Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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Online publication date: 09 September 2002

To cite this Article Sabah, E. and Çelik, M. S.(2002) 'ADSORPTION MECHANISM OF QUATERNARY AMINES BY SEPIOLITE', Separation Science and Technology, 37: 13, 3081 — 3097
To link to this Article: DOI: 10.1081/SS-120005658
URL: http://dx.doi.org/10.1081/SS-120005658

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SEPARATION SCIENCE AND TECHNOLOGY, 37(13), 3081–3097 (2002)

ADSORPTION MECHANISM OF QUATERNARY AMINES BY SEPIOLITE

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ABSTRACT

A series of adsorption tests examined the uptake of typical quaternary cationic surfactants, dodecyltrimethylammonium bromide and hexadecyltrimethylammonium bromide from water by a clay mineral, sepiolite. Adsorption tests conducted under different conditions revealed that sepiolite is highly receptive to adsorption of cationic surfactants. Adsorption of cationic surfactants on sepiolite exhibits two distinct regions. The first stage is characterized by low rate and is governed through an ion-exchange process between ammonium ions and magnesium ions in the octahedral sheet. The second stage is ascribed to a combination of chain–chain interactions through van der Waals forces and ion-exchange process. The incorporation of surfactant ion is elaborated on the basis of experimental data and thermodynamic equations.

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Key Words: Adsorption; Clay minerals; Sepiolite; Cationic surfactants; Amines; Waste water treatment

INTRODUCTION

Contamination of wastewaters stemming from industrial sites such as mining and chemical industries is still a challenging problem. In particular, transport of toxic chemicals through soil and contamination of both soil and ground and surface waters is of imminent threat to human life and environment. Even in the United States, the most developed country in the world, approximately 52 billion liters of heavy-metal-bearing wastewaters are generated currently. Cationic surfactants, mainly those of aliphatic and aromatic amines used in the manufacture of pigments, dyestuffs, rubber products, and agriculture chemicals[1,2] are also used in the flotation of silicates, soluble salts, and oxide minerals.

Contamination of wastewaters and soil with toxic ions is a complex problem. The removal of these contaminants has received considerable attention in recent years. Conventional methods of removing organic contaminants include chemical precipitation, ion exchange, filtration, and electrochemical treatment.[3] More sophisticated techniques like solvent extraction, biosorption, and ultrafiltration are either expensive or cannot cope with high concentrations of contaminants. All these methods have significant disadvantages such as incomplete ion removal, high energy requirements, and production of toxic sludge or other waste products that require further disposal.

For relatively less-contaminated waters, absorbents such as active carbon or cation-exchange resins are used to abate wastewaters.[4] The use of some natural clay minerals like zeolites in water treatment has attracted interest as these minerals are abundant and also cheap commodities.[5,6] However, their industrial utilization requires answers to some basic questions: the ability of regeneration and their economic feasibility.

Sepiolite is a natural clay mineral with the formula of magnesium hydrosilicate [$(Si_{12})(Mg_9)O_{30}(OH)_6(OH_2)_4H_2O$] and exhibits a fibrous structure composed of talclike ribbons.[7] This unique structure imparts sepiolite a fibrous matrix with channels (3.6×10.6 Å) oriented in the longitudinal direction with a theoretical surface area of 900 m^2/g. Such interior channels allow the penetration of organic and inorganic ions together with solutes into the crystal structure of sepiolite.[8] In addition to their high surface area, sepiolite exhibits relatively high ion-exchange properties, which generate great potential to remove heavy metals and those organics with cation base such as ammonia. Sepiolite is used in a

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variety of industries including cosmetics, ceramics, detergency, paper, and paint. The great sorption capacity of these minerals makes them invaluable alternative materials to other sorbents in processes such as wastewater treatment.[8]

A number of investigators have studied the sorptive properties of various organic cationic reagents with sepiolite. These include adsorption of aniline on sepiolite,[9] interaction of amines on sepiolite and palygorskite by infrared measurements,[10] and removal of aromatic amines from aqueous solutions by activated sepiolite.[11] Amongst others, uptake of ammonia[12] and adsorption of primary amines[13] are some of the examples related to our studies. However, no study to date has been done on the adsorption of quaternary amines onto sepiolite.

It is therefore the objective of this study to investigate the ability of uptake of typical quaternary amine surfactants, dodecyltrimethylammonium bromide (DTAB), and hexadecyltrimethylammonium bromide (HTAB) on sepiolite and elucidate the adsorption mechanism using experimental and thermodynamic data.

EXPERIMENTAL

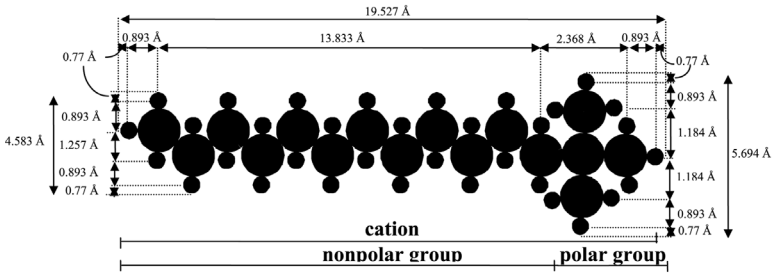
The sepiolite sample used in this study was received from Mayas Mining Co. in Sivrihisar, Turkey. This brown sepiolite ground to $-65\,\mu$m produced the average particle size (d_{50}) of $1.98\,\mu$m as determined by Zetasizer. The x-ray diffraction together with the chemical analysis given in Table 1 indicates that calcite and dolomite are the major impurities accompanying sepiolite.[14] The surface area of untreated sepiolite was found to be $68\,m^2/g$ by means of BET method using nitrogen as the adsorbent.

The study used DTAB ($C_{12}H_{25}N(CH_3)_3Br$) and HTAB ($C_{16}H_{33}N(CH_3)_3$-Br) as the cationic absorbents and $C_{12}H_{25}SO_4Na$, sodium dodecylsulfate (SDS), as the anionic surfactant for the analysis of cationic surfactant. The schematic view of the cationic surfactant molecules is shown in Fig. 1. All chemicals were purchased from Fluka AG of Switzerland and specified to be of high purity. Distilled and deionized water with a conductivity value of less than 2×10^{-6} mhos/cm was used in all experiments. Experiments were conducted at 25°C unless otherwise specified.

Adsorption tests were conducted in 20 or 40 mL glass vials. A sepiolite sample of 500 mg was mixed in 10 cc or its multiples with a solid to liquid ratio of

Table 1. Chemical Analysis of Sepiolite Sample Used in This Study

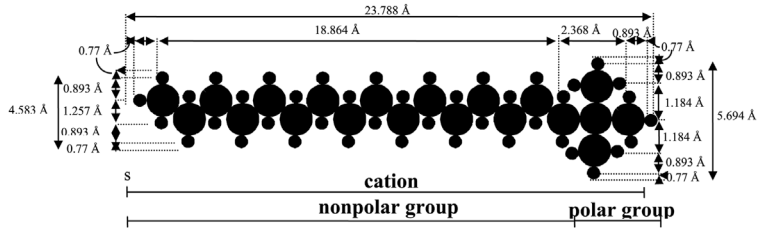
Component	SiO_2	MgO	CaO	Al_2O_3	Fe_2O_3	Na_2O	K_2O	TiO_2	LOI
% by weight	51.93	24.20	0.12	1.52	0.70	0.12	0.33	0.08	21.00



Cross-sectional area of polar group ≅ 25.45 Å^2
Cross-sectional area of nonpolar group ≅ 16.49 Å^2
Cross-sectional area of molecule ≅ 111.19 Å^2

Carbon
Nitrogen
Hydrogen

(a) $CH_3(CH_2)_{11}N(CH_3)_3Br$



Cross-sectional area of polar group ≅ 25.45 Å^2
Cross-sectional area of nonpolar group ≅ 16.49 Å^2
Cross-sectional area of molecule ≅ 135.45 Å^2

Carbon
Nitrogen
Hydrogen

(b) $CH_3(CH_2)_{15}N(CH_3)_3Br$

Figure 1. Molecular structure of (a) dodecyltrimethylammonium bromide and (b) hexadecyltrimethylammonium bromide.

0.05. The vials were shaken for 2 hr in a shaker and centrifuged for 15 min. The supernatant was analyzed for the cationic surfactant by a two-phase titration technique originally applied to anionic surfactants using dimidium bromide and disulfine blue as indicators.[15] This technique is based on the formation of a

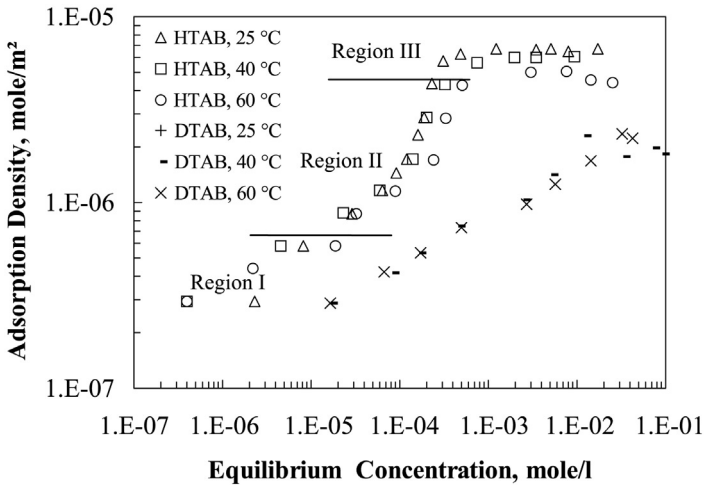


Figure 2. Adsorption isotherms of sepiolite/DTAB system at different temperatures (natural pH of 8.5, 2 hr conditioning time, *S*/*L* ratio of 0.05).

complex between an anionic surfactant (SDS) and a cationic reagent dodecylamine hydrochloride (DAH). This complex is soluble in chloroform and changes from blue to pink in the presence of indicators. The adsorption density was calculated by the formula given elsewhere[13] as follows:

$$\Gamma = (C_i - C_r)V/(mS \times 1000) \quad (1)$$

where C_i and C_r represents the initial and residual concentrations in mol/L, m the amount of solid in grams, V the volume of the solution in mL, S the specific surface area of sepiolite, and Γ the adsorption density in mol/m^2.

RESULTS AND DISCUSSION

Adsorption of Cationic Surfactants on Sepiolite

The adsorption isotherms of sepiolite/DTAB and sepiolite/HTAB systems at different temperatures are shown in Fig. 2. The adsorption isotherms are marked by three distinct regions of different slopes. Each region corresponds to a certain mechanism as will be described later. While the dependence of temperature is not apparent in the rising branch of the isotherm, significant differences are observed in the plateau adsorption densities, e.g., for DTAB, $6.18 \times 10^{-6}\, M/\mathrm{m}^2$, at 25°C, an average of about $2 \times 10^{-6}\, M/\mathrm{m}^2$ at 40 and 60°C

are noted. The corresponding residual concentrations at the plateau are 3.90×10^{-2}, 3.90×10^{-2}, and $3.20 \times 10^{-2}\,M$ for 25, 40, and 60°C, respectively; these values are close to the critical micelle concentration of $1.56 \times 10^{-2}\,M$ reported by Ottewill.[16]

The cross-sectional area of a DTAB molecule in Å/molecule can be calculated as

$$\text{Cross-sectional area} = 10^{20}/\Gamma_{\max} A \tag{2}$$

where $\Gamma_{\max}$ is the adsorption density at the plateau region and A is the Avagadro number. Using the values given in Fig. 1, the cross-sectional area of DTAB is found to be 27 Å/molecule, which is in agreement with the cross-sectional area of 25 Å/molecule reported for an amine molecule.[17] The effect of temperature is also reflected in the surface coverages (θ) while θ at 25°C is 0.92, at 40 and 60°C is reduced down to about 0.3 indicating that at higher temperatures the surfactant adsorption on sepiolite surface exhibits patches. These values for both surfactants are listed in Table 2.

Previous studies indicated that sepiolite undergoes acid–base interactions at pH 8.5 and the Mg^{2+} concentration increases significantly in the acidic pH region. Zeta potential measurements yielded an isoelectric point (IEP) of about 5.[21] Adsorption isotherms obtained with HTAB (16 CH_2 groups) compared to that obtained with DTAB (12 CH_2 groups) exhibited differences in the rising branch in accord with the corresponding free energies of adsorption due to additional CH_2 groups. Interestingly, this finding clarifies the controversy that it is adsorption rather than absorption that governs the uptake of chemicals onto sepiolite.[8] Indeed, the molecular structure given in Fig. 1 was depicted with the aim of identifying whether the molecule itself could be directly accommodated in the channels in the form of absorption. The adsorption results against chain length definitively ruled out this possibility, as the adsorption of a higher chain length amine should have exhibited

Table 2. Thermodynamic Data Obtained from Adsorption Isotherms of DTAB/Sepiolite and HTAB/Sepiolite Systems as a Function of Temperature

	Temperature (°C)	Plateau Adsorption Density $\Gamma_{\max} \times 10^{-6}$ (M/m^2)	Equilibrium Concentration (M)	Cross-Sectional Area (Å^2)	Degree of Coverage (θ)
DTAB (C_{12})	25	6.18	3.90×10^{-2}	27	0.92
	40	1.84	3.40×10^{-2}	90	0.28
	60	2.35	3.20×10^{-2}	70	0.36
HTAB (C_{16})	25	6.68	1.22×10^{-3}	25	1
	40	6.05	3.50×10^{-3}	27	0.92
	60	5.00	3.10×10^{-3}	33	0.75

even lower adsorption due to the larger size of the molecular structure and their exclusion from smaller pores. This finding confirms that some type of physical or chemical bond dictates the adsorption process.

Thermodynamic Evaluation of the Adsorption Process

The adsorption mechanism (i.e., chemical or physical) is often an important indicator to describe the type and level of interactions between the adsorbate and the adsorbent. If adsorption decreases with increasing temperature, it may be indicative of physical and the reverse is generally true for chemisorption. However, there are a number of contradictory cases in the literature.[18] In sepiolite/DTAB system, the decrease in adsorption with increasing temperature and fast adsorption kinetics, (e.g., adsorption of DTAB and HTAB on sepiolite takes place in less than 5 min) may suggest the presence of physical adsorption.[13] Nevertheless, this alone is not sufficient to determine the type of adsorption. The type of adsorption may be determined through thermodynamic quantities such as free energy of adsorption (ΔG^{o}_{ads}) and the heat of adsorption (ΔH^{o}_{ads}) both of which can be obtained from the adsorption data given in Figure 2.

A general adsorption isotherm for surfactant adsorption at the solid/liquid interface, taking into account the effect of size ratio (n) and lateral interaction coefficient (a) between adsorbed molecules, has the following form:[19]

$$\frac{\theta}{(1-\theta)^n}\exp(-2a\theta) = KC \tag{3}$$

where

$$K = \frac{1}{55.5}\exp(\Delta G^{o}_{ads}/RT) \tag{4}$$

is the adsorbability of the surfactant molecule at infinitively low coverage, C is the equilibrium concentration in mol/L, θ is the degree of surface coverage of the mineral with the collector molecule at (Γ/Γ_{max}), R is the gas constant (8.1314), T is the temperature in K, and Γ_{max} is the adsorption density at the plateau. The free energy of adsorption can be calculated from Eq. (4) as a function of θ.

The calculation of ΔG^{o}_{ads} has been made using four models: the Flory–Huggins, Frumkin, Modified Frumkin, and Langmuir equations. If the adsorption data obey these equations, the above parameters, i.e., (n, a, and K) are plugged into Eqs. (3) and (4) and ΔG^{o}_{ads} is calculated. Equation 3 is essentially the modified version of Frumkin equation with the size ratio of n taken into account. The value of n in the case of the Flory–Huggins[19,20] and modified Frumkin equations depend on the size of the adsorbate. The cross-sectional area of the DTAB molecule is approximately 27 $Å^2$. The value of n is defined as the ratio of

cross-sectional area of the adsorbate molecule to the cross-sectional area of the water molecule, which is 12.5 $Å^2$, i.e., $27/12.5 \approx 2$. The a and n values for different equations are given below:

Equation	n	a
Flory–Huggins	2	0
Frumkin	1	1
Modified Frumkin	2	1
Langmuir	1	0

For instance, by rearranging Eq. (3) and taking the logarithms for $n = 2$ and $a = 1$, the modified Frumkin equation is obtained:

$$\ln\left(\frac{\theta}{C(1-\theta)^2}\right) = 2a\theta + \ln K \tag{5}$$

The a and K values can be determined graphically from a plot of $\ln \theta/C(1-\theta)^n$ vs. θ (for $n = 2$) for the modified Frumkin equation. The resultant straight line has a slope of $2a$ and an intercept of $\ln K$. The results plotted in this manner are given in Fig. 3.

Similarly, if $a = 0$ and $n = 1$, the Langmuir equation is obtained in the following form:

$$\ln\left(\frac{\theta}{C(1-\theta)}\right) = 2a\theta + \ln K \tag{6}$$

The results of Langmuir Equation are shown in Fig. 4. The slopes and intercepts of the straight lines in Figs. 3 and 4 and others, which are not shown here for the sake of brevity, have been used to determine the value of ΔG^{o}_{ads} with the results presented in Table 3.

While ΔG^{o}_{ads} determines the affinity of the mineral surface towards the surfactant molecules at very low coverage, a represents the strength of lateral interaction forces between the amine molecules adsorbed on the surface. A positive value of a indicates a repulsive interaction between the polar heads and a negative value of a represents the chain–chain interactions. The negative a values in Table 3 indicate the presence of chain–chain interactions among the nonpolar molecules. The magnitude of a indicates the extent of interactions. The larger a values in the case of C_{16} amine compared to C_{12} amine again supports the significance of chain–chain interactions in the system; the value of a increases with both the chain length and the degree of coverage. In fact, the larger

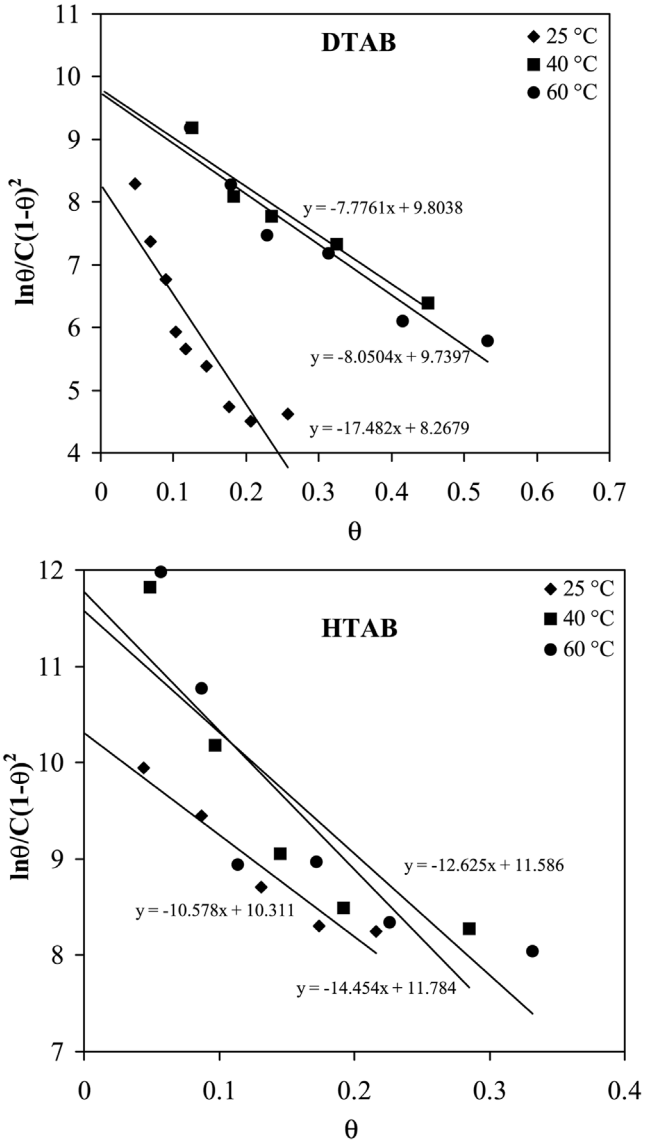


Figure 3. Illustration of Modified Frumkin Equation based on the data in Fig. 2.

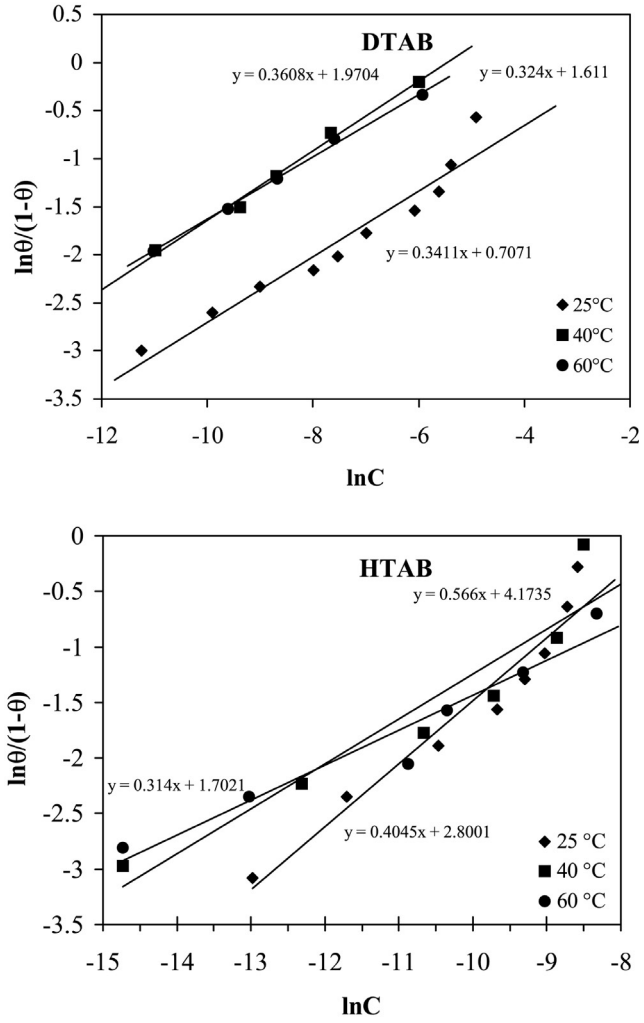


Figure 4. Illustration of Langmuir Equation based on the data in Fig. 2.

magnitude of *a* value corresponds to the more perpendicular orientation than those of lower *a* values.[19] It is evident from Table 3 that the values obtained in the Frumkin and the modified Frumkin equations yield larger free energy of adsorption values. Since the modified Frumkin equation takes into account both the size ratio and the lateral interaction coefficient, it appears to make better predictions than the Frumkin equation.

Table 3. Thermodynamic Data Calculated for Various Adsorption Models for Two Different Quaternary Amines of Different Chain Length

	Temperature (°C)	Langmuir ΔG_{ads} (kJ/mol)	Flory–Huggins ΔG_{ads} (kJ/mol)	Frumkin		Modified Frumkin	
				ΔG_{ads} (kJ/mol)	a	ΔG_{ads} (kJ/mol)	a
DTAB (C_{12})	25	−8.90	−10.31	−14.44	−3.38	−14.85	−2.62
	40	−11.15	−12.98	−16.02	−4.48	−16.13	−3.89
	60	−12.16	−13.55	−17.06	−4.61	−17.04	−4.03
HTAB (C_{16})	25	−13.19	−13.43	−15.34	−4.77	−15.39	−5.29
	40	−12.84	−12.34	−16.46	−6.94	−16.66	−6.32
	60	−12.31	−13.17	−17.59	−7.82	−17.69	−7.23

Another very important thermodynamic parameter in determining the type of adsorption is the heat of adsorption (ΔH^{o}_{ads}). This can be obtained from the Clausius Clapeyron Equation.[18]

$$\frac{d \ln K}{d(1/T)} = -\frac{\Delta H^{o}_{ads}}{R} \tag{7}$$

Using this equation, $\ln K$ vs. $1/T$ are shown in Fig. 5. The slopes of these lines have been substituted in Eq. (7) to calculate the ΔH^{o}_{ads} for each model. The results of the modified Frumkin equation only are presented in Table 4 along with the entropy values calculated using Eq. (8) given below:

$$\Delta G = \Delta H - T\Delta S < 0 \tag{8}$$

The adsorption process is composed of two contributions—enthalpic and entropic, which characterize whether the reaction is spontaneous or not. Since the modified Frumkin equation was selected to characterize the adsorption of cationic surfactants onto sepiolite best, only the results of these calculations are presented in Table 4. An examination of Table 4 reveals that ΔH^{o}_{ads} is rather small when compared to the total adsorption energy. However, the entropic contribution is even larger than the free energy of adsorption. Therefore, it is plausible to say that the adsorption of cationic surfactants onto sepiolite is entropically governed.

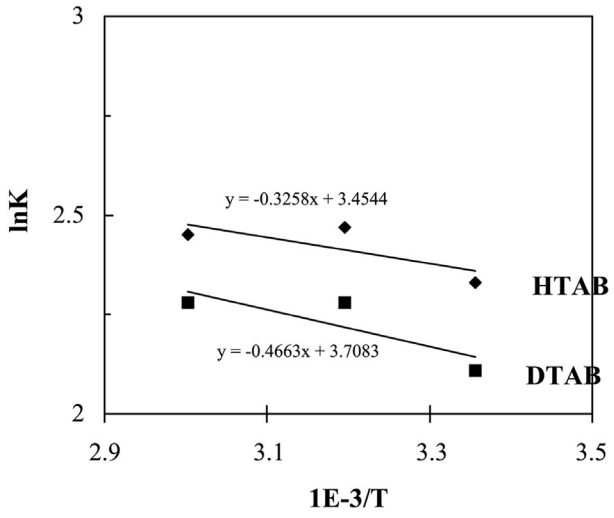


Figure 5. Heat of adsorption data for sepiolite/DTAB system using Modified Frumkin and Langmuir models.

Table 4. Thermodynamic Values Calculated for DTAB and HTAB Adsorbed onto Sepiolite

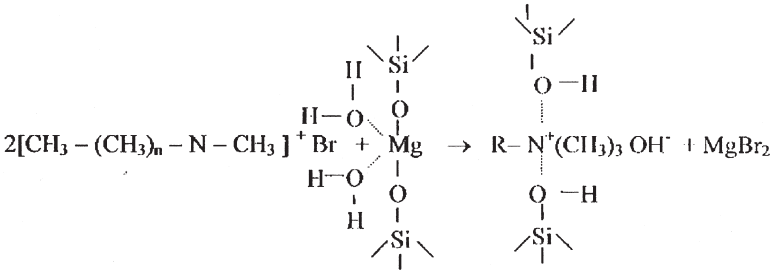
System	$1/T$ (°K)	Γ_{max} (M/m^2)	Modified Frumkin Equation ΔG^o_{ads} (kJ/mol)	ΔH^o_{ads} (kJ/mol)	$-T\Delta S^o_{ads}$ (kJ/mol)
DTAB/Sepiolite	3.35×10^{-3}	6.18×10^{-6}	−14.36	8.29	22.65
	3.19×10^{-3}	2.29×10^{-6}	−16.03	8.29	24.32
	3.00×10^{-3}	2.35×10^{-6}	−17.04	8.29	25.33
HTAB/Sepiolite	3.35×10^{-3}	6.68×10^{-6}	−15.39	3.58	18.97
	3.19×10^{-3}	6.03×10^{-6}	−16.46	3.58	20.04
	3.00×10^{-3}	5.09×10^{-6}	−17.55	3.58	21.13

Mechanism of Adsorption Process

Aromatic amines and primary amines are well known to adsorb via hydrogen bonding.[9] However, quaternary amines such as DTAB used in this study has no affinity to form hydrogen bonding. Therefore, the decrease obtained cannot be solely attributed to the loss of hydrogen bonding.

The adsorption isotherms in Fig. 2 also show two distinct regions, each characterized by different adsorption rates and mechanisms. In the first stage, adsorption takes place at a lower rate and is governed by an ion-exchange process. However, the adsorption continues to take place with increasing DTAB concentration. In the second stage, the adsorption is mainly characterized by chain–chain interactions through van der Waals forces. But the ion-exchange process still continues to take place at a similar rate as the magnesium release continues even in the plateau region.

The ion-exchange mechanism of DTAB and HTAB onto sepiolite can be depicted as follows:



where $n = 11$ for DTAB and $n = 15$ for HTAB.

The free energy of adsorption (ΔG^{o}_{ads}) is composed of a number of contributing forces. Among them, ΔG^{o}_{elec}, ΔG^{o}_{chem}, ΔG^{o}_{solv}, $\Delta G^{o}_{ion-exchange}$, and $\Delta G^{o}_{chain-chain}$, are relevant.[22,23] Here ΔG^{o}_{elec} is the electrostatic contribution to the total energy, $\Delta G^{o}_{chain-chain}$, or $\Delta G^{o}_{CH_2}$ represents the interaction due to association of hydrocarbon chains of the adsorbed surfactant molecule at the interface, ΔG^{o}_{chem} reflects the free energy change due to the formation of chemical bonds such as covalent bonds with the surface, ΔG^{o}_{solv} is the contribution of the solvation effects on the polar head of the adsorbate, and $\Delta G^{o}_{ion-exchange}$ represents the exchange of similar ions (e.g., cations or anions) on the surface with those in the bulk. In our system, $\Delta G^{o}_{ion-exchange}$, and $\Delta G^{o}_{chain-chain}$ are responsible for the adsorption reactions in the first and second regions of the adsorption isotherm. The ion exchange occurs between Mg^{2+} on the surface and positively charged amine group in the bulk. The formation of hydrogen bond between the zeolitic water and bound water has been proposed for a number of cationic surfactant systems such as primary amines.[10,13] However, the quaternary amines, which are surrounded by electron repulsive CH_3 constituents and the absence of vacant electrons make it impossible for the hydrogen bond to form. The significant increase in magnesium ion concentration in Fig. 6 clearly shows that ion-exchange mechanism is the mechanism responsible for the adsorption in the first region. The significant increase in the slope of adsorption isotherm in the second

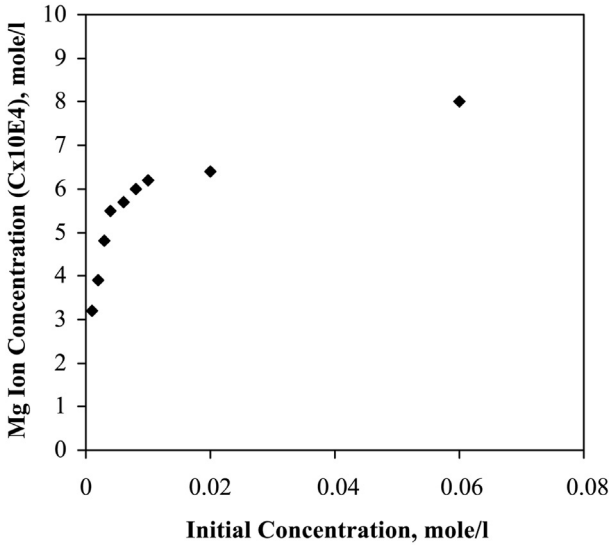


Figure 6. The released magnesium ion concentration as a function of initial DTAB concentration under the adsorption conditions of Fig. 2.

region is ascribed to the chain–chain interactions among the adsorbed amine molecules. Although C_{12} and C_{16} amines have different chain lengths and consequently sizes, both form monolayer at the plateau region at 25°C and are incorporated into the pores of sepiolite. The average pore size of sepiolite used in this study is 37 Å and the diameter of the amine polar head is 5.69 Å. This indicates that both amine surfactants have no difficulties to be accommodated in the pores of sepiolite. It should be noted that the whole molecule need not get into the pore but rather the polar part. Correspondingly, the lateral interaction coefficient for HTAB is larger than DTAB indicating that the longer adsorbed molecules have greater affinity to be adsorbed at lower surfactant concentrations. Indeed this is well shown in Figure 2 where the adsorption isotherm for HTAB is much higher in the second region of the isotherm.

CONCLUSIONS

Adsorption studies conducted on sepiolite resulted in the following salient points.

1. Adsorption of cationic surfactants on sepiolite exhibits two distinct regions. The first stage is characterized by low rate and governed through an ion-exchange process between ammonium ions and magnesium ions in the octahedral sheet. The second stage is ascribed to a combination of chain–chain interactions through van der Waals forces and ion-exchange process.
2. Calculations using a surface area of 68 m^2/g for sepiolite surface and a cross-sectional area of 27 $Å^2$/molecule for DTAB molecule reveal that a monolayer coverage is reached.
3. Calculated thermodynamic quantities, (i.e., the free energy of adsorption, the heat of adsorption, and the entropy) using the Frumkin, modified Frumkin, Flory–Huggins, and Langmuir models indicate that the adsorption process is physical in nature and mainly controlled by the entropic contribution. The Modified Frumkin model is found to yield more realistic values compared to other models. Under these premises, ΔG^{o}_{ads} value of -3.5 and 4 Kcal/mole and ΔH^{o}_{ads} value of 1.98 and 0.86 kcal/mol for DTAB and HTAB, respectively. Such small values of ΔH^{o}_{ads} and relatively large entropic contribution of (-5 to 6 kcal/mol) indicate the physical nature of the adsorption process.

REFERENCES

1. Haley, T.J. Benzidine Revisited: A Review of the Literature and Problems Associated with the Use of Benzidine and Its Congeners. Clin. Toxicol. **1975**, *8*, 13–42.
2. Golab, I.; Althaus, W.A.; Wooten, H.L. Fate of C-14 Trifluralin in Soil. J. Agric. Food Chem. **1979**, *27*, 163–179.
3. Corapcioglu, M.O.; Huang, C.P. The Adsorption of Heavy Metals onto Hydrous Activated Carbon. J. Water Res. **1987**, *21*, 1031–1044.
4. Seco, A.; Marzal, P.; Gabaldon, C.; Ferrer, J. Study of the Adsorption of Cd and Zn onto an Activated Carbon. Sep. Sci. Technol. **1999**, *34*, 1577–1593.
5. Katoh, M.; Katayama, K.; Tomida, T. Effect of Temperature on Air Adsorption onto Alkali Metal-Ion Exchanged ZSM-5 Zeolites. Sep. Sci. Technol. **1999**, *35*, 599–608.
6. Panayotova, J. Kinetics and Thermodynamics of Copper Ions Removal from Wastewater by Use of Zeolite. Waste Manag. **2001**, *21*, 671–676.
7. Brindley, G.W. X-Ray and Electron Diffraction Data for Sepiolite. Am. Miner. **1959**, *44*, 495–500.
8. Alvarez, A. Sepiolite: Properties and Uses. In *Developments in Sedimentology*; Singer, A., Galan, E., Eds.; Elsevier: Netherlands, 1984; 253–285.
9. Gonzalez-Pradas, E.; Valverde-Garcia, A.; Villafranca-Sanchez, M.; del Rey Bueno, F. Adsorption of Para-substituted Anilines from Cyclohexane Solution on Sepiolite. Adsorption Sci. Technol. **1987**, *4*, 79–85.
10. Shuali, U.; Bram, L.; Steinberg, M.; Yariv, S. Infrared Study of the Thermal Treatment of Sepiolite and Palygorskite Saturated with Organic Acids. Thermochim. Acta **1989**, *148*, 445–456.
11. Gonzalez-Pradas, E.; Valverde-Garcia, A.; Villafranca-Sanchez, M. Removal of Aromatic Amines from Aqueous Solution by Activated Sepiolite. J. Chem. Technol. Biotechnol. **1990**, *47*, 15–22.
12. Bernal, M.P.; Lopez-Real, J.M. Natural Zeolites and Sepiolite as Ammonium and Ammonia Adsorbent Materials. Bioresour. Technol. **1993**, *43*, 27–33.
13. Sabah, E.; Saglam, H.; Kara, M.; Çelik, M.S. Uptake of Cationic Surfactants by a Clay Absorbent: Sepiolite, Proceedings of Southern Hemisphere Meeting, Buenos Aires, May 6–9, 1997; 277–280.
14. Powers, G.W. The Volumetric Determination of Organic Sulfates or Sulfonates by the Double Indicator Method. *Communication C-225*; Amoco Production Co.: Tulsa, 1970; 1–4.
15. Reid, V.W.; Longman, G.F.; Heinerth, E. *Determination of Anionic Active Detergents by Two-Phase Titration*. Tenside **1967**, *4*, 292–294.

16. Ottewil, R.H. Adsorption of Nonionic Surfactants. In *Nonionic Surfactants*; Schick, M.J., Ed.; Dekker: New York, 1967; Ch. 19, 627–653.
17. Harkins, W.D.; Florence, R.T. Interactions in Mixed Monolayers on Aqueous Solutions. J. Chem. Phys. **1938**, *6*, 847–854.
18. Çelik, M.S.; Yoon, R.H. Adsorption of Poly(Oxyeyhylene)Nonylphenol Homologues on a Low-Ash Coal. Langmuir **1991**, *7*, 79–86.
19. Yehia, A.; Miller, J.D.; Ateya, B.G. Analysis of the Adsorption Behavior of Oleate on Some Synthetic Apatites. Miner. Eng. **1993**, *6*, 79–86.
20. Dhar, H.P.; Conway, B.E.; Joshi, K.M. Thermodynamics of Electrochemical Adsorption of Organic Substances. Electrochim. Acta **1973**, *18*, 789.
21. Sabah, E. Adsorption Mechanism of Quaternary Amines by Sepiolite. Ph.D. Dissertation, Osmangazi University, Eskisehir, Turkey.
22. Fuerstenau, D.W.; Raghavan, S. Some Aspects of the Thermodynamics of Flotation. In *Flotation A.M. Gaudin Memorial Volume*; Fuerstenau, M.C., Ed.; SME Publication: New York, 1976; Vol. 1, 21–65.
23. Çelik, M.S.; Somasundaran, P. Effect of Chainlength on Dissolution of Calcium Sulfonate Precipitates. J. Colloid Interface Sci. **1988**, *122*, 163–170.

Received January 2002