INVESTIGATION OF ADSORPTION BEHAVIOR OF PHOSPHONIUM SALTS ONTO Na-MONTMORILLONITE

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Abstract. Montmorillonite is an important clay mineral due to its cation exchange capacity and technological properties such as swelling and gelling. It has been widely used in many scientific applications like organoclay. Adsorption studies, involving montmorillonite in the presence of variety of organic compounds, like ammonium and phosphonium salts, are very important because of their application in organoclay and polymer nanocomposites. These materials have a high thermal resistivity. Different types of phosphonium salts, including hexadecyl triphenyl phosphonium bromide (HTPB), hexadecyl tributyl phosphonium bromide (HTBPB), and tetraphenyl phosphonium bromide (TPB), were used to investigate their adsorption on Na-montmorillonite. They have different structures and TPB contains only one aromatic part without any organic chain, HTBPB possess an organic chain with three branches while HTPB has an organic chain and an aromatic part. The adsorption of the surfactants was supplemented with other properties such as zeta potential, surface tension, and ability to flocculation. The results indicated that the adsorption behavior of these surfactants depended on their structure.

Keywords: Na-montmorillonite, phosphonium salts, adsorption

Introduction

Montmorillonite is a widely used clay mineral in scientific studies such as adsorption, preparation of organoclay and nanocomposites of high exchange capacity, and other physicochemical properties due to the sandwich-type 2:1 crystal lattice structure. The layers of montmorillonite are connecting each other due to weak van der Waals forces, water molecules as well as cations presence between them (Bergaya et al. 2006; Grim 1968; Lagaly 1993; Mittal 2009; Van Olphen 1977). Since the net surface charge of montmorillonite is always negative (Sondi et al. 1997), it can be modified with cationic surface active agents via ion exchange mechanism. Modification processes, based on cation exchange and properties of organoclay and nanocomposite, have been performed for a long time in literature.

In the current of era of nanotechnology, new types of materials have been discovered, which have brought a significant technological progress. Production of nanoclays and organoclays (organically modified layered silicates) has been a turning point for nanotechnology. The use of nanoclays in polymer matrix as a strengthen phase, as a rheological agent, and as a water treatment reagent (Patel 2006) accelerated this process. Application of nanocomposites has become very popular and many studies, particularly about layered silicate composites, hybrid or nanocomposites, were started by the Toyota research group in the 1980's (Okada and Usuki 2006) and has been continued until now.

The studies started with improvement of mechanical and thermal stability of the organoclays and have been continued with application of barriers (LeBaron et al. 1999; Usiki et al. 1992; Ray and Okamoto 2003). Academic and patent based studies with nanocomposites produced with clay minerals are quickly used in industrial applications such as thermoplastics. For example, organophilic montmorillonites are used as filler for nanocomposites because of their low prices and useful properties. Montmorillonite, which is hydrophilic, can be converted to hydrophobic using quaternary ammonium salts (Lagaly 1986; Hartwig et al. 2003), silane compounds (Silva et al. 2011), phosphonium salts (Hartwig et al. 2003), imidazolium (Abate et al. 2008), and pyridinium reagents by cationic exchange to form organomontmorillonite which is compatible with polymers. With addition of organoclay into polymer, nanocomposite structure being filled with clay is formed due to exfoliation and intercalation of clays in the matrix. Initially, the studies were done for improvement of mechanical and barrier properties of the organoclays (Messermith and Giannelis, 1995; Osman et al 2007) and later changed to investigation of thermal properties (Abdallah and Yilmazer 2012; Calderon 2008; Gilman et al. 2000; Xie et al. 2001 and 2002). The studies showed that while ammonium and silane compounds improved mechanical properties, phosphonium, imidazolium and pyridinium compounds improved thermal properties of organoclays or nanocomposites (Awad et al. 2004; Byrne and McNally 2007; Hartwig 2003; Patro et al. 2009).

Phosphonium, imidazolium and pyridinium cations have higher strength, when compared with ammonium ions, in terms of the thermal properties (Mittal 2012). Phosphonium salts, which have high thermal stability, are very important compounds, which become popular because of their usages in organoclay and polymer nanocomposites. Besides, there have been many studies about the use of phosphonium compounds for ionic liquids (Byrne and McNally 2007), eutectic solvents (Kareem et al. 2012), humidity sensor (Son and Gong 2002), and antibacterial applications (Wu et al 2011).

In this study, adsorption characteristics of phosphonium salts, due to their thermal resistance in comparison to other organics, on montmorillonite, was investigated in detail. It is suggested that the reason for thermal stability of organoclays prepared by using phosphonium salts depends on their aromatic structure (Abdallah and Yilmazer 2013). In this study, three different phosphonium surfactants were used. The first one

was composed of one aromatic head without any organic chain, another one had an organic chain with three branches, and the last one had an organic chain and aromatic head. Therefore, the effect of surfactants structure on adsorption on montmorillonite was also studied.

Materials and methods

Materials

The sodium-montmorillonite (Na-MMT) sample used in this study was obtained from Resadiye, Tokat region in northeast Turkey. Hexadecyl triphenyl phosphonium bromide (HTPB), hexadecyl tributyl phosphonium bromide (HTBPB), and tetraphenyl phosphonium bromide (TPB) were provided by Welink International Enterprise Limited, China. The chemical compositions of these surfactants are shown in Table 1. Millipore Milli-Q Synthesis ultrapure water (18.2 mΩ) was used for all experiments, except during physical purification process of the sample carried out by means of a Falcon concentrator.

Table 1. Specifications of the surfactants used in this study

Surfactant	Molecular formula	Molecular weight, g/mol	Structure
Hexadecyl Triphenyl Phosphonium Bromide (HTPB)	$C_{34}H_{48}BrP$	567.62	
Hexadecyl Tributyl Phosphonium Bromide (HTBPB)	$C_{28}H_{60}BrP$	507.65	
Tetraphenyl Phosphonium Bromide (TPB)	$C_{24}H_{20}BrP$	419.30	
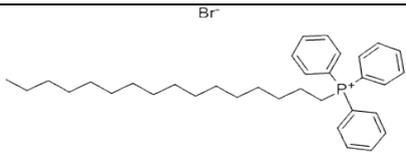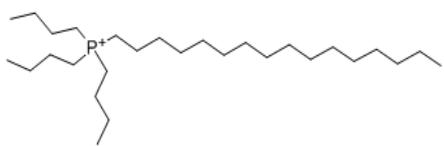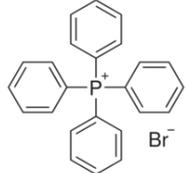
Methods

Sample characterization

The sample was purified in order to increase its adsorption capacity. The purification of montmorillonite was carried out by using a laboratory type Falcon Z40 model concentrator with a centrifuge force of 300 G, which is suitable for an effective

beneficiation in a short time compared to a number of physical methods such as sedimentation, decantation, centrifuge, and hydrocyclone. The raw and purified samples were characterized using several methods. For example, mineralogical compositions of the samples were determined by the X-Ray diffraction (XRD) technique with Shimadzu XRD 6000 (Cu(K$_\alpha$) radiation). Major elemental analyses of the samples were performed by the Rigaku Rix-3000 instrument. Technological properties of the raw and purified samples were obtained with cation exchange capacity (CEC), swelling and gelling index, and water adsorption capacity tests.

The CEC's of the raw and purified Na-montmorillonite were determined by using the methylene blue test based on the ASTM standard (ASTM C 837, 2003). The swelling index tests were performed in several graduated cylinders. For this purpose 2-g samples of ground (-38 μm) and dried (at 105 ^{o}C) montmorillonite were slowly added into 100 cm^3 of ultrapure water for 1 h to avoid aggregation of the samples. The suspension was left undisturbed for 24 h while the volume of the sediment was continuously recorded as swelling index.

The gelling index of the samples was also determined by using graduated cylinders. A certain amount of the samples (from 0.5 to 1.3 g) was added into 10 cm^3 of water, and shaken for 5 min. The samples were left for a day to allow the suspension to gel. After 24 h, the cylinders were bent 45° to let the suspensions to flow out. The amount of samples in the suspensions, which allows the flow more than a minute was determined and the ratio of 10 (cm^3)/sample amount (g) was defined as the gelling index.

In the case of the water adsorption tests, 20 g dried (at 105 ^{o}C), crushed, and screened montmorillonite granules (–4+1 mm) was added into 1000 cm^3 water. The Na-montmorillonite samples were steeped into water for 20 min by putting them into reservoir which was cylindrical in the cross-section and a 1 mm open sieve space. The sample was kept in a hanger for 20 min to remove the excessive water from the clay surfaces, then the sample was weighed, and the adsorbed water was determined.

Adsorption experiments

The adsorption experiments were conducted in 100 cm^3 glass bottles. The purified Na-montmorillonite suspension at the solid ratio of 1% was stirred using a magnetic stirrer for 30 min at 500 rpm. A desired amount of surfactant solution was added into the suspension and the experiments were carried out for 1 h. After the adsorption, the suspension was transferred into a 50 cm^3 test tube, and subjected to centrifuge at 5000 rpm in order to obtain a clear solution of surfactants. The solution was filtered through a 0.23 μm filter. The final concentration of the surfactant solution was measured by a UV/visible spectrometer (PG Instrument Ltd, London, UK, Model T80) at wavelengths of 199, 197, and 192 nm for HTPB, TTPB, and TPB, respectively. A calibration curve for each surfactant was obtained as seen Figs. 1, 2, and 3.
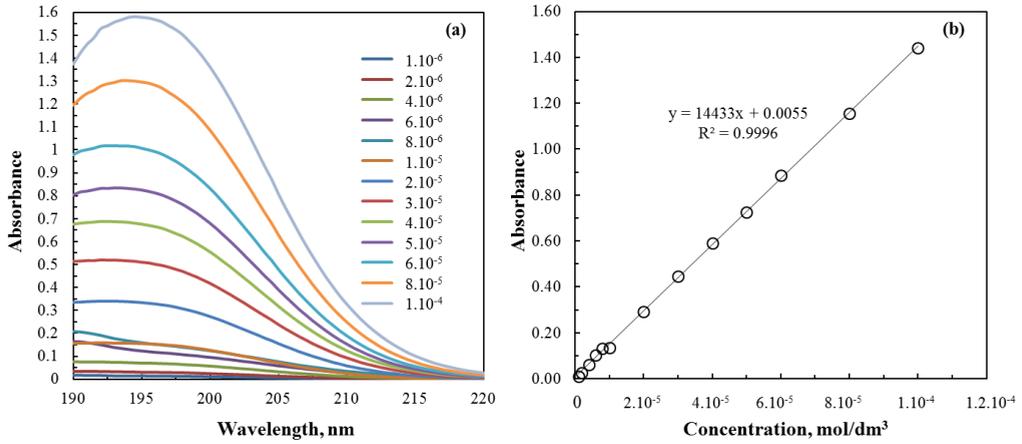
Fig. 1. (a) UV spectra for HTPB at different concentrations
(b) Calibration curve (absorbance values at 199 nm)
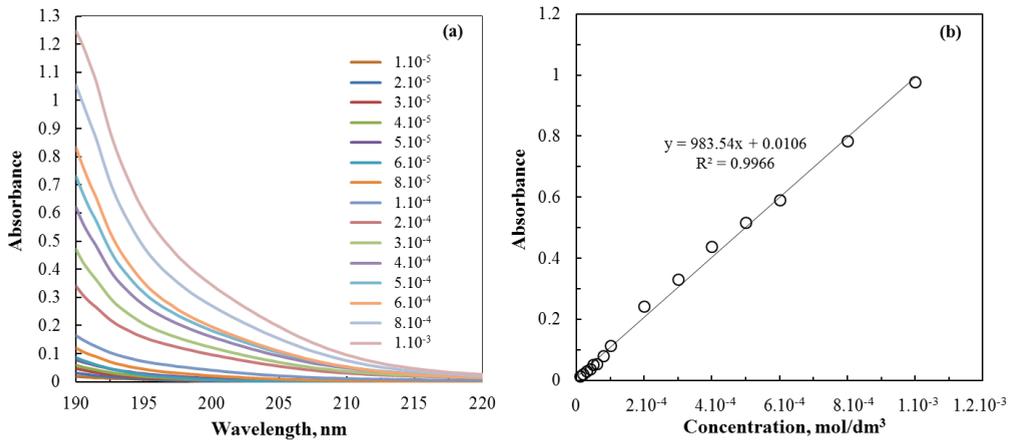
Fig. 2. (a) UV spectra for HTBPB at different concentrations
(b) Calibration curve (absorbance values at 192 nm)

Additionally, the equations obtained from these calibration curves were used to calculate the residual concentration of the surfactants.

The adsorption density was calculated by means of the following formula:

$$\Gamma = \frac{(C_i - C_e)V}{m} \tag{1}$$

where C_i is the initial concentration (mol/dm^3), C_e equilibrium concentration (mol/dm^3), V solution volume (dm^3), m solid amount (g), and Γ adsorption density (mol/g).
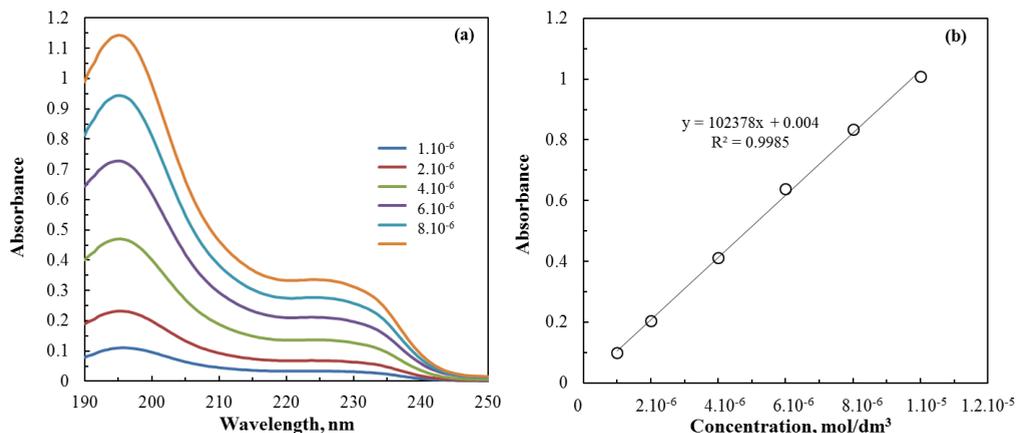
Fig. 3. (a) UV spectra for TPB at different concentrations
(b) Calibration curve (absorbance values at 197 nm)

Zeta potential measurements

The zeta potentials of the samples in the presence of the phosphonium salts were determined using a ZetaPlus instrument (Brookhaven Instruments, Holtsville, NY). First, the sample was added into the surfactant solution at the desired concentration (solid ratio of 0.1 %), and stirred using a magnetic stirrer at 500 rpm for 30 min. Next, the suspension was centrifuged for 5 min at 5000 rpm in order to make solid-liquid separation. Then, a 5 cm^3 of clear solution was taken from the top of the suspension, and mixed with a small amount of solid taken from the bottom of the tube, and this suspension was shaken for 10 times by hand. Finally, the suspension was transferred to the measurement cell, and ten measurements at each surfactant concentration were performed. An average value of these measurements was used further on and the average error was about 3%. The experiments were carried out at room 23 °C.

Surface tension measurements

The surface tension measurements were carried out by using an optical tensiometer with a fully computer-controlled apparatus (Theta Lite, Attension, Finland). In this method, a drop hanging down was generated, the drop profile was captured, digitized and the image data processed. The digitized drop profiles were fitted numerically with the solution of the Young–Laplace equation to obtain the surface tension value. In addition, the critical micelle concentration (CMC) of each surfactant was also determined from the surface tension measurements.

Flocculation experiments

The flocculation experiments were carried out with the suspensions in the presence of HTPB, HTBPB and TPB solutions ranging from 10^{-6} mol/dm^3 to 10^{-2} mol/dm^3 to

determine the critical phosphonium salt concentration. The experiments were carried out at a solid ratio of 0.1 %. The suspensions were first homogenized in an ultrasonic bath for 3 min, and left for 24 h overnight. Finally, the critical flocculation concentration for each surfactant was determined based on the level of maximum settling.

Results and discussions

Results

Sample characterization

The mineralogical analysis of the raw and purified samples indicated that the samples contain smectite (S) (Na-montmorillonite having basal spacing for raw and purified clay of 12.45 Å and 11.62 Å, respectively) as the main mineral with impurities such as quartz (Q), feldspar (F), calcite (C) and opal-CT (O) (Fig. 4).
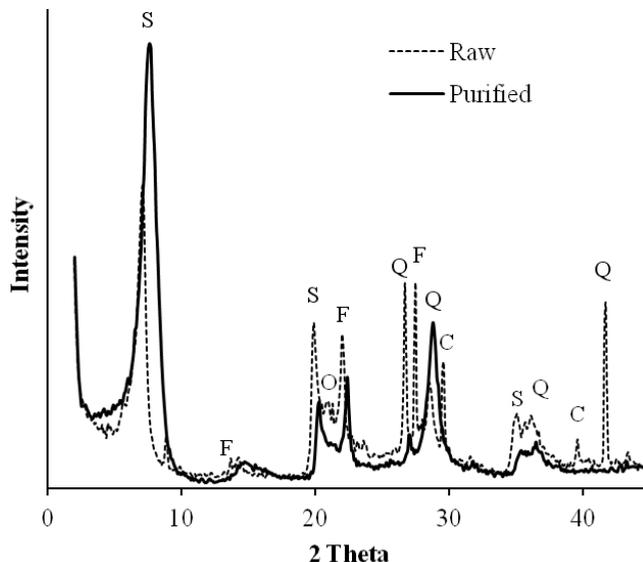
Fig. 4. XRD patterns of raw and purified Resadiye Na-montmorillonite

After the purification, significant amounts of feldspar was removed as seen from the chemical analysis and the XRD patterns of the samples presented in Table 2 and Fig. 4. A decrease in the CaO content of the sample is clearly seen in Table 2.

The results of the characterization test for the samples are shown in Table 3. The results indicated that the purification of the raw sample using a Falcon separator significantly increased cation exchange capacity (CEC), swelling, gelling index, and water adsorption capacity of Na-MMT (Table 3).

Table 2. Chemical composition of the raw and purified Na-MMT

Component	Raw Na-MMT Mass, %	Purified Na-MMT Mass, %
SiO_2	64.1	65.9
Al_2O_3	15.6	16.9
Fe_2O_3	3.6	4.8
MgO	1.8	2.0
CaO	3.1	0.7
Na_2O	2.5	2.7
K_2O	1.1	0.4
TiO_2	0.2	0.2
P_2O_5	0.1	0.1
MnO	0.1	0.1
LOI	7.6	5.8
Total	99.8	99.6

Table 3. Technological properties of the raw and purified Na-MMT

Sample	CEC (meq/g)	Swelling (cm^3)	Gelling index	Water adsorption capacity (%)
Raw	0.78	23.0	11.8	240.8
Purified	0.98	40.0	20.0	543.6

Adsorption experiments

A series of adsorption experiments was carried out to determine the adsorption isotherms of Na-montmorillonite/phosphonium salts (Fig. 5).

As seen from Fig. 5, the adsorption isotherms for surfactants exhibit three regions: a low adsorption region, linear increase region, and finally plateau region. When the results are analyzed carefully, it can be seen that the HTPB adsorption capacity of Resadiye Na-montmorillonite $1.8 \cdot 10^{-3}$ mol/g (1.8 meq/g). Higher adsorption capacities than these values showed the effect of ion exchange reactions as well as ion adsorption by considering that the cation exchange capacity of the same product is 0.98 meq/g. The HTBPB adsorption capacity was calculated as $1 \cdot 10^{-3}$ mol/g (1 meq/g). The adsorption capacity of HTPB and HTBPB showed both ion exchange capacity and ion adsorption reaction if considered that the cation exchange capacity as 0.98 meq/g. Besides, their adsorption capacities, when close to the CEC value, cause a bilateral (double) layer formation. The TPB adsorption capacity of Na-montmorillonite was identified as $1.2 \cdot 10^{-3}$ mol/g by analyzing the adsorption isotherm. The ion exchange and ion adsorption reactions are effective as the adsorption capacity is higher than the CEC

values (0.98 meq/g). However, the aromatic structured TPB was absorbed mainly on the surface due to the low equilibrium concentration in the solution.
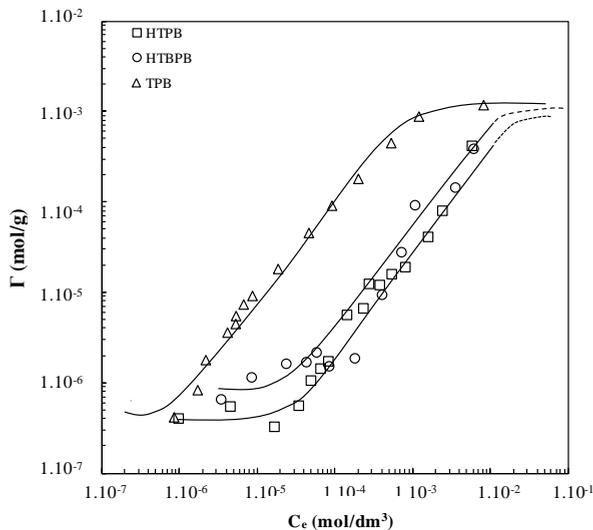
Fig. 5. Adsorption isotherms for phosphonium salts on Na-montmorillonite

According to the adsorption isotherms of HTPB and HTBPB on Na-montmorillonite the cation exchange as well as ion adsorption reactions are present. In addition, the adsorption capacities, which are nearly equal to the CEC values, showed the existence of a monolayer and a bilayer due to a function of its concentration between layers. This is also consistent with the study of Patel (2007). The adsorption value of TPB, which showed a much higher value than the CEC of 0.98 meq/g of the Resadiye Na-montmorillonite, indicates that the ion adsorptions as well as ion exchange reactions are apparent. However, the low equilibrium concentration of the TPB implies that the aromatic surfactant adsorbed only on the surfaces by building monolayers between the Na-MMT sheets.

The adsorption density values of HTBPB and HTPB are nearly equal and the shape of the isotherms shows similarities by considering the adsoption isotherm curves. In the case of HTBPB and HTPB, this could be explained by the chemical composition of both of the surfactants and their molecular surface area.

The study of adsorption isotherms shows that the ion exchange, which is pointed by the initial portion of the curve, takes a long time to complete the process. The isotherm of the TPB is rather different than other phosphonium salts as a result of its tendency to adsorption acceleration. However, this depends on its moleculer area which is different for other surfactant and also on its aromatic structure that includes one head group.

In conclusion the TPB adsorption capacity of Resadiye Na-montmorillonite is greater than that of HTPB and HTBPB. This depends on the chemical structures of the surface active agents. It is well known that TPB has a rounded shape whereas HTPB and HTBPB have a long chained form (Table 1). A similar trend is shown in Fig. 5 for

HTPB and HTBPB in contrast to the ion exchange duration for TPB, which is completed much earlier. In addition, when considering TPB, it can be seen that the ion exchange capacity is accomplished soon, and the surfactants adsorb by moving quickly onto the surface.

The results obtained from the adsorption experiments with the phosphonium salts were considered in the accordance with the models of Langmuir and Freundlich adsorpsion isotherms (Freundlich 1926; Langmuir 1926). The plots of the Langmuir and Freundlich isotherms are illustrated in Table 4 and Fig. 6. The parameters such as K_L and a_L for the Langmuir equation (Eq. 2) and K_f and $1/n$ for the Freundlich equation (Eq.3), were calculated and listed in Table 4. The results indicated that adsorption of phosphonium salts on Na- montmorillonite shows a better distribution according to the Freundlich model where a standard deviation is close to 1. On the other hand, only adsorption of TPB on montmorillonite is consistent with the Langmuir model when compared to others (Table 4). This can be attributed to its structure because it is composed of only one aromatic head rather than chain structure

$$q_e = \frac{K_L a_L C_e}{1} + a_L C_e \tag{2}$$

$$q_e = K_f C_e^{\frac{1}{n}} \tag{3}$$

where K_L – Langmuir isotherm constant, $dm^3\ g^{-1}$, a_L – Langmuir isotherm constant, $dm^3\ mol^{-1}$, K_f – Freundlich isotherm constant, $dm^3\ g^{-1}$, n – Freundlich isotherm constant, $dm^3\ mol^{-1}$.

Table 4. Langmuir and Freundlich adsorpsion model parameters

	Langmuir				Freundlich		
	K_L	a_L	$q_m = K_L/a_L$	R^2	K_f	$1/n$	R^2
HTPB	0.028	−90.279	−0.0003	0.3413	0.99	0.0693	0.9372
HTBPB	0.019	−138.314	−0.0001	0.2936	0.99	0.0599	0.9501
TPB	1.078	338.675	0.0032	0.9383	1.0	0.7907	0.9958

The zeta potential measurements of Na-montmorillonite as a function of the equilibrium concentration of phosphonium salts are shown in Fig. 7. The zeta potential of purified Na-montmorillonite was measured as -50 mV at natural pH. After the modification of the sample at low concentrations of the surfactants, this value increased to -60 mV. With increasing surfactant concentration, the zeta potential value started to decrease and reached zero point of charge at $3 \cdot 10^{-3}\ mol/dm^3$, $4 \cdot 10^{-3}\ mol/dm^3$, and $1 \cdot 10^{-3}\ mol/dm^3$ for HTBPB, HTPB, and TPB, respectively. Finally, above these concentrations, the zeta potential of the clay reached +60 mV.
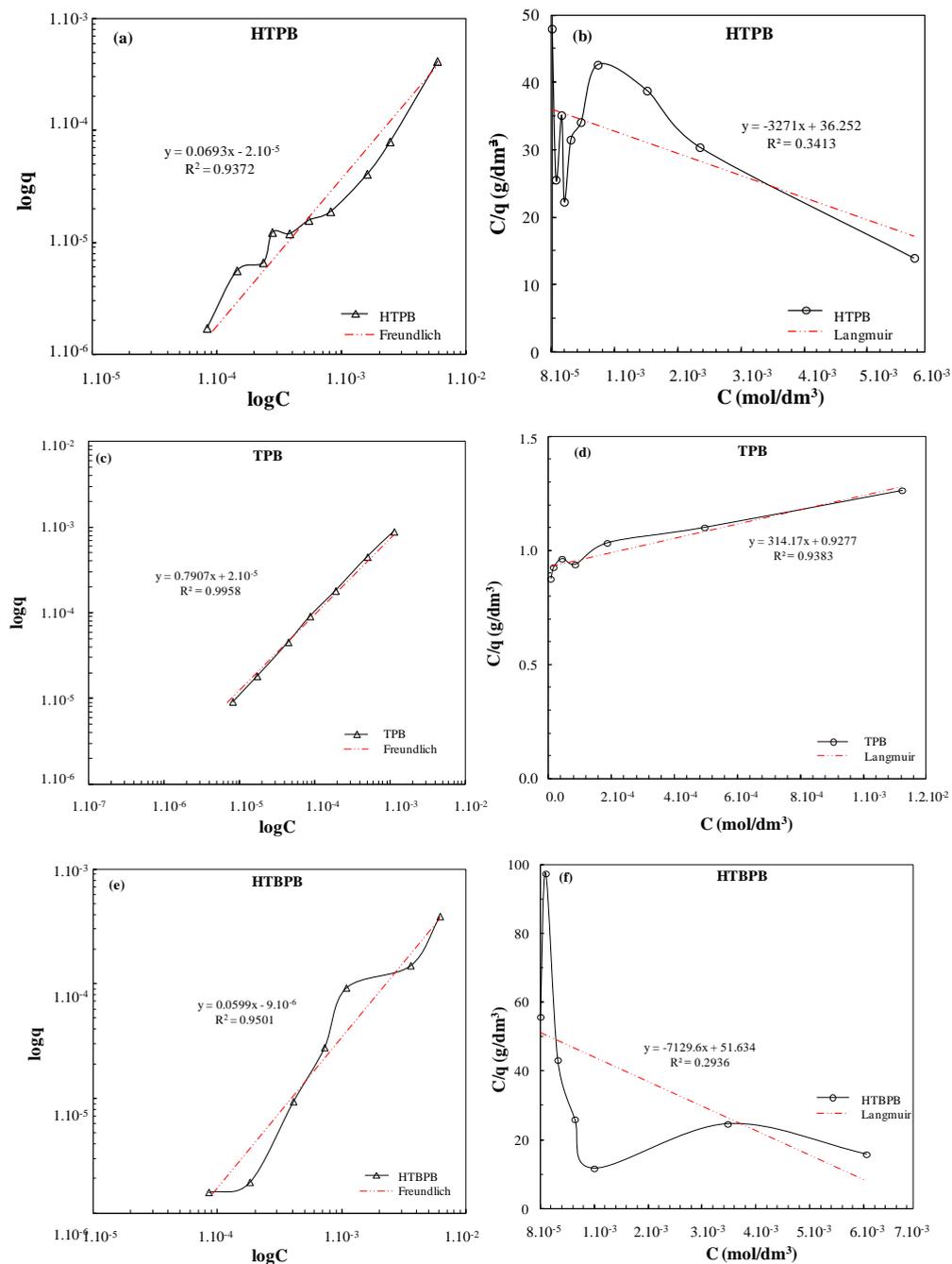
Fig. 6. Freundlich (a)(c)(e) and Langmuir (b)(d)(f) plots for phosphonium salts

K. Cinku, B. Baysal

According to the zeta potential and the adsorption isotherm profiles for the modified Na-montmorillonite, it can be seen that the adsorption reached plateau at concentrations where the zeta potential reached positive values (Figs 5 and 7). The parallel increase of the charge with the surfactant concentration confirmed adsorption of the phosphonium salts on montmorillonite.
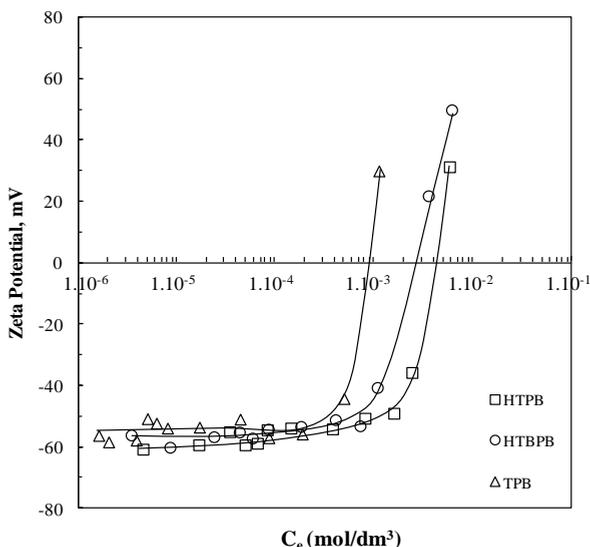
Fig. 7. Effect of surfactant concnetration on zeta potential of Na-montmorillonite

The surface tension of aqueous solutions of HTPB and HTBPB at different concentrations was measured and the results are presented in Fig. 8. As can be seen in Fig. 8, the surface tension decreases with an increase in the surfactant concentrations, and finally reaches the equilibrium point at a specific surfactant concentration. This concentration is known as the critical micelle concentration (CMC). The CMC for HTPB was found to be $2–3\cdot10^{-3}$ mol/dm^3, which is consistent with the results of Verma and Ghosh (2010), whereas it is $2\cdot10^{-3}$ mol/dm^3 for HTBPB (Fig. 8). On the other hand, the CMC for TPB could not be measured because of its chemical composition showing no hydrocarbon tail and a high Kraft point and it crystallizes at room temperature in a short period time. However, it gives rise to flocculation when subjected to interaction with clay in water. For this reason, an empirical approach is developed for determining the surface tension based upon the critical coagulation concentration conception (Lagaly and Ziesmer 2003).
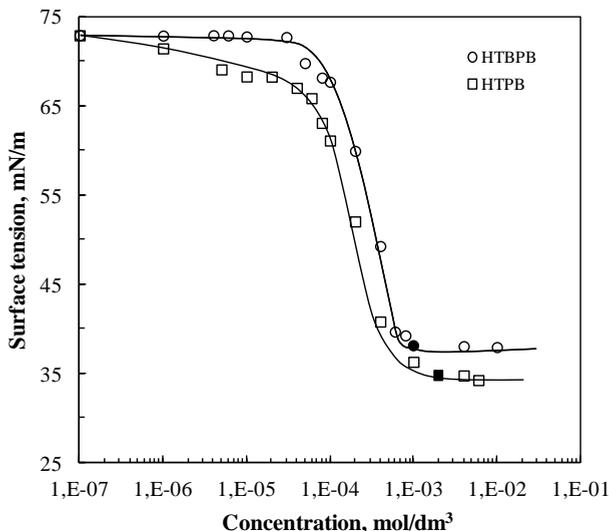
Fig. 8. Surface tension of HTPB and HTBPB solutions at room temperature

The critical flocculation concentration (CFC) test showed that the CFC values were found to be $2-3 \cdot 10^{-4}$ mol/dm^3, $2 \cdot 10^{-4}$ mol/dm^3, and approximately $2 \cdot 10^{-4}$ mol/dm^3 for HTPB, TPB, HTBPB, respectively. It is also interesting to note that there is an approximately ten-fold difference between the CFC and CMC values for HTPB and HTBPB. Additionally, as already mentioned, it was not possible to measure the surface tension of TPB due to its high Kraft point, which causes its crystallization even at room temperature because of lack of the tail part. From this point of view, the CMC value for TPB can be accepted as $2 \cdot 10^{-3}$ mol/dm^3 by applying the CFC test.

It can be concluded that the results obtained from this study showed a great consistency when considering adsorption isotherms, zeta potential measurements, and the CMC test curves (Figs 5, 7 and 8) along with the CFC test results.

Conclusions

In this study, the adsorption of selected phosphonium salts (HTPB, HTBPB, and TPB) on Resadiye sodium montmorillonite (Na-MMT) which was purified with a Falcon concentrator was investigated in detail. The characterization tests for the raw and pure samples showed that the clay mineral used in this study is a good quality sodium montmorillonite due to its swelling volume of 23–39 cm^3, a high gelling index of 11.8–20, and a characterisitic (d_{001}) smectite peak of 11 Å and 12 Å.

The adsorption experiments with HTPB, HTBPB, and TPB showed that the maximum adsorption densities for HTPB, HTBPB and TPB on Na-MMT were found to be $1.8 \cdot 10^{-3}$, $1 \cdot 10^{-3}$ and $1.2 \cdot 10^{-3}$ mol/g, respectively. These results were also supported

with zeta potential, surface tension and critical flocculation concentration (CFC) measurements. The difference in the adsorption capacity among the surfactants was attributed to their structures, especially the variations in their polar parts. The chain lenghts of the surfactants were 16 C, except TBP, and the the adsorption capacity widely depended on the difference of the surface area of the head that forms the polar part.

It is concluded that the technological properties of Na-montmorillonite can be improved using mineral processing equipment such as a Falcon concentrator. Additionally, the adsorption properties of the phosphonium salts on the purified Na-montmorillonite obtained from this study will be fundamental in the case of production of organoclay/nanocomposites modified with these surfactants which has a higher thermal stability.

Acknowledgements

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