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Fuel Processing Technology 81 (2003) 57–66

FUEL PROCESSING TECHNOLOGY

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The investigation of adsorption thermodynamics and mechanism of a cationic surfactant, CTAB, onto powdered active carbon

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Received 21 March 2002; received in revised form 1 July 2002; accepted 19 December 2002

Abstract

In this study, the adsorption mechanism of cethyltrimethylammonium bromide (CTAB), a cationic surfactant, onto powdered active carbon (PAC) from aqueous solution was investigated and also some thermodynamic quantities such as isosteric adsorption enthalpy and entropy for this system were determined. In addition, the mechanistic and thermodynamic results of the experiments were supported with the surface zeta potential measurements. It was found that 5 min is sufficient in order to reach adsorption equilibrium. The adsorption of CTAB onto active carbon/water interface mainly takes place through ion exchange, the ion pairing and hydrophobic bonding. The predominant mechanisms in the lower CTAB concentrations are probably ion exchange and ion pairing. The hydrophobic bonding mechanism predominates with the increasing CTAB concentration. It was determined that the signs of isosteric adsorption enthalpy (ΔH_ξ) and isosteric adsorption entropy (ΔS_ξ) for adsorption of CTAB onto PAC are negative and positive, respectively. As temperature increases, the amount of CTAB adsorbed is decreased indicating the exothermic nature of adsorption process. This decreasing verifies the negative sign expected of $(\Delta H_{ads})_\xi$. As a result of the adsorption, since the number of the water molecules surrounding the hydrocarbon tails of CTAB molecules decreases and thus the degree of freedom of the water molecules increases, the positive sign of $(\Delta S_{ads})_\xi$ points out the hydrophobic bonding mechanisms.
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Keywords: Adsorption; CTAB; Powdered active carbon; Zeta potential; Hydrophobic interaction

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doi:10.1016/S0378-3820(03)00002-X

1. Introduction

Adsorption of surfactants at the solid/liquid interface has been extensively studied during the last four decades. One reason for this interest is the importance of surfactant adsorption on solid surfaces in many industrial applications in order to improve efficiency and economy. Therefore, it is essential to understand the mechanism of adsorption. It is a complex phenomenon that depends on a number of factors such as pH, electrolyte content, temperature, surfactant structure and the nature of the activated carbon used.

Activated carbon is an adsorbent that is widely used in adsorption processes. Activated carbon consists of a network of interconnected pores of varying sizes which are classified according to their diameter; micropores <2.0 nm, mesopores 2-50 nm and macropores >50.0 nm. The pores provide a large internal surface area, typically ranging from 800 to 1200 m^2/g, which enables activated carbon to adsorb contaminants from water. It has been reported that the internal structure of active carbon depended on its starting material and the mode of activation. The difference in pore structure and size distribution results in different adsorption properties [1,2].

Powdered active carbon (PAC), a pure and carbon-based substance, was chosen as adsorbent. Although there are many studies on the adsorption of surface-active agents and other chemical materials onto active carbon/water interface, these have not been directly focused on the relation between the values of zeta potentials of carbon particles and cethyltrimethylammonium bromide (CTAB) adsorption. There is no study that investigated the thermodynamics of adsorption of surfactant by taking the zeta potentials of surfaces as reference. In physical processes in which coals and similar heterogeneous materials are used, the impurity in heterogeneous substances complicates the investigation of adsorption mechanism. Therefore, it is clear that the results obtained by using PAC is important in terms of evaluations of results obtained for heterogeneous systems.

The aim of the present work is to study the adsorption mechanism of CTAB, a cationic surfactant, onto PAC from aqueous solution, and also to determine some thermodynamic quantities such as isosteric adsorption enthalpy and entropy for CTAB-active carbon system. In addition, the mechanistic and thermodynamic evaluations of the experimental results have been supported with the measurements of zeta potential of surfaces.

2. Experimental

In the study, as adsorbate, a cationic surfactant, cethyltrimethylammonium bromide (CTAB), which have a long hydrocarbon chain and is one of the most popular cationic surfactants was chosen [3–11]. CTAB was crystallized three times with $CHCl_3$ prior to use. A commercial powdered active carbon (PAC) with a BET surface area of 900 m^2/g and particle size of 150 μm ($<80\%$) (Merck cat. no. 2184) was used as adsorbent.

Batch adsorption experiments for the study of the adsorption kinetics were carried out in 100-ml, glass-stopperred, round-bottom flasks immersed in a thermostatic shaker bath. For this, 0.1 g of active carbon was mixed with 100 ml of the aqueous solutions of the various initial concentrations (30, 60, 90, 120, 150, 180, 240 and 300 mg/l) of CTAB. The flasks with its contents were then shaken for the different adsorption times at 298 K. At the

end of the adsorption period, the contents of flasks were divided in two parts. One part was filtered through filter paper and then the supernatant was centrifuged twice for 15 min at 3750 min^{-1}. A second part of carbon/water suspension was used for the measurements of zeta potential of the carbon particles.

The concentration of CTAB in the supernatant solution was determined by using a double-beam UV spectrophotometer at 375 nm and in the presence of 0.02 ml of 0.1% picric acid in 0.002 M NaOH and 0.40 ml of 1,2-dichloroethane per 1.0 ml of the supernatant [12]. It was found that the calibration curve was very reproducible and linear over the concentration range used in this study. The amount of the 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 active carbon/water suspensions were carried out by using Zeta Meter 3.0+ in their natural pH. The correction for temperature differences of the values of zeta potentials were performed by using following equation (Eq. (1)):

$$\xi_d(\mathrm{mV}) = C_T \xi_0 \tag{1}$$

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, zeta meter was calibrated by using Min-U-Sil standard solution.

In order to obtain the adsorption isotherms, 0.1 g of PAC was kept in contact with 100 ml of aqueous solution having different initial concentrations of CTAB at 298 K for 20 min. The additional experiments in which the effects of temperature on the adsorption of CTAB were investigated have been carried out at the range of temperature changing from 298 to 348 K. For the different temperatures, the values of zeta potential of the solid particles and the amounts of CTAB adsorbed were determined as in the previous step.

3. Results and discussion

As can be seen from Fig. 1, the adsorption of CTAB onto the surface of active carbon has taken place very quickly parallel to the increasing initial concentration of CTAB until first 5 min. After this adsorption time, the adsorption rate exhibits the tendency to be constant. Therefore, it can be said that in order to reach adsorption equilibrium, the adsorption time of about 5 min is sufficient. The relative shorter equilibrium adsorption time in this study can be attributed to the intensive physical interactions between CTAB molecules and/or CTA^+ ions and the surface of active carbon. For the adsorption processes in which physical interaction is predominant, it has been reported that the time required for reaching adsorption equilibrium is extremely short [13–15].

Fig. 2 shows that as the adsorption time increases, the values of zeta potential of particles in active carbon/water suspensions have different tendencies in terms of both magnitude and sign in all initial concentrations of CTAB at 298 K.

In the case of the initial CTAB concentration of 30 mg/l, after an adsorption period of about 40 min, the values of zeta potential of the carbon particles do not significantly

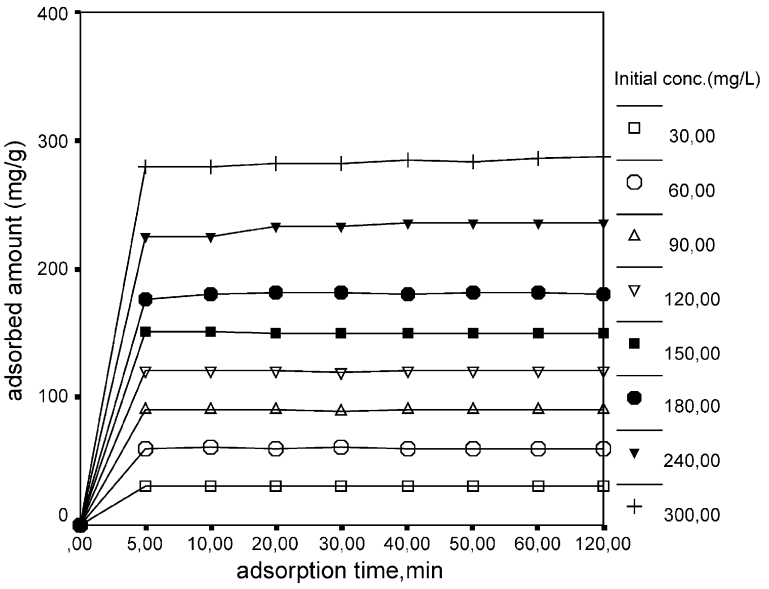

Fig. 1. The variation of CTAB adsorption with time at different initial CTAB concentrations at 298 K.

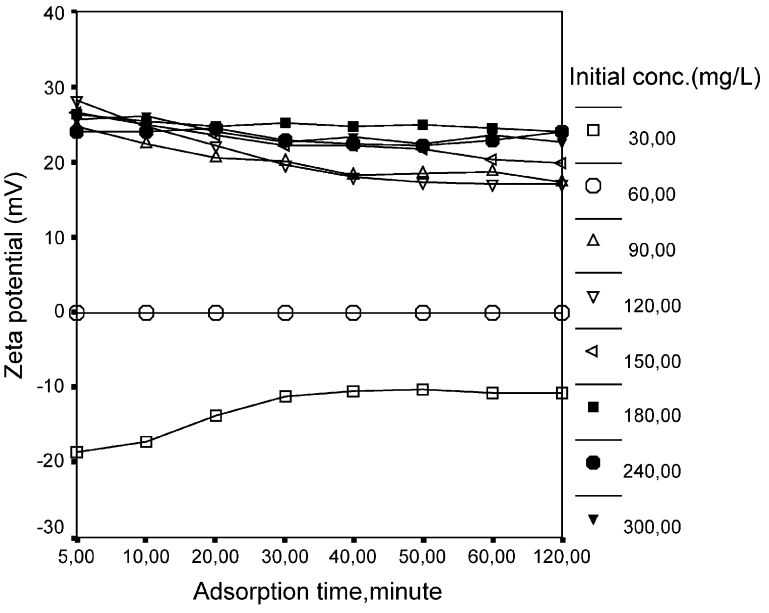

Fig. 2. The variation of zeta potentials with adsorption time at 298 K.

change, but the adsorption efficiency is still high. This is probably because the adsorption of CTAB molecules predominantly occurs through the diffusion from macropores to both micropores and mesopores depending on the difference of the concentration of CTAB molecules within these pores [16]. These behaviors have not been observed in the cases of the middle and higher CTAB concentrations. The adsorption of CTAB onto active carbon/water interface mainly takes place through the mechanisms of the ion exchange, ion pairing and hydrophobic bonding. However, in the lower CTAB concentrations, adsorption probably takes places predominantly through ion exchange and ion pairing. As can be seen from Fig. 2, in the cases of the higher CTAB concentrations, the sharp changes in the values of zeta potential of the particles occur. Whereas, in the case of initial CTAB concentration of 60 mg/l, the zeta potential values of the particles do not change with the increasing adsorption time, indicating that the predominant mechanism of adsorption is ion pairing. The hydrophobic bonding mechanism begins to predominate with increasing CTAB concentration. This is probably because the interactions between the hydrophobic carbon surface and the CTA^+ ions are effective in the shorter adsorption time.

From Figs. 3 and 4, it can be clearly seen that in the case of the isotherm at 298 K, the increase in the equilibrium CTAB concentration up to 0.3 mg/l causes an increase in surface charge of the particles and achieving a constant value of zeta potential of 24 mV (see Fig. 4). Thus, it can be said that the adsorption mainly proceeds through the electrostatic adsorption mechanisms (i.e. ion exchange and/or ion pairing) at the lower concentrations. However, after reaching to the equilibrium CTAB concentration of 0.3 mg/l, the hydrophobic interactions between the hydrophobic surface of active carbon and the hydrocarbon tails of CTAB molecules begin to predominate on the adsorption process.

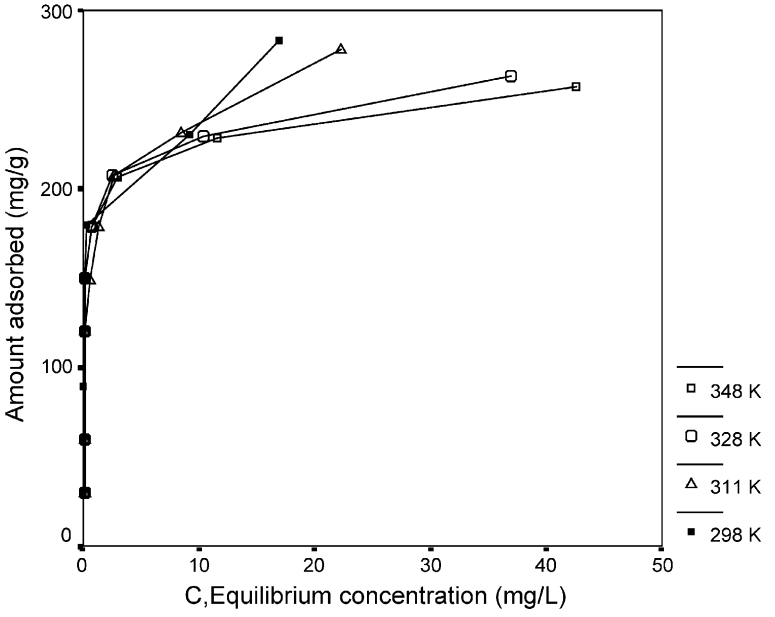

Fig. 3. Adsorption isotherms for the various temperatures.

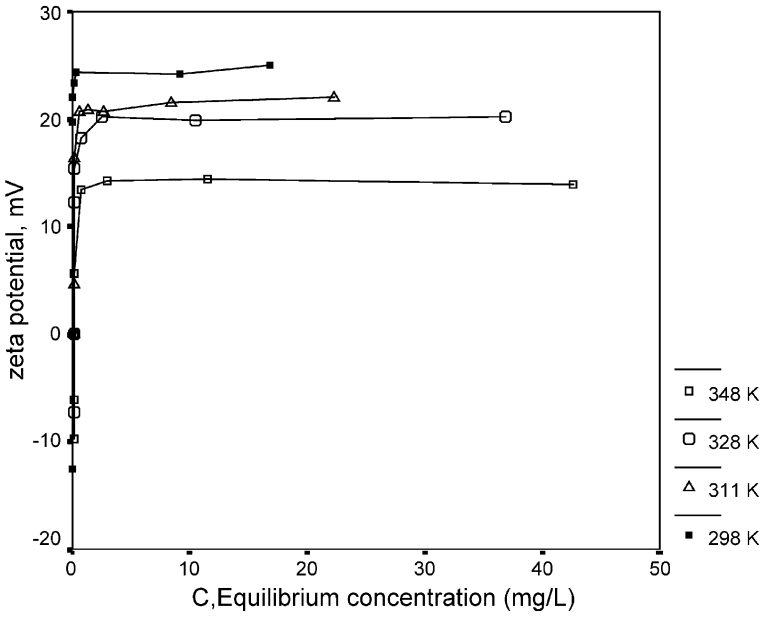

Fig. 4. The variation of zeta potential values with equilibrium concentrations for the various temperatures of 20 min.

After the equilibrium CTAB concentration of 0.32 mg/l, adsorption efficiency decreases whereas the amounts of CTAB adsorbed continuously increase and also the values of zeta potential of the particles stay constant. This suggests that the adsorption of CTAB onto the surface of active carbon in the cases of the higher equilibrium concentrations occurs as extremely compact and perpendicular to the surface. Similar results are reported previously about the adsorption of charged surface active agents to the surfaces of the highly charged solid adsorbents [17–22].

Although the amounts of CTAB adsorbed at 298 and 311 K are relatively close to each other, the surface potentials of the particles are significantly different. This difference can be attributed to the change of the adsorption mechanism (from ion exchange to ion pairing and hydrophobic bonding). As can be seen from Figs. 3 and 4, the zeta potential values of carbon particles increase by about 18 and 14 mV with the increase in equilibrium CTAB concentration at 328 and 348 K, respectively. This indicates that the increase in temperature could cause to reach the zero point of charge at lower concentrations.

In addition, the experimental data have been applied to the Langmuir adsorption model [23]. The results are graphed in Fig. 5. As can be seen from Fig. 5, the adsorption of CTAB onto PAC shows a high fitness to Langmuir model.

Thermodynamic quantities for the adsorption of CTAB onto PAC surface have been determined by considering the certain amounts of surfactant adsorbed. These are isosteric adsorption enthalpy, $(\Delta H_{ads})_\zeta$, and isosteric adsorption entropy, $(\Delta S_{ads})_\zeta$, which were statistically calculated by using least squares method and experimental data. These quantities were calculated by using Eqs. (2) and (3) [24]. In these calculations, the

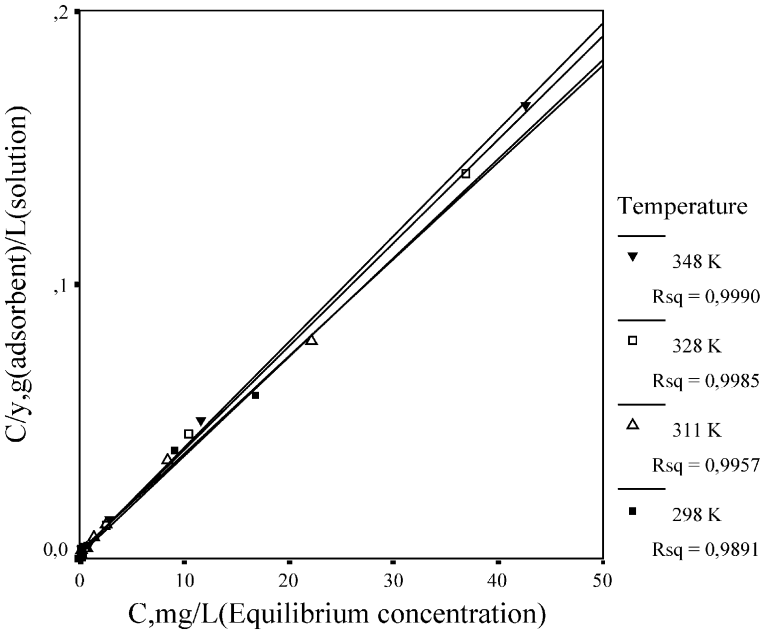

Fig. 5. Langmuir adsorption isotherms and *R*-square values for the various temperatures.

amounts of the surfactant adsorbed at the different temperatures correspond to the different equilibrium surfactant concentrations in which zeta potential values of carbon particles exhibit the tendency to be constant.

$$\frac{\mathrm{d}(\ln C)}{\mathrm{d}\left(\frac{1}{T}\right)} = \frac{(\Delta H_{\mathrm{ads}})}{R} \tag{2}$$

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

From experimental adsorption isotherms for CTAB adsorption on PAC at different temperatures, the isosteric enthalpy of adsorption, ΔH_{ads}, can be determined by using the slope obtained from the plot of ln$C$ values versus $1/T$ (Fig. 6). C and T in these equations represent the equilibrium CTAB concentration and absolute temperature, respectively. The isosteric entropy of adsorption, ΔS_{ads}, can also be determined by using the slope of the plot of ln$C$ values versus ln$T$ (Fig. 7). As can be seen from Table 1, the equilibrium concentrations used in the calculation of ΔH_{ads} and ΔS_{ads} are not values corresponding to the monolayer surface cover, but in these equilibrium concentrations, the values of zeta potential of the carbon particles begin to be constant.

From Table 1, it can be seen that the signs of ΔH_{ζ} and ΔS_{ζ} for adsorption of CTAB onto PAC are negative and positive, respectively. As temperature is increased, the amount of

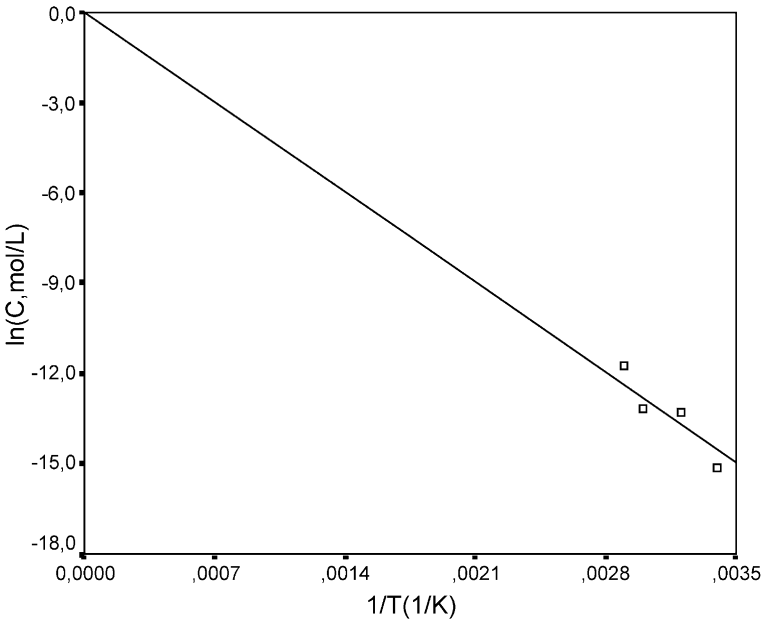

Fig. 6. The plot of ln$C$ values versus 1/T.

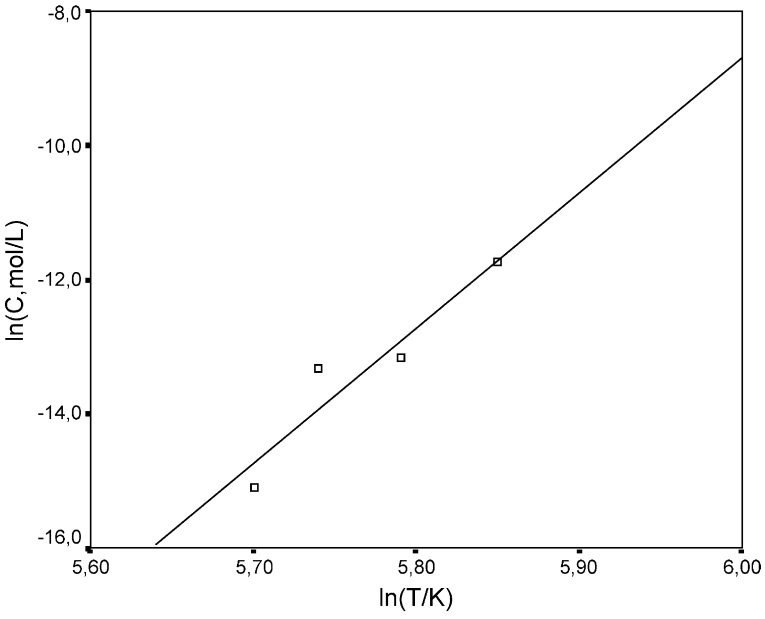

Fig. 7. The plot of ln$C$ values versus ln$T$.

Table 1
Amounts adsorbed and zeta potential values for the various temperatures and also thermodynamics quantities for active carbon/CTAB system

		Temperature (K)			
		298	311	328	348
Amount adsorbed, y^a (mg/g)		118	149	179	207
Zeta potential, ζ (mV)		22.0	20.7	18.2	14.3
Isosteric adsorption enthalpy, $(\Delta H_{ads})_\zeta$ (kJ mol^{-1})	$r=0.943$	−48.86			
Isosteric adsorption entropy, $(\Delta S_{ads})_\zeta$ (kJ mol^{-1} K^{-1})	$r=0.948$	0.168			

[a] The values in which zeta potential of the carbon particles begin to be constant.

surfactant adsorbed is decreased, implying the exothermic nature of adsorption process. This decreasing also verifies the negative sign expected of $(\Delta H_{ads})_\zeta$. For the hydrophobic bonding mechanisms, both theoretical and experimental studies indicate that the reorientation or restructuring of water around nonpolar solutes or surfaces is very unfavorable in terms of entropy, since it disturbs the existing water structure and imposes a new and more ordered structure on the surrounding water molecules [25]. As a result of adsorption of CTAB onto the hydrophobic surface of active carbon, the number of the water molecules surrounding the hydrocarbon tails of CTAB molecules decreases and thus the degree of freedom of the water molecules increases. Therefore, the positive sign of $(\Delta S_{ads})_\zeta$ indicates the presence of the mechanisms of hydrophobic bonding. As a result, it can be said that the adsorption results obtained by investigating activated carbon/CTAB system will shed light on adsorption processes in which similar adsorbents and adsorbates are used.

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