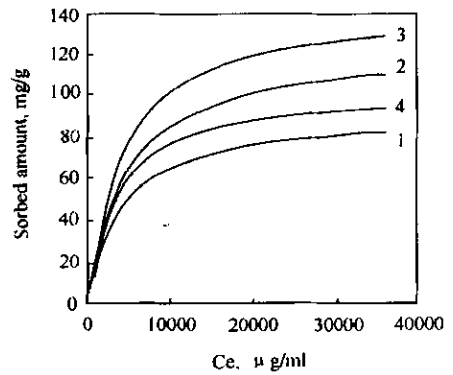


Fig. 6 Effects of composition of dual-cation on adsorption contribution to sorption of aniline to dual-cation organobentonites

1. 40TMAB/20DTMAB; 2. 40TMAB/20BDTDAC; 3. 40TMAB/20CTMAB; 4. 40TMAB/20OTMAB

### 3 Conclusion

Partition and adsorption contribution to sorption of organic compounds to dual-cation organobentonites can be described quantitatively as follows:  $Q_A = a \ln C_c + b - K_{oc} \cdot f_{oc} \cdot C_c$ ,  $Q_P = K_{oc} \cdot f_{oc} \cdot C_c$ .

Partition contribution to sorption of organic pollutants is increased linearly with the equilibrium concentration increasing; adsorption is increased nonlinearly with equilibrium concentration, and conforms to Langmuir isotherm. The contribution of adsorption ( $Q_A$ ) to sorption of organic compounds to dual-cation organobentonites is larger than contribution of partition ( $Q_P$ ) at low relative concentrations; namely, when  $C_c < C_0$ ,  $Q_A > Q_P$ . The contribution of partition to sorption of organic compounds to dual-cation organobentonites is larger than contribution of adsorption at high relative concentrations; namely, when  $C_c > C_0$ ,  $Q_A < Q_P$ .

Partition contribution to sorption of organic compounds to dual-cation organobentonites is increasing as the amounts of DTMA cations exchanged onto the bentonite increases from 0% to 60% of cation-exchange

capacity. Namely, 40TMAB/60DTMAB > 40TMAB/40DTMAB > 40TMAB/20DTMAB > 40TMAB. Partition contribution to sorption of organic compounds to dual-cation organobentonites is increasing with increasing alkyl-chain of organic cations exchanged onto the bentonite. Namely, 40TMAB/20DTMAB > 40TMAB/20TPAC > 40TMAB/20CTMAB > 40TMAB/20OTMAB. Adsorption contribution to sorption of organic compounds to dual-cation organobentonites is related to the alkyl-length and amount of long-cation quaternary exchanging onto the bentonite. Adsorption contribution is also related to the properties and concentration of organic compounds.

$C_e$  is equilibrium concentration when the contributions of adsorption and partition to sorption of organic compounds to dual-cation organobentonites is equal.  $C_0$  is diagnostic parameter of sorption, and the value is related to the composition and ratio of dual-cation organobentonite, and properties of organic compounds.

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