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Thermodynamics and mechanism of cetyltrimethylammonium adsorption onto clayey soil from aqueous solutions

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ABSTRACT

In this study, the adsorption mechanism of cetyltrimethylammonium bromide (CTAB), a cationic surfactant, to a clayey soil from aqueous solution was investigated as a function of ionic strength, pH, temperature, CTAB equilibrium concentration, and stirring speed. In addition, both kinetics and thermodynamic evaluations of the adsorption data were supported with measurements of particle zeta potential and suspension electrical conductivity. The amount of cetyltrimethylammonium bromide adsorbed to clayey soil increased with increasing CTAB equilibrium concentration, temperature and ionic strength, but was not affected from pH and stirring speed. The isosteric enthalpy and entropy changes were calculated as 28.27 kJ mol^{-1} and -0.091 kJ mol^{-1} K^{-1}, respectively. This positive enthalpy value indicates that the adsorption process was endothermic. The negative and quite small isosteric entropy change indicates that the orderless of adsorption system slightly decreases with adsorption of CTA$^+$ ions to the clayey soil. In addition, it was found that the kinetic data agrees very well to the pseudo-second-order kinetic model, indicating the presence of effective electrostatic interactions between the charged active sites on the surface and CTA$^+$ ions. The measured zeta potential values of particles support this result. Addition of the neutral electrolyte, NaCl, increased the adsorption efficiency and effectiveness of ionic surfactants due to decreased electrical repulsion between free CTA$^+$ ions and similarly charged adsorbed ions. Polyvalent cations, such as Al^{3+} and Ca^{2+}, tend to compete for adsorption with CTA$^+$ ions, but the increased ionic strength of the media favored adsorption of CTA$^+$ ions.

1. Introduction

Adsorption of surfactants at the solid–liquid interface is critical for many traditional processes such as detergency, wetting and mineral flotation as well as the newer fields of templated surfaces and nanotechnology. The past decade has seen the extension of surfactant applications to such high-technology areas, such as electronic printing, magnetic recording, biotechnology, microelectronics, and viral research [1]. The application of surfactants can also produce environmental pollution and raises a series of problems for wastewater treatment plants [2]. Furthermore, surfactants adsorb readily onto crystal surfaces, owing to their surface activity, leading to crystal growth inhibition [3–5]. From this perspective, surfactants should be removed from selected stages of industrial processes or wastewater treatment systems. Surfactant removal from industrial wastewaters is a major environmental problem because it is difficult to treat such waters by conventional methods. One of the characteristic features of surfactants is their tendency to adsorb at interfaces in an oriented fashion [1]. The adsorption of surface-active materials onto a solid surface from an aqueous solution is an important process both scientifically and technologically in many situations, including those in which we may want to remove unwanted materials from a system (detergency), change the wetting characteristics of a surface or stabilize a finely divided solid system in a liquid where stability may otherwise be absent [6]. Surfactant adsorption has been studied extensively. Additionally, several materials have been investigated as surfactant adsorbents. These include layered double hydroxides [7,8], zeolites [7], activated carbons [9], silica [10], alumina [5,7,8,11–13], polymers [14], and natural and synthetic fibers [15].

In relatively recent years, there has been an increasing interest in utilizing natural clay materials for the removal of toxic metals and some organic pollutants from aqueous solutions [16,17]. One type of clay mineral is bentonite, which exists as discrete deposits in most continents of the world. It was created primarily in volcanic eruptions millions of years ago, when volcanic ash settled in shallow seas and overtime became bentonite clay. In Jordan, specifically the areas of Mahes and Al-Rashadyeh, bentonite is available

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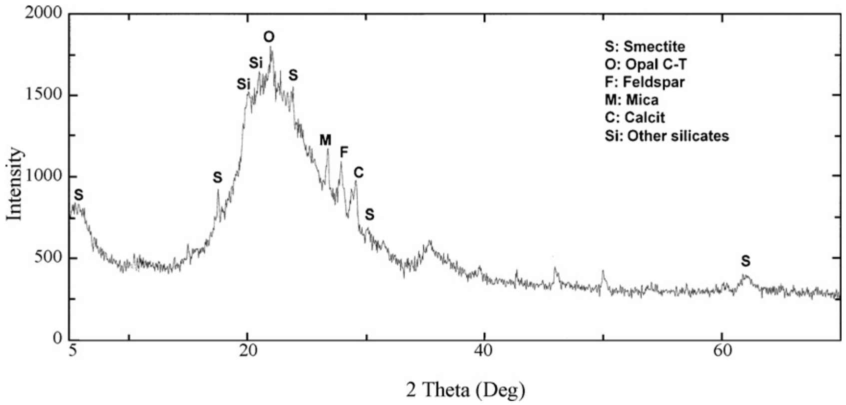

Fig. 1. Random powder-mount X-ray diffraction pattern for the clayey soil.

in large amounts. Bentonite has the potential to be used as a low-cost sorbent since it is naturally available and has a high surface area [18].

In the present paper, the adsorption of cetyltrimethylammonium bromide (CTAB) onto clayey soil surfaces from aqueous solution was investigated. This study is of interest in detergency from two points of view. Cationic surfactants are known as bactericides [11] and fabric softeners [12] and proper incorporation of these two characteristics in a detergent formulation would be of great interest. The adsorption of surfactants at the solid–liquid interface is strongly influenced by a number of factors: (i) the nature of the structural groups on the solid surface, (ii) the molecular structure of the surfactant being adsorbed (the adsorbate), and (iii) the aqueous phase pH, electrolyte concentration, additives, and temperature [1]. Particularly, the modification of clay and clayey soil with the various ions and preparation of organo-clay using cationic surface active substances such as CTAB are required knowledge of the nature of interactions of ion–clay and surfactant–clay. Therefore, in this work, the adsorption of CTAB, a cationic surfactant, onto a clayey soil was studied as a function of equilibrium concentration, stirring speed, pH, ionic strength, and temperature. In addition, both the kinetic and thermodynamic evaluations of the adsorption data have been supported with particle zeta potential and suspension electrical-conductivity measurements.

2. Experimental

2.1. Materials

In this study, the cationic surfactant, CTAB also known as hexadecyltrimethylammonium bromide was used as adsorbate. CTAB has a long hydrocarbon chain and is one of the most popular cationic surfactants [3–11]. CTAB was re-crystallized three times from $CHCl_3$ prior to use. The clayey soil sample taken from Erzurum region in Turkey was not purified prior to usage and it consists of smectite clay mineral and opal C–T, amorphous material, feldspar, mica, and calcite and quartz in minor quantities. XRD measurement of the clayey soil was performed using Rigaku 2200D/max (Rigaku Corporation, Tokyo, Japan) powder diffractometer equipment with a Cu Kα radiation source. X-ray diffraction spectrum of clayey soil sample is given in Fig. 1. The determined minerals in the clayey soil were showed on XRD pattern. The used clayey soil, apart from smectite, also contains non-clay minerals and this minerals and their quantity significantly effect XRD peaks' shape and breadth. The intensity of smectite peaks depending on its quantity is relatively low. XRF analysis and physical properties such as cation exchange capacity, liquid limit, plasticity index, density of clayey soil support these results (see Table 1).

Table 1
Physical properties of clayey soil

Main clay mineral	Smectite
Cation exchange capacity (mequiv./100 g dry soil)	34.4
Specific gravity (g/cm^3)	1.85
Organic matter content (%)	2.22
Moisture (%)	4.51
Liquid limit, w_L (%)	89
Plastic limit, w_P (%)	68
Plasticity index, I_p	21
Unified soil classification (USCS)	MH
BET (N_2) surface area (m^2/g)	30.0
Average pore diameter (μm)	0.0342
Total pore surface area (m^2/g)	28.91

The sample was air-dried and then sieved to give a 180–450 μm size fraction using ASTM Standard sieves. Chemical composition of the clayey soil was determined by Rigaku RIX-3000 X-ray fluorescence spectrometry (Rigaku Corporation, Tokyo, Japan). The results are given in Table 2. The cation exchange capacity (CEC) of the clayey soil sample was determined by the ammonium acetate method [19]. All chemicals used in this study were obtained from Merck. BET surface area and porosity measurements of the clayey soil sample were determined by Micrometrics FlowSorb II-2300 and Autopore II 9220 Hg Porosimeter (max. Hg pressure 40,000 psi) (Micrometrics Instrument Corp., Norcross, GA, USA) respectively.

2.2. Method

Batch adsorption kinetics experiments were carried out in 100-ml, glass-stopperred, round-bottom flasks immersed in a thermostatic shaker bath. A 0.2-g sample of clayey soil was mixed with 100 ml aqueous solutions of CTAB with various initial con-

Table 2
Chemical composition of the clayey soil

Constituent	Percentage present
SiO_2	84.40
Al_2O_3	4.32
Fe_2O_3	2.02
MgO	0.44
CaO	0.53
Na_2O	0.39
K_2O	0.52
TiO_2	0.18
P_2O_5	0.09
MnO	<0.01

centrations (30, 60, 90, 120, 150, 180 and 210 mg/L). The flasks and contents were then shaken for the different adsorption times at 293, 313 and 333 K at natural pH (5.6). The effect of pH was investigated at 293 K for 30 min. The pH adjustments were done using concentrated HCl and NaOH solutions. In the experiments, the stirring speed was kept constant at 90 rpm, except in experiments that examined the effect of stirring speed. The effect of stirring speed was investigated at 293 K for 180 mg/L initial CTAB concentration with various stirring speeds (90, 120 and 150 rpm) at different adsorption times. The effect of ionic strength on CTAB adsorption were investigated by using three electrolytes, NaCl, $CaCl_2$ and $AlCl_3$, at three different concentrations (0.01, 0.02 and 0.03 mol/L) at 293 K for 30 min. At the end of each adsorption period, the flask contents were divided into two parts. One part was passed through Whatman 40 filter paper and the filtrate was centrifuged twice for 15 min at 3750 rpm. The second part of the clayey soil/water suspension was used for zeta potential and electrical conductivity measurements.

The concentrations of CTA^+ in the supernatant solution were determined using a double-beam UV spectrophotometer at 375 nm with 0.02 mL of 0.1% picric acid in 0.002 M NaOH and 0.40 mL of 1,2-dichloroethane added per 1.0 mL of the supernatant [20]. It was found that the calibration curve was very reproducible and linear over the concentration range used in this study. The amount of CTAB adsorbed was calculated from the concentrations in solution before and after adsorption. Blanks containing no CTAB were used for each series of experiments.

The zeta potential measurements of solid particles in clayey soil/water suspensions were carried out by using a Zeta Meter 3.0+ (Zeta-Meter, Inc., Staunton, VA, USA) at the unadjusted pHs. The zeta potential values were corrected for temperature differences using the following equation (Eq. (1)):

$$\zeta_\mathrm{d}\ (\mathrm{mV}) = C_\mathrm{T}\,\zeta_0 \tag{1}$$

where ξ_d, C_T, ξ_0 represent the corrected zeta potential value, correction factor related to temperature and the measured zeta potential value, respectively. In addition, prior to each measurement, the zeta meter was calibrated using a Min-U-Sil standard solution. Min-U-Sil is a natural air-floated silica produced by crushing sandstone. Its average diameter is about 1.1 μm. A suspension of 100 mg/L of Min-U-Sil in a 100 mg/L sodium chloride solution is easy to prepare and gives reasonably consistent results. This suspension was allowed to stand for 1 h to reach equilibrium before use. The average zeta potential of the Min-U-Sil standard solution was between −50 and −42 mV with a standard deviation of 4–6 mV.

The conductivity of clayey soil/water suspension was measured using a WTW LF 521 Karl Kolb conductometer (WTW Inc., Weilheim, Germany) after adsorption under the same conditions as the zeta potential measurements.

3. Results and discussion

3.1. *The effect of time, equilibrium CTAB concentration and temperature*

The adsorption of CTAB to the clayey soil sample was investigated at a constant stirring speed of 90 rpm, at time intervals ranged from 10 to 1440 min, and with initial CTAB concentrations ranged from 30 to 210 mg/L. The equilibration time necessary for adsorption was found to be approximately 30 min which indicates rapid adsorption occurred.

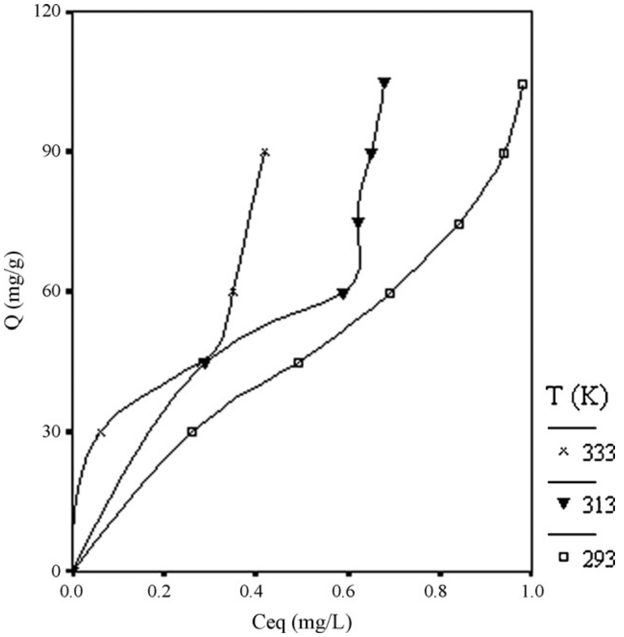

Fig. 2. Isotherms for adsorption of CTAB at three different temperatures.

To investigate variations in CTAB adsorption with equilibrium concentration, experiments were carried out by varying initial CTAB concentrations from 30 to 210 mg/L at three temperatures for 30 min and a constant stirring speed of 90 rpm (Fig. 2). There are number of mechanisms by which surface-active solutes may adsorb onto solid adsorbents from aqueous solution. In general, adsorption of surfactants involves (i) ion exchange, (ii) ion pairing, and (iii) hydrophobic interactions [9,21]. Ion exchange is the replacement of counter ions of the adsorbent by similarly charged surfactant ions. Ion pairing involves the adsorption of surfactant ions from solution onto oppositely charged sites unoccupied and/or the interaction between the hydrophobic parts of adsorbed surfactant ions and the tails of monomeric surfactant ions in the solution (hemimicelle formation). Hydrophobic bonding occurs when the combination of mutual attraction between hydrophobic groups of the surfactant molecules and their tendency to escape from an aqueous environment becomes large enough to permit them to adsorb onto the solid adsorbent by aggregating their chains. Adsorption of surfactant molecules from the liquid phase onto or adjacent to other surfactant molecules already adsorbed on the solid adsorbent also may occur by this mechanism [1]. At low CTAB concentrations, the surfactant adsorbs mainly by ion exchange or ion pairing, possibly with the hydrophobic group more or less prone on the adsorbent [9,21]. In this case, the charge density or potential at the Stern layer of the solid remains almost constant. As seen from Fig. 2, adsorption efficiency was generally increased with increasing temperature. In the 293 K isotherm, CTAB adsorption initially increased rapidly with increases in equilibrium concentrations, slowed at intermediate concentrations, then rapidly increased at high equilibrium concentrations. The isotherms at 313 and 333 K exhibited similar tendencies. The dispersion of highly negatively charged clay particles became more effective at higher temperatures. This facilitated the adsorption of CTA^+ ion onto the clay surface. The greater temperatures also lead to the more dehydration of the CTA^+ ions. Thus, these ions could easily reach active sites on the clay matrix.

3.2. *The effect of temperature on the zeta potential and conductivity*

Fig. 3a–c shows the changing of zeta potential and conductivity values with equilibrium concentrations of CTAB for three

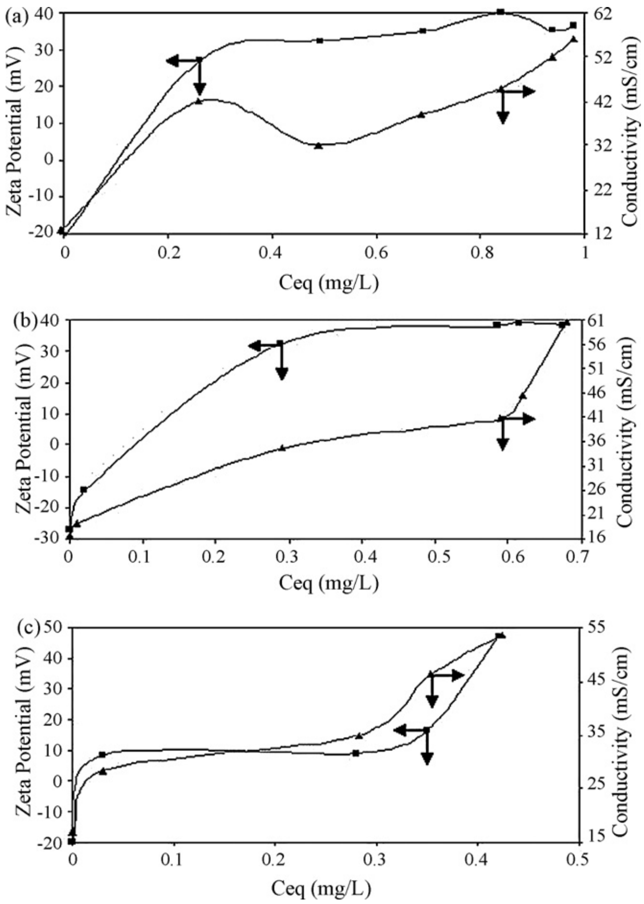

Fig. 3. Equilibrium CTAB concentration effects on particle zeta potential and suspension electrical conductivity at (a) 293 K, (b) 313 K and (c) 333 K.

temperatures. At higher equilibrium CTAB concentrations and at 293 and 313 K, adsorption increased, but the zeta potentials did not change very much. This indicates that CTAB adsorption mainly takes place through cooperative adsorption. Namely, it can be said that the adsorption proceeds through the lateral hydrophobic interactions between the hydrophobic tails of CTAB molecules. At lower equilibrium CTAB concentrations, it can also be suggested that the adsorption takes place through the mechanisms of the ion exchange and ion pairing between CTA$^+$ ions and active sites on clay surface. However, after reaching surface saturation at intermediate equilibrium CTAB concentrations, cooperative adsorption begins to predominate. Especially, the observed relative increase in conductivity values at higher CTAB concentrations and the apparent relative decrease at intermediate CTAB concentrations might indicate more compact packing on the adsorbent surface. This leads to the removal of other co-ions and counter ions from the surface. Similar results were reported previously about the adsorption of charged surface-active agents to the surfaces of the highly charged solid adsorbents [22–27].

As can be seen from Fig. 3a–c, the changes in both conductivity and zeta potential values were parallel until equilibrium concentrations at which either conductivity or zeta potentials starts to deviate from the normal curve. These changes in Fig. 3a–c have a similar tendency to changes in the isotherm shapes at Fig. 2. The zeta potential values at 333 K were quite low and positive until an equilibrium concentration of 0.35 mg/L was attained. The uttermost increase observed after this point can be attributed to the increase in the tendency of cooperative adsorption that depends temperature. Such an adsorption leads to an intensive dehydration of the CTA$^+$ ions. This situation may also be explained by endothermic nature of adsorption. The increase in temperature might increase the capability of CTA$^+$ ions to reach to the surface and/or increase dehydration of the hydrophilic part of CTAB. It was reported that temperature increase generally increases the adsorption of nonionic species [1], while it decreases adsorption of ionic species, particularly anionic [7,28]. The increase in the adsorption of CTAB with increasing temperature could be attributed to the hydrophobic bonding or/and formation of hemimicelle as to the adsorption of non-ionic species.

Thermodynamic quantities for the adsorption of CTAB onto clayey soil surface have been calculated by considering the certain amounts of surfactant adsorbed. These are isosteric adsorption enthalpy, $(\Delta H_{ads})_q$, and isosteric adsorption entropy, $(\Delta S_{ads})_q$, which were statistically calculated by using least squares method and experimental data. These quantities were calculated using Eqs. (2) and (3) [9]. These calculations were based on the same amount of adsorbed surfactant at different temperatures that corresponded to different equilibrium surfactant concentrations where adsorption efficiencies were highest.

$$\frac{d(\ln C)}{d(1/T)} = -\frac{\Delta H_{ads}}{R} \tag{2}$$

$$\frac{d(\ln C)}{d(\ln T)} = \frac{\Delta S_{ads}}{R} \tag{3}$$

From experimental adsorption isotherms for the clayey soil sample at different temperatures, the isosteric enthalpy of adsorption, ΔH_{ads}, and the isosteric entropy of adsorption ΔS_{ads}, can be determined from the slope of a plot of $\ln C$ values versus $1/T$ and from plots of $\ln C$ versus $\ln T$. The quantity $-\Delta H_{ads}$ is the differential molar enthalpy of adsorption which is also termed as the isosteric enthalpy of adsorption. Thus, the isosteric heat of adsorption ΔH can be taken with the opposite sign [29,30]. The C and T in these equations represent the equilibrium CTAB concentration and absolute temperature, respectively.

The isosteric enthalpy change was calculated to be 28.27 kJ mol^{-1}. This positive enthalpy value indicates that the adsorption process was endothermic, but it was not chemisorption. The calculated entropy value (−0.091 kJ mol^{-1} K^{-1}) was quite small and negative. This was an expected result due to adsorption of free CTA$^+$ ions on the surface, and thus the CTA$^+$ ions were more ordered. Especially, the adsorption occurred at higher concentrations led to great dehydration of the CTA$^+$ ions and to decrease of the number of water molecules surrounding the hydrocarbon tails of CTAB molecules and thus the degrees of freedom of water molecules increased. As a result, it can be said that the adsorption process was physical in nature and controlled by entropy.

3.3. The effect of pH

Surfaces possessing highly charged groups in aqueous solvents are especially sensitive to environmental conditions such as pH, ionic strength and temperature. This usually causes marked changes in the adsorption of ionic surfactants onto charged solid adsorbents. As the pH of the aqueous phase is lowered, a solid surface will usually become more positive or less negative because of proton adsorption from solution onto charged sites. This leads to an increase in anionic surfactant adsorption and a decrease in cationic surfactant adsorption depending on the sign of surface charge. The reverse is true when the pH of the aqueous phase is increased. The effects of pH are observed markedly in mineral oxides, such as silica and alumina, and in wool and other polyamides [1,21], due to the potential determining ions of H$^+$ and OH$^-$.

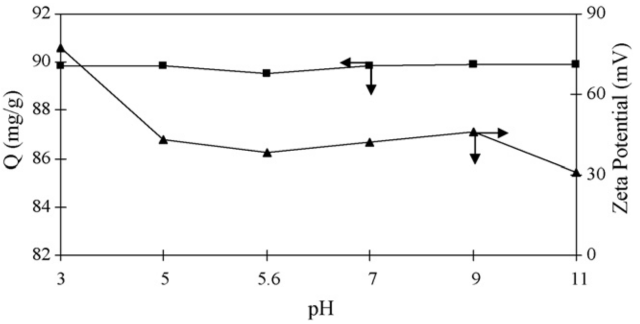

Fig. 4. Suspension pH effects on particle zeta potential and amount of CTAB adsorbed at 293.

Variations in particle zeta potential and CTAB adsorption with suspension pH indicate that CTAB adsorption was almost the same throughout the pH range, while particle zeta potentials at the lower pH range were quite high (Fig. 4). This indicates that there was no competition between the H^+ and CTA^+ ions. As the aqueous phase pH was decreased, the solid surface became more positive and a decrease in the adsorption of cationic surfactants, such as CTAB, might be expected due to the repulsion between the similar charges. However, the highly positive particle zeta potential values measured in this pH range clearly indicate H^+ ion adsorption [31], decarbonatation [32] and hydrolysis of metal oxides in the clay matrix. The last two processes (decarbonatation and hydrolysis) might facilitate CTA^+ transport to the interlayers of the clay and compensate the possible decrease in CTAB adsorption due to first process (H^+ adsorption).

The conductivity values were quite high at lower and higher pHs, whereas the particle zeta potential values decreased as suspension pH was increased (Fig. 5). This might be attributed to the existence of $Al(OH)_n$ hydrolysis products at higher pHs, the high affinity of CTA^+ ion for active sites on the surface, and the partial adsorption of OH^- ions onto the surface.

3.4. *Effect of stirring speed*

With increased stirring speed, the efficiency and effectiveness of adsorption was almost unaffected (Fig. 6). This indicates that the adsorption rate in the clayey soil/CTAB system did not depend on the rate of surfactant ion diffusion from the bulk solution to the adsorbent surface. Therefore, the adsorption kinetics of the clayey soil/CTAB system was investigated with regard to the effectiveness of interaction between active sites and surfactant ions. It was found that the experimental results were highly consistent with pseudo-second order rate kinetics (Table 3). Very large rate constants were obtained at low initial concentrations especially for two different temperatures (Table 3). The pseudo-second-order kinetic model agrees very well with the kinetics behavior for the adsorption of CTAB at clayey soil/water interface under different temperatures. The observed high adsorption rate at low concentrations clearly indicates the importance of CTA^+ orientation at the surface. It is thought that the temperature increase positively affected the adsorption of CTA^+ ions by improving the conformity between the orientation of ions and free active sites. Increasing temperature gradually desolvated the head group making it less hydrophilic and more compact. Thus, surface adsorption saturation values also were increased by increasing the freedom of movement of the alkyl tails of adsorbed CTA^+ with increased temperature.

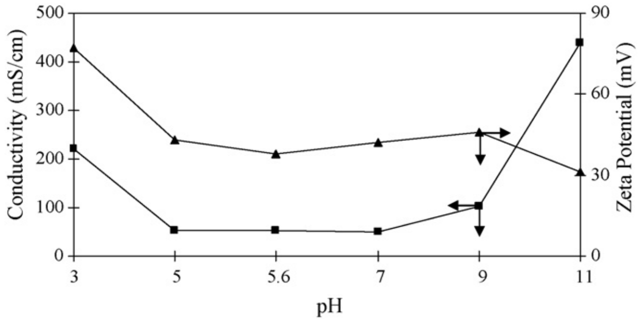

Fig. 5. Suspension pH effects on particle zeta potential and suspension electrical conductivity at 293 K.

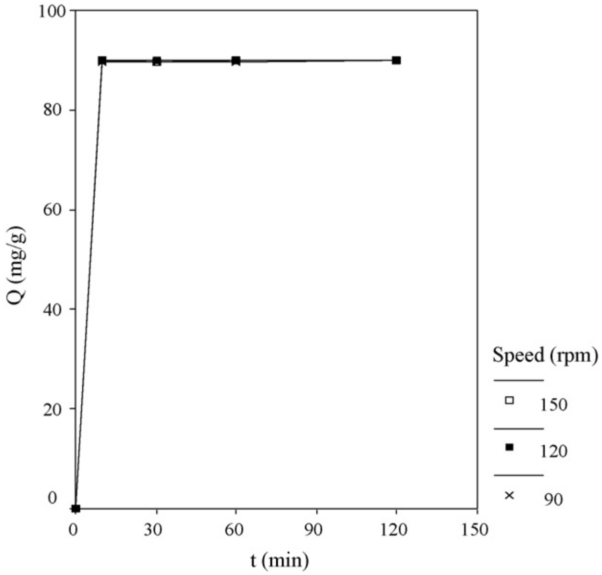

Fig. 6. Effect of adsorption time and stirring speed on amount of CTAB adsorbed.

3.5. *The effect of electrolyte*

The effect of electrolyte additions on CTAB adsorption at the clayey soil/water interface considering the suspension electrical

Table 3
Pseudo second-order kinetic values calculated for CTAB adsorption

Temperature (K)	Initial concentration (mg/L)	k_2 ($g\,mg^{-1}\,s^{-1}$)	r_2
293	30	3.23	0.997
	60	0.306	0.993
	90	0.164	0.980
	120	0.224	0.983
	150	0.143	0.978
	180	0.073	0.980
	210	0.081	0.979
313	30	3.13	0.998
	60	2.30	0.999
	90	0.219	0.986
	120	0.116	0.997
	150	0.105	0.984
	180	0.118	0.985
	210	0.142	0.986
333	30	6.89×10^{-5}	0.978
	60	1.76×10^{-9}	0.967
	90	1.27×10^{-6}	0.982
	120	1.92×10^{-7}	0.994
	150	1.44×10^{-9}	0.992
	180	2.66×10^{-8}	0.976
	210	3.25×10^{-8}	0.965

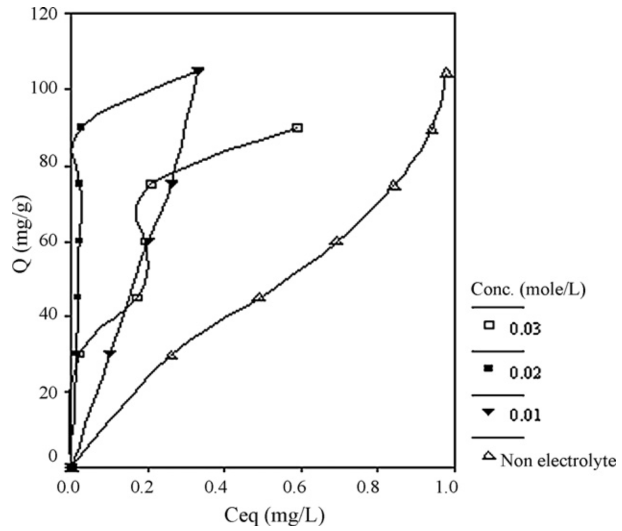

Fig. 7. Effect of NaCl on CTAB adsorption.

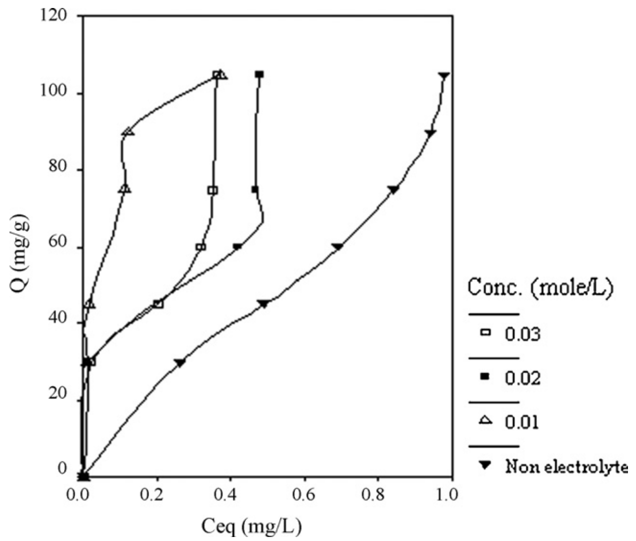

Fig. 9. Effect of $CaCl_2$ on CTAB adsorption.

conductivity, and particle zeta potential values were investigated. The experiments were carried out using the electrolytes, NaCl, $CaCl_2$ and $AlCl_3$ at different concentrations at 293 K for 30 min (Figs. 7–12). In addition, the electrical double-layer thickness, often called the Debye length, was calculated using Eq. (4) [1]. Electrical conductivity values for three electrolytes and CTAB solutions alone were measured at different concentrations (Table 4).

$$\frac{1}{\kappa} = \left[\frac{\varepsilon_r \varepsilon_0 RT}{4\pi F^2 \sum_i C_i Z_i^2} \right]^{1/2} \tag{4}$$

where R is gas constant, T is absolute temperature, F is Faraday constant, C is the molar concentration of an ion in the solution phase, $\varepsilon_r = \varepsilon / \varepsilon_0$ is relative static permeability.

The adsorption of an ionic surfactant to a solid surface of similar charge was enhanced in the presence of an electrolyte. The effect of counter ion valence in enhancing adsorption followed the *Schulze–Hardy* rule. At low electrolyte concentrations, a thicker electrical double layer caused enhanced clay dispersion. Hence, the diffusion of CTA^+ ions into the inner parts of the interlayer and clay surface occurred more easily. When a comparison was made between the electrical conductivity values of CTAB solutions and the electrolyte solutions in Table 4 and Figs. 8, 10 and 12, it was concluded that predominant mechanism of adsorption was ion-exchange. The increased electrolyte concentration led to a decrease in the dispersibility of the particles due to shrinking of the electrical double layer. However, the higher ionic strength might have caused an increased tendency of the long hydrophobic groups of CTA^+ ions to escape from the bulk solution to the surface due to increased interfacial tension. There was a competition between these two effects. Adsorption efficiency rapidly increased even for Na^+ ions which cannot specifically adsorb (Fig. 7). As seen from Fig. 7, the addition of NaCl leads to modifications in the isotherm forms. The initial slopes of isotherms are larger compared to no-electrolyte for all NaCl concentrations. The increase in the equilibrium concentration does not cause to a significant variation of electrical conductivity for three different NaCl concentrations. But, as expected, the values of electrical conductivity increase with increasing NaCl concentration (Fig. 8). The conductivity values measured in NaCl solutions were slightly lower than that of measured after CTAB adsorption, whereas particle zeta potential values significantly changed (Table 4, Fig. 8). Hence, it can be said that addition

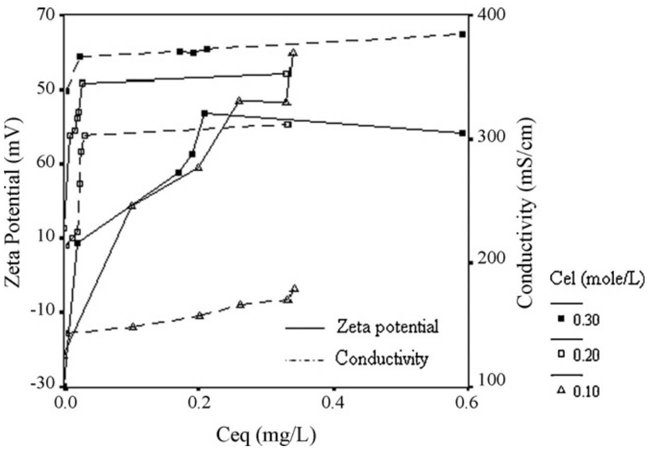

Fig. 8. Effect of CTAB equilibrium concentration and NaCl on particle zeta potential and suspension electrical conductivity.

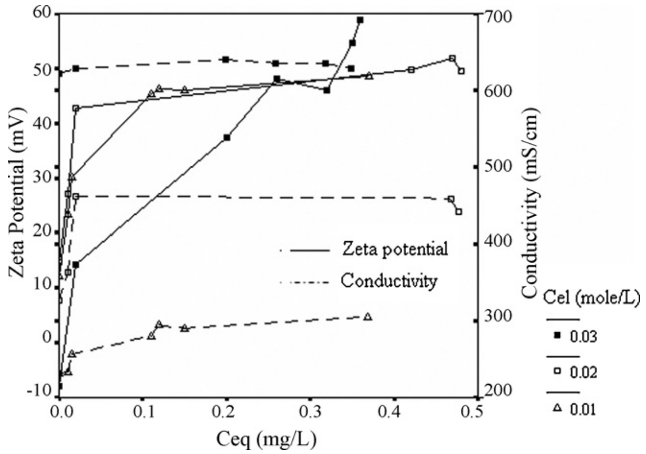

Fig. 10. Effect of CTAB equilibrium concentration and $CaCl_2$ on particle zeta potential and suspension electrical conductivity.

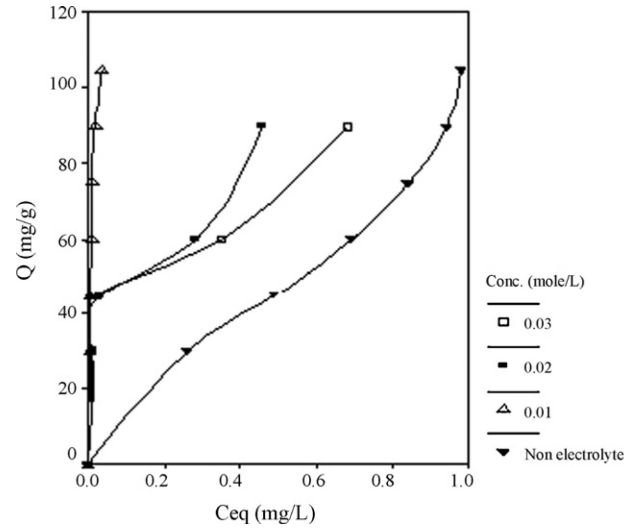

Fig. 11. Effect of $AlCl_3$ on CTAB adsorption.

of the neutral electrolyte, NaCl, increased the adsorption efficiency and effectiveness of ionic surfactants due to decreased electrical repulsion between free CTA^+ ions and similarly charged adsorbed ions. The decreased repulsion between free ions and adsorbed ions might have permitted more compact packing. This effect was presumably due to increased attraction between Cl^- ions in aqueous solution and positive sites on the clay surface. It has been stated that the major driving forces for adsorption of ionic surfactants to oxide surfaces are electrostatic interaction between the headgroups and the surface and hydrophobic interactions between the alkyl chains [33].

Fig. 9 shows the adsorption isotherms of CTAB in existence of $CaCl_2$ at 293 K. As seen, $CaCl_2$ addition change the isotherm forms and the isotherm slope is especially the largest at low $CaCl_2$ concentration. Fig. 10 illustrates that the variation of equilibrium concentration with the values of zeta potential and electrical conductivity is different for three $CaCl_2$ concentrations. The increase in the equilibrium concentration does not lead to an apparent change, especially at high $CaCl_2$ concentrations, while the increasing salt concentration have been increased the measured conductivity values. On the other hand, the values of zeta potential increase with increasing equilibrium concentration for three $CaCl_2$ concentrations and these values reach to a maximum. Polyvalent cations, such as $Al^{3+}$and Ca^{2+}, tend to compete for adsorption with CTA^+ ions, but the increased ionic strength of the media favored adsorption of CTA^+ ions. Also, the tendency for specific adsorption depends on the electrolyte valence (Figs. 7, 9 and 11). For the higher valence electrolyte, Al^{3+} and Ca^{2+}, the tendency for increased CTAB adsorption efficiency shifted to the higher concentration range. The particle zeta potentials in the presence of 0.03 M Ca^{2+} ions were higher than for 0.03 M Al^{3+} ions (Figs. 10 and 12). The relative increase in the zeta potential values in the presence of Ca^{2+} ions was partially related to increased CTA^+ ion adsorption (Fig. 10). However, higher electrical conductivity values were measured in the presence of Al^{3+} and Ca^{2+} ions. These values were closer to those measured in the electrolyte solution without CTAB. This suggests that the increased CTAB adsorption efficiency drastically depended on the ionic strength of the media. The relatively increased polyvalent cation adsorption also affected CTAB adsorption efficiency. Although, normally, a decrease in adsorption efficiency is expected in the presence of Al^{3+} ions, the increased tendency of CTA^+ ions to escape from bulk solution to the surface paralleled increases in ionic strength. The presence of the electrolyte might have led to greater CTAB adsorption. This can also be seen by comparing particle zeta potential and electrical conductivity values (Table 4, Figs. 8, 10 and 12). Fig. 11 shows the adsorption isotherms of CTAB in existence of $AlCl_3$ at 293 K. As seen, the initial slopes of isotherms at low equilibrium concentrations are higher than no-electrolyte for all $AlCl_3$ concentrations. But, at middle and high $AlCl_3$ concentrations, the isotherm slopes approaches to isotherm slope of no-electrolyte with increasing equilibrium concentration. Fig. 12 illustrates that the variation of zeta potential and electrical conductivity values with equilibrium concentration are different for three $AlCl_3$ concentrations. As seen, the increase in the equilibrium concentration does not change the values of electrical conductivity. But, these values increase with increasing $AlCl_3$ concentration. The zeta potential values of particles increase steeply at low equilibrium concentrations then do not clearly change at higher concentrations.

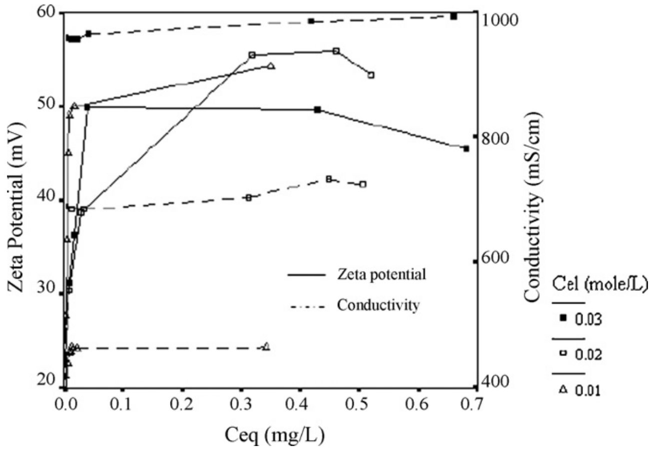

Fig. 12. Effect of CTAB equilibrium concentration and $AlCl_3$ on particle zeta potential and suspension electrical conductivity.

Table 4
The values of electrical double layer thickness and electrical conductivity

Non-electrolyte		NaCl			$CaCl_2$			$AlCl_3$		
C (CTAB) (mg/L)	Λ (mS/cm)	C (mol/L)	Λ (mS/cm)	$1/K$ (nm)	C (mol/L)	Λ (mS/cm)	$1/K$ (nm)	C (mol/L)	Λ (mS/cm)	$1/K$ (nm)
30	9.5	0.01	143	3.04	0.01	235	1.76	0.01	416	1.02
60	13.3									
90	20.0	0.02	232	2.15	0.02	418	1.24	0.02	570	0.72
120	25.8									
150	32.1	0.03	340	1.76	0.03	529	1.02	0.03	1054	0.59
180	37.0									
210	43.0									

4. Conclusion

This study investigated the adsorption mechanism of cethyltrimethylammonium bromide CTAB, a cationic surfactant, onto the clayey soil sample from aqueous solution as a function of ionic strength, pH, temperature, CTAB equilibrium concentration, and stirring speed. In addition, both kinetics and thermodynamic evaluations of the adsorption data were supported with measurements of particle zeta potential and suspension electrical conductivity. The main findings of the study could be summarized as follows:

1. The adsorption equilibrium time was found approximately 30 min indicating a rapid adsorption occurred through physical interactions.
2. The amount of cetyltrimethylammonium bromide adsorbed onto the clayey soil sample increased with increasing in equilibrium CTAB concentration, temperature and ionic strength, but was not affected from pH and stirring speed.
3. The isosteric enthalpy change was calculated as 28.27 kJ mol^{-1}. The calculated entropy value (-0.091 kJ mol^{-1} K^{-1}) was negative and quite small.
4. The pseudo-second-order kinetic model agrees very well with the kinetics behavior for the adsorption of CTAB at the clayey soil/water interface under different temperatures.
5. Addition of the neutral electrolyte, NaCl, increased the adsorption efficiency and effectiveness of ionic surfactants due to decreased electrical repulsion between free CTA$^+$ ions and similarly charged adsorbed ions.
6. Polyvalent cations, such as Al^{3+}and Ca^{2+}, tend to compete for adsorption with CTA$^+$ ions, but the increased ionic strength of the media favored adsorption of CTA$^+$ ions.

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