Adsorption thermodynamics of stearic acid onto bentonite

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Abstract

Adsorption equilibrium of stearic acid onto natural bentonite with Turkish origin was studied at the temperatures of 298, 308 and 318 K. SEM and XRD analysis show that the bentonite used as adsorbent is composed of microcrystal and porous structure. The specific surface area was determined by BET method as $38.6 \, m^2/g$. The adsorption of stearic acid onto bentonite was conformed to the Langmiur and Freundlich isotherms. The equilibrium parameter, R_L revealed that the bentonite is a good adsorbent for stearic acid. The sorption capacity of bentonite studied decreases with increasing temperature. However, it is concluded that the adsorption capacity of bentonite for the stearic acid under the same experimental conditions is in comparable level in terms of that of the rice husk ash given in literature. Thermodynamic parameters, ΔG_{ads}°, was calculated to be between -21.8 and $-22.8 \, kJ \, mol^{-1}$. ΔH_{ads}° and ΔS_{ads}° were found to be $-9.2 \, kJ \, mol^{-1}$ and $42.4 \, J \, mol^{-1} \, K^{-1}$, respectively. These parameters obtained as a function of temperature indicate that the adsorption of stearic acid onto bentonite was a spontaneous and an exothermic process. An FT-IR study on the adsorbed material was used to verify the interaction of the stearic molecule with bentonite after adsorption process.
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1. Introduction

The use of fatty acids is widely accepted in the pharmaceutical and food industry. Many drugs and foods contain fatty acids and they are often subjected to thermal treatment during processing, storage and preparation. Moreover, stearic acid as a saturated fatty acid are attractive phase change material for thermal energy storage applications due to the properties of high latent heat storage, melting and solidifying at a nearly constant temperature, good chemical stability and non-toxicity [1,2]. These properties make it important industrial material.

The use of adsorbent clay for bleaching of stearic acid has considerably increased [3]. There are a few studies on the adsorption of different fatty acids in literature. Proctor and Palaniappan [4,5] showed the ability of rice husk ash (RHA) to absorb free fatty acid from soy oil. Saleh and Adam [6] reported that the fatty acids adsorbed on RHA could be easily eluted out by acetone and they suggested that the adsorption of fatty acids takes place by physisorption. Adam and Chua [7] indicated that the adsorption of saturated fatty acid on RHA chemically modified with Al(III) ion using the sol–gel technique follows to the Langmiur isotherms. Topallar and Bayrak [8] investigated the adsorption isotherms of myristic, palmitic and stearic acid on rice hull ash and they showed the adsorption of all fatty acids studied on the rice hull ash followed to the Langmiur isotherms.

In this paper, the bentonite was used as adsorbent material. Bentonite is a good adsorbent for organic species because it exhibits a variety of attractive properties such as high specific surface area, high porosity and surface activity [9]. It is used as industrial raw material in more than 25 application areas, including the production of selective adsorbants, bleaching earth, catalyst beds, carbonless copy paper and medication [9]. They are also used as binders in foundries and in ceramic production since they produce muds of high plasticity with water [10]. In particular, experience with drilling in the major oil producing countries has shown bentonite clay as the chief raw material that should be added in the preparation of drilling fluids [10].

In the present work, it is aimed to investigate the adsorption equilibrium of stearic acid on bentonite, which is not modified by chemical or thermal treatment, at 298, 308 and 318 K. This study

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was also undertaken to evaluate thermodynamic parameters of the adsorption at different temperatures above.

2. Experimental

2.1. Materials

In this study, bentonite which is not subjected to any chemical (expect water evaporation process) or thermal treatment, used as adsorbent in this study was obtained from Resadiye (Tokat, Turkey). The specific surface area of untreated bentonite was found to be $38.6\,m^2/g$ by BET method using nitrogen as an adsorbent (Quantachromosorb).

Natural bentonite was first dried and sieved form 200-mesh, then washed with distilled water several times to remove any dust and other water-soluble impurities. The washed sample was dried in electric oven at 378 K for 24 h and then placed in a desiccator before adsorption experiments. Stearic acid (98% purity) used as adsorbate was obtained from Merck company. All other chemicals used were of analytical grade.

2.2. Preparation of stearic acid stock solution

A 0.569 g stearic acid was dissolved in isooctane (AR grade from Merck Company) and made up 1000 mL with isooctane. This stock solution had a concentration of 2.00×10^{-3} M. A solution of 0.005 NaOH was prepared and standarized with potassium hydrogen phthalate (KHP) and phenolphthalein as indicator. It was then diluted to 0.0025 M NaOH. The indicator solution was prepared by dissolving about 0.8 g of phenolphthalein in 100 mL 1-propanol. This solution was heated to near boiling and NaOH solution was added drop by drop until the pink color permanently observed. This was used as solvent for the quantitative determination of the stearic acid during adsorption experiments.

2.3. Instrumentation

Dry adsorbent sample was characterized (KBr) by FT-IR (JASCO 430 model) spectroscopy. The chemical analysis was carried out by X-ray powder diffractometry (RIGAKU D-MAX 2200 model). The micrographs were obtained by a scanning electron microscopy (SEM; JEOL 6400 model).

2.4. Adsorption experiments

Samples of bentonite (predried at 378 K for 24 h and desiccated) of 0.1–0.8 g were weighed with the accuracy of ±0.1 mg

and transferred to 50.0 mL conical flasks with glass stoppers. Twenty milliliter stock solution of stearic acid was pipetted into each conical flask. The samples were shaken for 30 min by a mechanical shaker combined with a temperature controller (Arex, Velp Scientitica) at 298 K and 100 rpm shaking speed. Subsequently, all samples were equilibrated at this temperature in a thermostated water bath (LAUDA; KG. D-6970 model) for another 30 min until all adsorbent had settled to the bottom. At the end of 1-h period, a 5.00 mL of the supernatant was pipetted into 10.0 mL neutralized 1-propanol and titrated with 0.0025 M NaOH. In addition, a blank titration on 5 mL of the untreated stock fatty acid solution was carried out. In order to determine the adsorption parameters at different temperatures the above experiments were repeated at 308 and 318 K. A small portion of bentonite adsorbed with stearic acid was filtered and dried at room temperature for the FT-IR spectroscopic analysis.

3. Results and discussion

3.1. Characterization of the prepared adsorbent

Table 1 presents chemical composition and ignition loss of natural bentonite used as adsorbent in this study. It can be noted from Table 1 that the adsorbent mainly consist of 59.6% SiO_2 and 15.4% Al_2O_3 components.

The SEM micrographs obtained at $350\times$ and $1500\times$ magnifications were shown in Fig. 1a and b. It can be obviously seen from both figures that the bentonite have porous structure. The adsorbent was also characterized by FT-IR spectroscopic analysis before and after adsorption process and the spectra obtained was given in Fig. 2. Before adsorption, the broad bands at 3415, 3478 and $3550\,cm^{-1}$ is due to the O—H stretching vibration of the silanol (Si—OH) groups from the solid and HO—H vibration of the water molecules adsorbed on the silica surface. The spectral bands at 1617 and $1639\,cm^{-1}$ reflect the bending H—OH bond of water molecules, which are retained in the silica matrix and not removing at 378 K. The strong band at $1099\,cm^{-1}$ represents the Si—O—Si groups of the tetrahedral sheet. While the band at 790, 620 and $480\,cm^{-1}$ are due to the deformation and bending modes of the Si—O bond [10,11].

As also seen in Fig. 2, after adsorption of the stearic acid the Si—O—Si bond of the adsorbent has shifted from 1099 to $1120\,cm^{-1}$ and the deformation and bending band of the Si—O bond at 790, 620 and $480\,cm^{-1}$ have also shifted to 798, 626, and $512\,cm^{-1}$. The O—H stretching vibration band of the silanol (Si—OH) at 3415, 3478 and $3550\,cm^{-1}$ have shifted to 3421, 3482 and $3555\,cm^{-1}$, respectively. These frequency

Table 1
Chemical composition of untreated bentonite used as adsorbent in present study

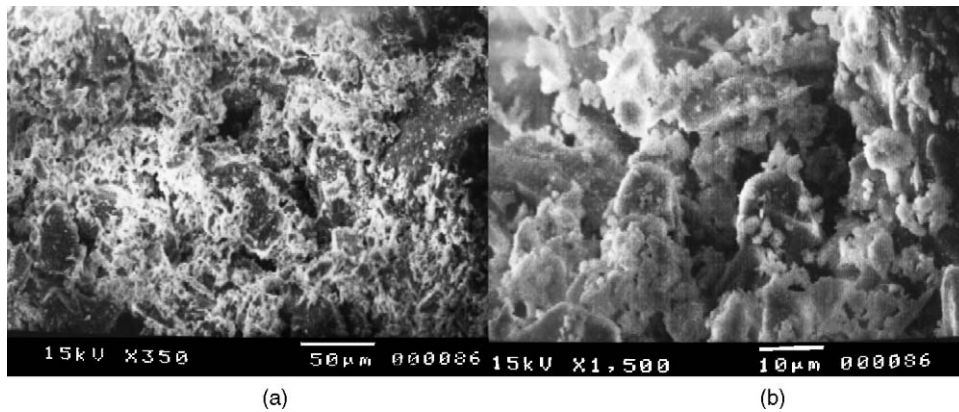| Chemical composition (%)									Ignition loss (at 1000 °C)
SiO$_2$	Al$_2$O$_3$	K$_2$O	MgO	Fe$_2$O$_3$	CaO	TiO$_2$	Na$_2$O	P$_2$O$_5$	
59.6	15.4	1.2	2.6	3.9	3.6	0.5	1.9	0.2	11.1

Fig. 1. The SEM micrographs of bentonite (a) at 350× magnification and (b) at 1500× magnification.
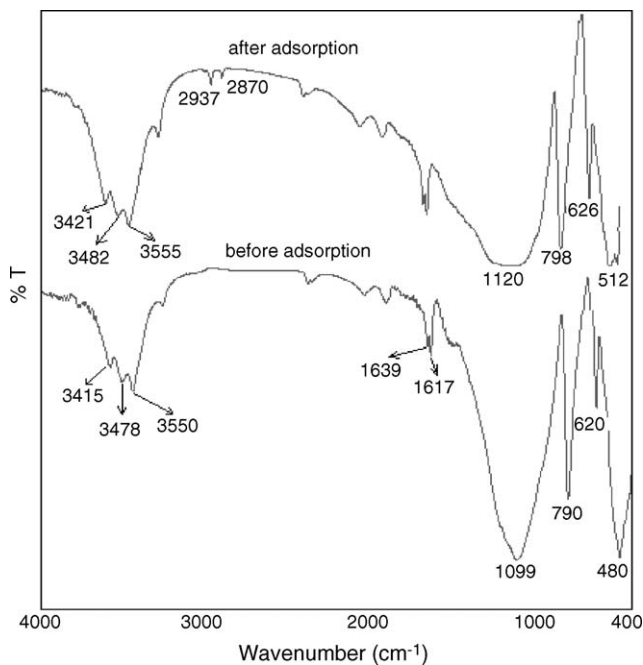

Fig. 2. The FT-IR spectra of bentonite before and after adsorption.

shifts observed are clear evidence for interaction of stearic acid molecules with silanol groups as seen in Fig. 3.

The similar observations were reported for the adsorption of different fatty acids onto rice husk ash [7]. Moreover, the bands at 2870 and 2937 cm^{-1} observed after adsorption is because of the stretching vibration of C–H bond of stearic acid (Fig. 2). This is another evidence of the adsorption of stearic acid onto bentonite.
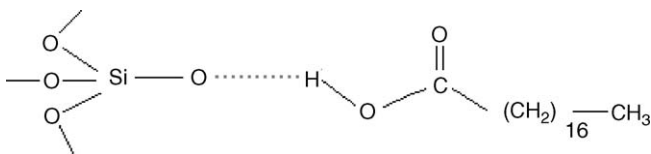

Fig. 3. Interaction of stearic acid molecules with silanol groups.

3.2. Adsorption isotherms

The Langmiur and Freundlich adsorption isotherms are the equations most frequently used to represent data on adsorption from solution. The Langmiur isotherm can be described by the linearized form

$$\frac{X_e}{q} = \frac{X_e}{q_m} + \frac{1}{K_L q_m} \tag{1}$$

where X_e (mg) is the amount of adsorbate in the solution at equilibrium and q (mg g^{-1}) is the amount of adsorbate adsorbed onto the adsorbent [7,8,12–15]. q_m (mg g^{-1}) is the amount of adsorbate adsorbed to form a monolayer coverage on the solid particles. K_L is the Langmiur adsorption equilibrium constant.

The essential characteristics of the Langmiur isotherm can be expressed in terms of a dimensionless equilibrium parameter R_L that is given by equation:

$$R_L = \frac{1}{1 + K_L C_0} \tag{2}$$

where C_0 is the initial amount of adsorbate [7]. R_L value between 0 and 1 indicate the suitability of the adsorbent for the adsorbate at the temperature studied. The linearized Freundlich adsorption isotherm by taking logarithms can be written:

$$\log q = \log K_F + \left(\frac{1}{n}\right) \log X_e \tag{3}$$

where q and X_e reflects the same parameters described in the Langmiur equation [12–15]. K_F and n are the Freundlich constants.

Fig. 4 shows the adsorption isotherms of stearic acid from isooctane solution at 298, 308 and 318 K. The curves are reached to almost a constant value of q (mg g^{-1}) at studied three temperatures and they indicate that the surface of adsorbent was covered with a monolayer of stearic acid molecules. The same adsorption type was observed for the different fatty acids onto the rice husk ash [7,8]. It can also be resulted from Fig. 3 that the adsorption pattern of stearic acid onto untreated bentonite is not influenced by temperature, but the adsorption capacity decreases with increasing temperature.
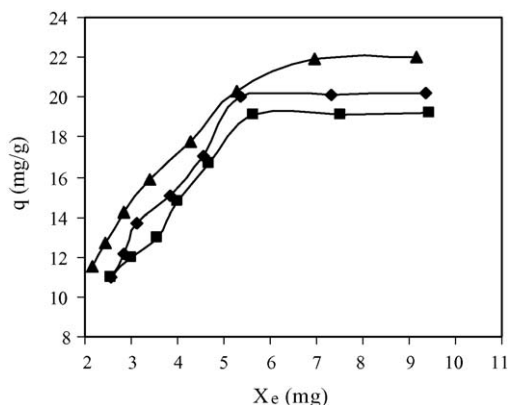
Fig. 4. The adsorption isotherm plots of q (mg g^{-1}) vs. X_e (mg) at different temperatures: (▲) 298 K; (♦) 308 K; (■) 318 K.
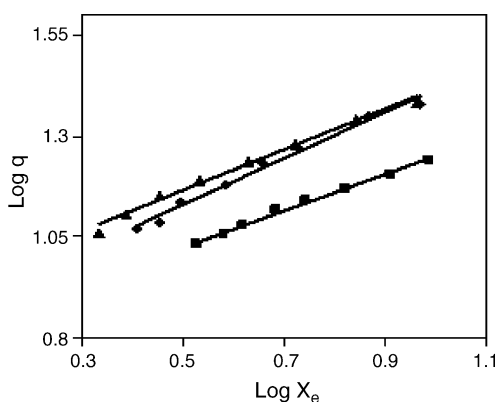
Fig. 5. Linearized Langmiur isotherms at different temperatures: (▲) 298 K; (♦) 308 K; (■) 318 K.
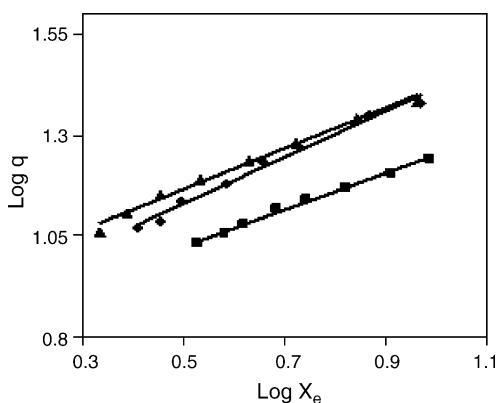
Fig. 6. Linearized Freundlich isotherms at different temperatures: (▲) 298 K; (♦) 308 K; (■) 318 K.

Figs. 5 and 6 show the plots of Langmiur and Freundlich isotherms in linearized form for the adsorption of stearic acid on untreated bentonite at 298, 308 and 318 K. It is observed from the plots in both graphs that adsorption behavior of the stearic acid on bentonite is in good agreement with the Langmiur and Freundlich isotherms with the correlation coefficient (R^2) (in the range of 0.9845–0.9955) at examined temperatures. The Langmiur and Freundlich parameters obtained from the plots in Figs. 5 and 6 are summarized in Table 2. The correlation coefficient, R^2, indicate that the adsorption data found for both isotherms follow on a straight line. The variation of the Langmiur adsorption equilibrium constant, K_L, the Freundlich adsorption constants, K_F and the amount of adsorbate in the solution at equilibrium q_m, with temperature exhibit that the adsorption of stearic acid on bentonite goes on an exothermic process. It can be noted that stearic acid was significantly adsorbed onto bentonite when the q_m value, 36.4 mg g^{-1} at 298 K in Table 2 is compared with the value (37.27 mg g^{-1}) obtained for the adsorption of stearic acid [8] and that (15.48 mg g^{-1}) obtained for the adsorption of palmitic acid on rice husk ash [7] at the same temperature. Moreover, the calculated Langmiur equilibrium parameter R_L between 0 and 1 shows the bentonite is good adsorbent for stearic acid from isooctane solution at studied temperatures.

3.3. Thermodynamic parameters

The free energy change of adsorption ΔG°_{ads} was calculated by using the equation:

$$\Delta G^\circ_{ads} = -RT \ln K_0 \tag{4}$$

where R is the universal gas constant and T is the Kelvin temperature [7,8,12,16,17]. K_0 is the thermodynamic equilibrium constant for the adsorption process was determined by plotting $\ln(q/X_e)$ versus X_e and extrapolating to zero X_e as suggested by Khan and Singh [12].

The other thermodynamic parameters, the enthalpy change ΔH°_{ads} and the entropy change ΔS°_{ads} were calculated from the slope and intercept of the plot of $\ln K_0$ against $1/T$ according to the equation:

$$\ln K_0 = \frac{\Delta S^\circ_{ads}}{R} - \frac{\Delta H^\circ_{ads}}{RT} \tag{5}$$

ΔH°_{ads} was obtained from the slope of the straight line and ΔS°_{ads} was determined from the intercept of the graph [7,16,17].

In order to evaluate the thermodynamic equilibrium constant K_0, the $\ln(q/X_e)$ values were plotted versus X_e values at 298, 308 and 318 K as seen in Fig. 7. The linear graphs were obtained for all the temperatures. The K_0 parameters obtained was used

Table 2
Langmiur and Freundlich constants and other derived parameters for the adsorption of stearic acid onto untreated bentonite at 298, 308 and 318 K

Temperature (K)	q_m (mg g^{-1})	Langmiur isotherm			Freundlich isotherm		
		K_L (mg^{-1})	R^2	R_L	K_F	n	R^2
298	36.4	0.22	0.9953	0.28	8.15	1.98	0.9898
308	35.7	0.20	0.9845	0.31	6.97	1.75	0.9880
318	35.1	0.18	0.9929	0.33	6.31	2.22	0.9955
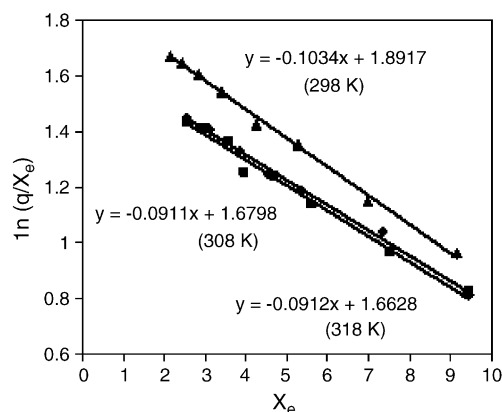
Fig. 7. Plots of $\ln(q/X_e)$ vs. X_e at different temperatures: (▲) 298 K; (♦) 308 K; (■) 318 K.

Table 3
Thermodynamic parameters for adsorption of stearic acid onto bentonite at 298, 308 and 318 K

Temperature (K)	K_0 (kg^{-1})	ΔG_{ads}° (kJ mol^{-1})
298	6630	−21.8
308	5460	−22.0
318	5270	−22.7

ΔH_{ads}°(kJ mol^{-1}) = −9.2; ΔS_{ads}°(J mol^{-1} K^{-1}) = 42.4.

to calculate ΔG_{ads}° function. The calculated thermodynamic parameters (ΔH_{ads}°, ΔS_{ads}°, and ΔG_{ads}°) at the temperatures above are given in Table 3. Fig. 8 shows the plot of $\ln K_0$ versus $1/T$.

By taking into the consideration of the decreases in the values of q_m, K_L, K_F and K_0 with rise in temperature, it can be concluded that the adsorption of the stearic acid molecules onto untreated bentonite is exothermic in nature. The Gibbs free energy change ΔG_{ads}° is in the range of −21.8 to −22.7 kJ mol^{-1} and it indicates that the process is spontaneous and considered as a physisorption interaction [18]. Moreover, based on the decrease in ΔG_{ads}° with increase in temperature, it can be
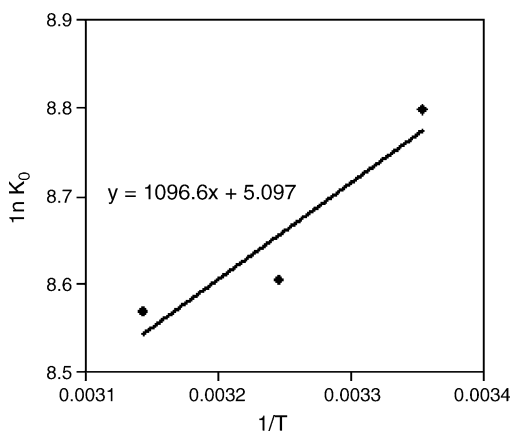
resulted that the interaction between the acid and bentonite at higher temperatures is weaker and thus the adsorption is less favorable. The ΔH_{ads}° (−9.2 kJ mol^{-1}) values is negative, which also exhibits the exothermic nature of the adsorption process of stearic acid onto bentonite. These results are contrary to the data given in the literatures [7,8]. It may be due to that the energy released during the adsorption is higher than that needed for extracting the solvent molecules from the porous network of bentonite by stearic acid. In addition, the positive ΔS_{ads}° (42.4 J mol^{-1} K^{-1}) have mean of an increase in disorder of the system during the adsorption. This is due to the physical interaction of stearic acid with the adsorption sites of bentonite.

4. Conclusion

The adsorption pattern of the stearic acid onto bentonite at 298, 308 and 318 K followed to the Langmiur and Freundlich isotherms and the isotherm shapes were not affected by the temperature. The sorption capacity of bentonite decreases with increasing temperature during the adsorption of stearic acid. These frequency shifts observed from the FT-IR spectroscopic analysis are clear evidence for the interaction of the stearic acid molecule with the bentonite. Adsorption equilibrium parameter, R_L, showed that the bentonite is a good adsorbent for the stearic acid. The decreases in the adsorption parameters (q_m, K_L, K_F, and K_0), and the negative ΔH_{ads}° reveal the exothermic adsorption process. Furthermore, the negative ΔG_{ads}° shows the adsorption of stearic acid onto bentonite is carried out spontaneously at studied temperatures. Based on the change in ΔG_{ads}° values it also concluded that the adsorption is less favorable with rise in temperature. It was finally resulted from the experimental findings that untreated bentonite is an efficient adsorbent for the adsorption of stearic acid from the isooctane solution at room temperature.

Acknowledgements

References

[1] A. Abhat, Solar Energy 30 (1983) 313.
[2] A. Sarı, Solar Energy 71 (2002) 365.
[3] A. Sarı, Energy Convers. Manage. 44 (2003) 2277.
[4] A. Proctor, C. Adhikara, G.D. Blyholder, J. Am. Oil Chem. Soc. 72 (1995) 331.
[5] A. Proctor, S. Palaniappan, J. Am. Oil Chem. Soc. 67 (1990) 15.
[6] M.I. Saleh, F. Adam, J. Am. Oil Chem. Soc. 71 (1994) 1363–1366.
[7] F. Adam, J.H. Chua, J. Colloid Interf. Sci. 280 (2004) 55.
[8] H. Topallar, Y. Bayrak, Turkish J. Chem. 23 (1999) 193.
[9] T. Alemdaroğlu, G. Akkuş, M. Önal, Y. Sarıkaya, Turkish J. Chem. 27 (2003) 675.
[10] G. Akçay, K. Yurdakuç, Turkish J. Chem. 23 (1999) 105.
[11] V.C. Farmer, The Layers Silicates in the Infrared Spectra of Minerals, Mineralogical Society, London, 1974, 331-363.

Fig. 8. Plot of $\ln K_0$ vs. $1/T$.

[12] A.A. Khan, R.P. Singh, Colloid Surf. 24 (1987) 33.
[13] A. Demirbas, E. Pehlivan, F. Gode, T. Altun, G. Arslan, J. Colloid Interf. Surface 282 (2005) 16.
[14] H.M. Park, D.J. Moon, J. Chem. Eng. Data 48 (2003) 908.

[15] J.H. Yun, D.K. Choi, Y.W. Lee, J. Chem. Eng. Data 45 (2000) 136.
[16] S. Tahir, N. Rauf, J. Chem. Thermodyn. 35 (2003) 2003.
[17] V.K. Gupta, P. Singh, N. Rahman, J. Colloid Interf. Sci. 275 (2004) 398.
[18] S.F. Özcan, B. Erdem, A. Özcan, J. Colloid Interf. Sci. 280 (2004) 44.