Thermodynamics and Kinetics of Fuel Oxygenate Adsorption into Granular Activated Carbon

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The removal of methyl *tert*-butyl ether (MTBE) and ethyl *tert*-butyl ether (ETBE) from water by granular activated carbon (GAC) was studied at different temperatures. Freundlich and Langmuir isotherm coefficients were developed based on linearized forms of the models. The results show the dependence of the isotherms with temperature. Data obtained from the kinetic studies were treated according to various kinetic models with the second-order model being the most suitable overall. Thermodynamic parameters (ΔG°, ΔH°, and ΔS°) for the adsorption process were calculated, and the results suggest that the nature of adsorption is endothermic, spontaneous, and favorable. According to the values of activation energy and enthalpy, the adsorption of both compounds in the studied GAC is in the range of physisorption.

Introduction

Oxygenated compounds are added to gasoline to improve fuel combustion efficiency and to lower exhaust emissions of CO and hydrocarbons. Examples of these compounds are alcohols (such as methanol, ethanol, isopropyl alcohol, isobutyl alcohol, and *tert*-butyl alcohol) and ethers (such as methyl *tert*-butyl ether (MTBE), ethyl *tert*-butyl ether (ETBE), *tert*-amyl methyl ether (TAME), and diisopropyl ether (DIPE)).[1] MTBE is the most important fuel oxygenate used worldwide and from 1998 in the USA and 2002 in the European Union was included in monitoring programs of volatile organic compounds (VOC). It is considered a unique contaminant owing to its ability to move readily throughout various environmental compartments and to its resistance to degradation.[2] On the other hand, the use of ETBE is increasing in Europe[3] and has environmental problems similar to MTBE. Due to their physicochemical properties, these kinds of compounds remain in groundwater for a long time. For this reason, the contamination of water resources by these kinds of organic chemicals is a problem of increasing concern.

Their physicochemical properties (high solubility, low Henry's law constant, and low octanol−water partition coefficient[4]) make it difficult for their treatment with conventional water cleaning technologies, including air stripping, advanced oxidation processes (AOP), and carbon adsorption.[5−8] Sutherland et al.[6] examined the treatment of MTBE using air stripping, advanced oxidation with (UV)/H_2O_2 and O_3/H_2O_2, and GAC adsorption in a pilot plant. The work concluded that at higher flow rates air stripping tended to be the most adequate treatment in terms of economy and efficiency. At lower rates, all the techniques were competitive, and the process selection could be based on other factors. Similar results were obtained by Baus et al.[8] Another material different to GAC has been used to adsorb ether such as perfluoroctyl alumina[9] or organic polymers such as Nafion.[10]

The several process variables that are involved in these techniques strongly affect their efficiency. One typical parameter that can vary more often is the temperature since usually these processes are carried out at environmental conditions. So, the efficiency in summer or in winter can differ in some order of magnitude. For this reason, improving the knowledge of the temperature dependence of the physicochemical properties that can affect the cleaning processes is important. Some temperature dependencies of physicochemical properties for these compounds are found in the literature. Arp and Schmidt obtained Henry's law constant for these ethers.[11] Gonzalez-Olmos et al.[12,13] studied the temperature dependence of water solubility, density, and speed of sound. Krahenbuhl and Gmehling report vapor pressure for ethers.[14] Vapor pressure is also published with vapor−liquid equilibria data for binary and/or ternary mixtures containing ethers in the works of Toghiani et al.,[15] Arce et al.,[16] and Loras et al.[17] However, few and poor systematic studies of the temperature dependencies on granulated carbon adsorption are found in the literature. The whole adsorption data disposable for these compounds are isothermal.

The literature reports only adsorption data at one temperature, and there exists an important lack of information about the temperature dependence of this process.

Yu et al.[18] examined the adsorption isotherm of MTBE, ETBE, and other fuel oxygenates at 22 °C using two bituminous-coal GACs (Calgon F400 and F600). These carbons are commonly used in drinking water treatment plants. Sutherland et al.[19] also studied the adsorption properties of the same GACs and compounds. They worked at environmental temperature and with mixtures of ethers, and thus GAC capacities for individual ethers were not determined. These two studies demonstrated that the relative affinity of F400 and F600 was higher for ETBE than for MTBE. Shih et al.[20] studied the ether adsorption process

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Table 1. Molecular Weight, Densities ρ, Speed of Sound u, Refractive Indices n_D, Water Solubility S_w, Henry's Law Constant K_{iH}, and Vapor Pressure p_i of the Chemicals at 298.15 K and Physicochemical Properties of GAC

		ρ (g·cm^{-3})	u (m·s^{-1})	n_D	S_w (g·L^{-1})	K_{iH} (m^3·Pa·mol^{-1})	p_i (kPa)
chemical	MW (g·mol^{-1})	lit.[a]	it.[b]	lit.[c]	lit.[d]	lit.[c]	lit.[e]
MTBE	88.150	0.734915	1035.89	1.366207	44.26	83.50	32.86
ETBE	102.176	0.735327	1034.28	1.373670	14.25	135.77	20.29

GAC	surface area (m$_2$·g^{-1})	particle diameter (mm)	efective size (mm)	iodine number (mg·g^{-1})
F400[f]	1050	1.0	0.6 to 0.7	1050

[a] Gonzalez-Olmos et al.[13] [b] Gonzalez-Olmos et al.[13] [c] Gonzalez-Olmos et al.[24] [d] Gonzalez-Olmos et al.[12] [e] Arp et al.[11] [f] Chemviron Data sheet[25]

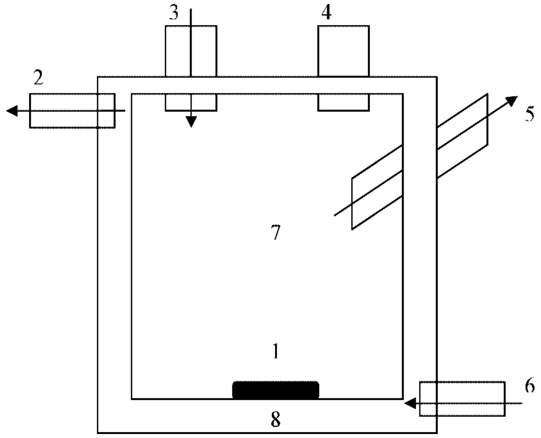

Figure 1. Schematic of adsorption cell. 1, Magnetic stirrer; 2, Outlet thermostatic bath water; 3, Polluted water inlet; 4, Thermometer inlet; 5, Take of sample; 6, Inlet thermostatic bath; 7, Adsorption compartment; 8, Thermostatic bath.

in the presence of other compounds such as BTEX or natural organic material (NOM) in real waters (surface and ground waters).

This work is part of a wider study related to theoretical and experimental analysis of thermophysical properties of fuel oxygenates.[12,13,21–24] Thus, as a continuation of our scientific work, the temperature dependence of isotherms and kinetics of ether adsorption in water at three temperatures (288.15, 298.15, and 308.15) K by a granulated activated carbon (GAC) (Filtrasorb F400) is reported. Isotherms were fit to the linearized form of both the Langmuir and Freundlich models. The kinetics was fit to first- and second-order and intraparticle diffusion models. Finally, thermodynamic parameters for the adsorption of MTBE and ETBE were calculated and discussed.

Experimental Section

Chemicals. Water was Millipore quality with organic carbon content < 5 ppb and resistivity of 18.2 MΩ·cm^{-1}. MTBE was supplied by Merck with purity better than 99.5 mol %. ETBE is provided by REPSOL-YPF and has purity higher than 97 mol %. The pure components were stored in vessels protected from the sunlight and at constant temperature. All products were degassed using ultrasound and dried on molecular sieves (pore diameter of (4 and $5 \cdot 10^{-10}$) m from Fluka) before use. The granulated activated carbon was a F400 supplied by Chemviron. Table 1 shows the values of the chemicals and GAC properties.

Adsorption Cell. Figure 1 shows a schematic diagram of the apparatus used for the adsorption isotherms and kinetic experiments. The adsorption cell consists of a jacketed vessel. The system was maintained at constant temperature ± 0.01 K with a Polyscience bath model 9010. The temperature inside the cell was measured with a digital platinum 100 Ω resistance thermometer with a precision of ± 0.01 K.

Isotherm Experiment Procedure. Stock solutions of MTBE and ETBE were prepared at (11 and 5.5) g·L^{-1}, respectively, in distilled and deionized water and stored at 4 °C in 250 mL bottles without headspace until use. Isotherm experiments were carried out in the adsorption cell without headspace to prevent volatilization losses at (288.15, 298.15, and 308.15) K. Different loads of GAC (1, 10, 25, 50, 75, and 100) g·L^{-1}) and constant initial concentration were used to obtain the different experimental points of the isotherms. Another additional experiment was carried out without any GAC to confirm no losses of analyte due to other mechanisms (volatilization, sorption to glass, abiotic degradation, etc.). Isotherms were conducted during 24 h based on the kinetics experiments that showed that more than 99 % of equilibrium was achieved for both ethers. The initial and final concentrations were determined by gas chromatography (GC).

Kinetic Experiment Procedure. Stock solutions of MTBE and ETBE were prepared at (9 and 3.5) g·L^{-1}, respectively, as explained before. The mass of GAC was kept constant in all the kinetic experiments at 50 g·L^{-1}. Adsorption of the fuel oxygenates at different temperature values on GAC was monitored by GC. Chromatographic data of each compound were obtained approximately in two-minute intervals from (0 to 10) min, five-minute intervals from (10 to 30) min, and fifteen-minute intervals from (30 to 90) min during the adsorption process.

Analytical Method. The concentration of dissolved hydrocarbon in water was measured by GC/FID. An amount of 2 μL of the aqueous phase (Direct Aqueous Injection) was taken using an Agilent D07-B1086 microsyringe and was automatically injected with an Agilent 7683 series injector into the GC. The GC used was a Hewlett-Packard 6890 operated with Chemstation. The column was a 30 m capillary column (DB-624, J+W scientific, 0.53 mm and 3 μm film thickness). The detector was a flame ionization detector (FID). For all measurements, the column temperature was set to 108 °C (isotherm) over 4 min. The FID temperature was 250 °C, and the injector temperature was 180 °C. Helium was used as the carrier gas (40 kPa) for all analyses. The flow parameters of other gases were set as fuel gas (hydrogen) 30 mL·min^{-1}, air 400 mL·min^{-1}, and makeup (nitrogen) 30 mL·min^{-1}.

Results and Discussion

Influence of the Temperature on the Adsorption Isotherms. Adsorption isotherm results for F400 were analyzed according to linearized forms of the Freundlich and Langmuir models.[26] The Freundlich model has the form

$$q_e = K C_{eq}^{\frac{1}{n}} \qquad (1)$$

where q_e is the equilibrium loading (mg·g^{-1}) and is obtained by the following equation

$$q_e = \frac{(C_0 - C_{eq})V}{m} \tag{2}$$

where C_{eq} is the equilibrium aqueous phase concentration (mg·L^{-1}); C_0 is the initial aqueous phase concentration (mg·L^{-1}); V (L) is the volume of adsorbate solution; m (g) is the mass of the GAC; and K and $1/n$ are the Freundlich constants. The linearized form of the Freundlich equation for regression was

$$\log q_e = \log K + \frac{1}{n} \log C_{eq} \tag{3}$$

Figure 2 shows the representation of this equation for both compounds at the three temperatures of study.

The Langmuir isotherm model has the form

$$q_e = \frac{q_{max} b C_{eq}}{1 + b C_{eq}} \tag{4}$$

where q_{max} and b are the Langmuir constants. The linearized form of the Langmuir equation for regression was

$$\frac{1}{q_e} = \frac{1}{q_{max} b} \cdot \frac{1}{C_{eq}} + \frac{1}{q_{max}} \tag{5}$$

Figure 3 shows the representation of this equation for both compounds at the three temperatures of study.

Reproducibility of the isotherms was assessed by examining the overlap of 95 % of confidence bands about the Freundlich regressions. The parameters of both fitting models are shown in Table 2. Isotherms on F400 showed that the relative sorptive affinity was higher for ETBE than for MTBE in the same way as that for the work of Yu et al.[18] The performance of the carbon is also better for higher temperatures, due to GAC activity increases, and the kinetics energy of the system is higher so the molecules have more energy to reach the surface of the carbon to be adsorbed. Finally, another important aspect is the hydrophobicity of both compounds, that as the work of Gonzalez-Olmos et al.[12] remarks increases with temperature. The reason for the higher affinity for ETBE is explained by the higher carbon content in the ETBE molecule that increases its hydrophobicity.

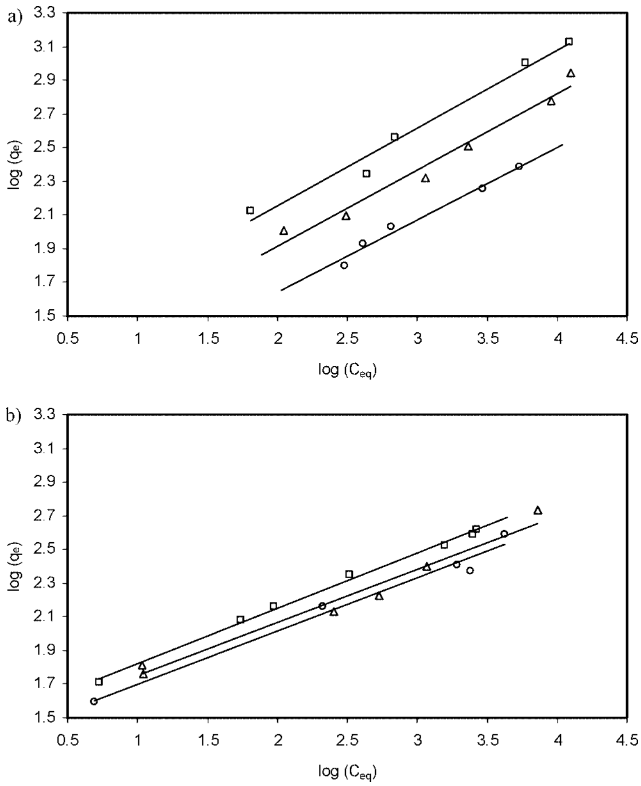

Figure 2. Isotherms for (a) MTBE and (b) ETBE adsorbed on F400 GAC with Freundlich model fit. Experimental results at □, 308.15 K; △, 298.15 K; and ○, 288.15 K.

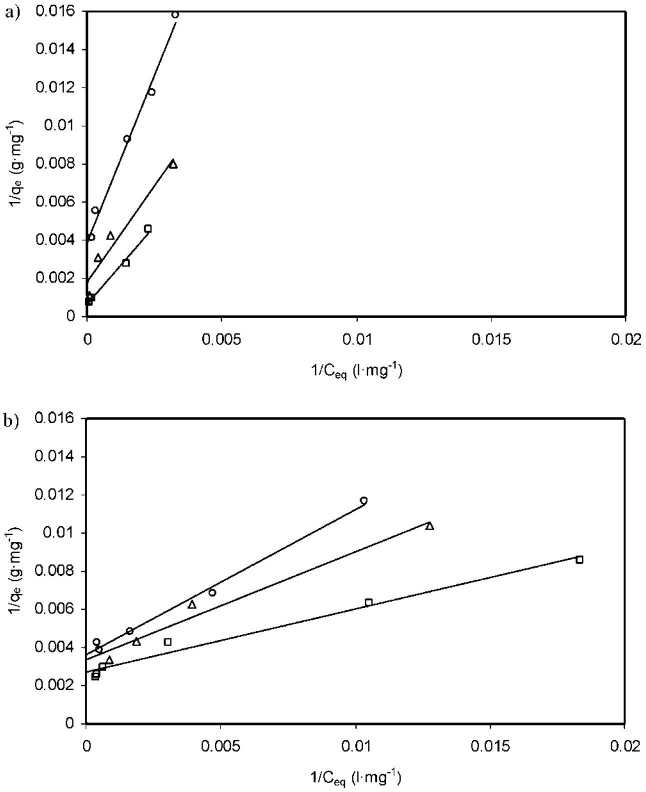

Figure 3. Isotherms for (a) MTBE and (b) ETBE adsorbed on F400 GAC with Langmuir model fit. Experimental results at □, 308.15 K; △, 298.15 K; and ○, 288.15 K.

Table 2. Parameters of Linear Langmuir and Freundlich Models for Fuel Oxygenate Adsorption Isotherms

	MTBE					
	Freundlich model			Langmuir model		
T (K)	$1/n$	K/(mg·g^{-1}) (L·mg^{-1})^(n^{-1})	r	qmax (mg·g^{-1})	b (L·mg^{-1})	r
288.15	0.430	6.056	0.979	263.158	1.082 E-3	0.989
298.15	0.453	10.149	0.970	555.556	0.899 E-3	0.946
308.15	0.461	17.088	0.979	1666.667	0.366 E-3	0.989

	ETBE					
	Freundlich model			Langmuir model		
T (K)	$1/n$	K/(mg·g^{-1}) (L·mg^{-1})^(n^{-1})	r	qmax (mg·g^{-1})	b (L·mg^{-1})	r
288.15	0.315	24.401	0.970	277.778	4.706 E-3	0.993
298.15	0.318	26.915	0.989	303.030	5.839 E-3	0.975
308.15	0.327	31.383	0.968	370.370	8.164 E-3	0.980

Comparison with Literature. The results of isotherm experiments have been compared with the literature available related with the adsorption of MTBE or ETBE onto a F400 GAC or a similar GAC. Only two works present data to compare with the experimental results presented in this work.[8,18] Comparing the fitting parameters of the Freundlich model shown in Table 3, it is possible to see how despite the difference of the initial concentrations the values of the parameters are very similar. It

Table 3. Comparison of the Parameters of Freundlich Model with the Literature

author	exptl	lit.[a]	lit.[a]	lit.[b]	exptl	lit.[a]	lit.[a]
compound	MTBE	MTBE	MTBE	MTBE	ETBE	ETBE	ETBE
type of carbon	F400	F400	F600	F300	F400	F400	F600
T/(K)	298.15	295.15	295.15	n/a	298.15	295.15	295.15
C_0/(mg·L^{-1})	11000	0.02	0.02	0.4	5500	0.05	0.05
Range C_f/(mg·L^{-1})	9108 to 110	0.015 to 0.0005	0.015 to 0.0005	0.4 to 0.018	4990 to 1033	0.021 to 0.0006	0.015 to 0.0005
$1/n$	0.453	0.692	0.708	0.64	0.318	0.622	0.493
K/(mg·g^{-1})(L·mg^{-1}) ^(n^{-1})	10.149	6.830	9.793	7.6	26.915	27.676	53.548

[a] Yu et al.[18] [b] Baus et al.[8]

Table 4. Rate Constants and Correlation Coefficients from Treatment of Adsorption Data According to Three Kinetic Models for Three Temperatures[a]

	kinetic model					
	first-order		second-order		intraparticle diffusion	
T/(K)	k_1	r	k_2	r	k_i	r
			MTBE			
288.15	0.2026	0.797	0.0478	0.980	0.0497	0.913
298.15	0.3583	0.824	0.1060	0.985	0.0477	0.802
308.15	0.3853	0.791	0.1165	0.982	0.0486	0.750
			ETBE			
288.15	0.3719	0.889	0.6342	0.988	0.0267	0.847
298.15	0.3580	0.549	0.9506	0.952	0.0249	0.794
308.15	0.5500	0.683	1.4944	0.992	0.0239	0.695

[a] $[k_1] = \text{min}^{-1}$; $[k_2] = \text{L}\cdot\text{g}^{-1}\cdot\text{min}^{-1}$; $[k_i] = \text{mg}\cdot\text{g}^{-1}\cdot\text{min}^{-0.5}$.

is important to take into account that little differences in values could be induced by differences in the operational conditions such as experimental temperature, the type of carbon (F600 and F300 are similar to F400), and in the preparation of the GAC.

Influence of the Temperature on the Kinetics Adsorption. Concentrations were plotted as a function of time. They are shown in Figure 4. Initial concentration in all experiments was adjusted to be the same to compare their adsorption behavior easily. Some probable kinetic models were applied to fit them to experimental data. These models include intraparticle diffusion,[27] which can be formulated as

$$q_t = k_i t^{\frac{1}{2}} \tag{6}$$

first-order which can be formulated as

$$\ln C - \ln C_0 = -k_1 t \tag{7}$$

and the second-order model which can be formulated as

$$\left(\frac{1}{C} - \frac{1}{C_0}\right) = k_2 t \tag{8}$$

where q_t is the amount of adsorbate adsorbed at any time; C is the concentration of adsorbate at any time; t is the time; and k_i, k_1, and k_2 are the rate constants for the diffusion, first-order, and second-order models, respectively. q_t is obtained from C_0 and C values by the following equation

$$q_t = \frac{(C_0 - C)V}{m} \tag{9}$$

The applicability of the three models was studied by drawing a linear plot of q_t versus $t^{1/2}$ for the intraparticle diffusion, ln(C) versus t for the first-order, and 1/C versus t for the second-order models. The rate constants of k_i, k_1, and k_2 obtained from the slopes of corresponding linear plots are given in Table 4 at different temperature values with correlation coefficients, r. When the correlation coefficients of the three models are compared for each temperature, it can be seen that it is better for a second-order model. On the whole, the fit of the experimental data to the second-order model seems to be excellent for both compounds because the r value is better. In addition, the kinetic study demonstrates that the reduction achieved for ETBE is higher and faster than for MTBE. That agrees with the literature and confirms the results obtained with the equilibria study. The effect of temperature improves slightly the efficiency in terms of kinetics and of removal efficiency. As in the case of the isotherm adsorption, the kinetics are improved by the temperature probably also explained by an increment of the kinetic energy of the system, increasing the transport molecular mechanisms in terms of diffusion and adsorption of ethers onto the solid carbon surface.

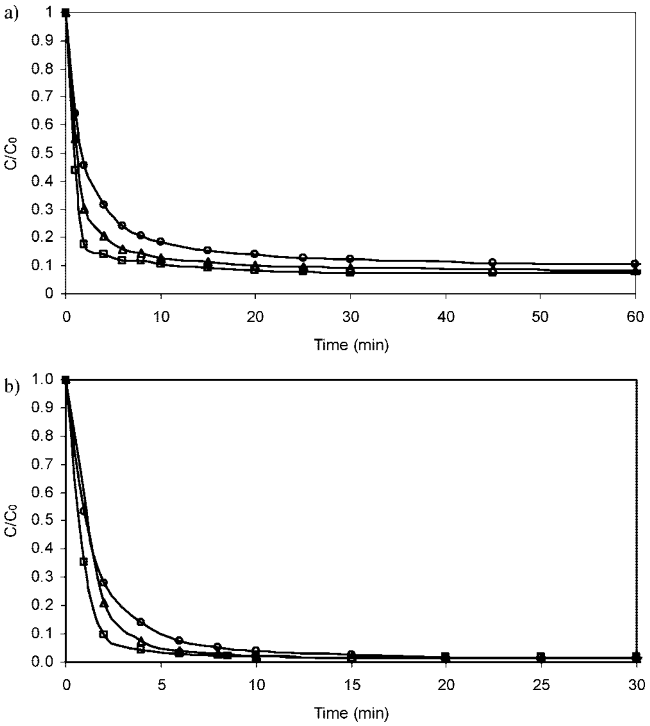

Figure 4. Effect of temperature on adsorption kinetics on F400 GAC for (a) MTBE and (b) ETBE. Experimental results at □, 308.15 K; △, 298.15 K; and ○, 288.15 K.

Thermodynamic Parameters. The kinetic constants of the second-order model can be fit to the Arrhenius equation

$$k_2 = A e^{\frac{-E_a}{RT}} \tag{10}$$

where R is the ideal gas constant; A is the frequency factor (min^{-1}); E_a is the activation energy (kJ·mol^{-1}); and T is the absolute temperature (K). The linear equation is obtained by taking the logarithm of eq 10.

$$\ln(k_2) = \ln A - \left(\frac{E_a}{RT}\right) \tag{11}$$

The activation energy for MTBE and ETBE adsorption determined from the slope of the linear plot of ln(k_2) versus 1/T is

Table 5. Thermodynamic Data for Adsorption of MTBE and ETBE onto F400

	MTBE		ETBE	
		ΔG°		ΔG°
T/(K)	K_c	(J·mol $^{-1}$)	K_c	(J·mol $^{-1}$)
	MTBE			
288.15	11.49	−5846	69.59	−10158
298.15	13.18	−6389	83.66	−10967
308.15	14.29	−6810	94.30	−11642
ΔH°/(J·mol $^{-1}$)	8050		11235	
ΔS°/(J·(mol·K)$^{-1}$)	48.29		74.32	
r	0.983		0.990	

(36 and 32) kJ·mol^{-1}, respectively. The low activation energy [(5 to 40) kJ·mol^{-1}] is characteristic for physisorption, while higher energy [(40 to 800) kJ·mol^{-1}] suggests chemisorption.[28] Therefore, the adsorption of these compounds is of a physical nature. Equilibrium constants, K_c, for the adsorption of MTBE and ETBE on F400 GAC were calculated by the following equation

$$K_c = \frac{M_{\text{ads}}}{C_{\text{eq}}} \tag{12}$$

where K_c is the equilibrium constant; M_{ads} is the adsorbed amount of adsorbate at equilibrium (mg·L^{-1}); and C_{eq} is the equilibrium concentration of adsorbate (mg·L^{-1}). The changes in the Gibbs free energy (ΔG°) were evaluated by

$$\Delta G^\circ = -RT \ln(K_c) \tag{13}$$

The changes of standard enthalpy (ΔH°) and entropy (ΔS°) were determined from the Van't Hoff equation

$$\ln(K_c) = -\left(\frac{\Delta H^\circ}{RT}\right) + \left(\frac{\Delta S^\circ}{R}\right) \tag{14}$$

ΔH° and ΔS° were obtained from the slope of the plot of ln(K_c) versus 1/T. The values of the thermodynamics parameters are listed in Table 5.

The negative values of free energy changes (ΔG°) confirm that the adsorptions of MTBE and ETBE into F400 GAC are spontaneous and thermodynamically favorable. The decreasing value of (ΔG°) with temperature indicates more driving force and results in more adsorption capacity at higher temperature. The positive enthalpy changes indicate that the adsorption is an endothermic process, and the enthalpy values for both ethers are smaller than 41.8 kJ·mol^{-1}. That indicates that the process is physisorption.[29] This result is in good agreement with the activation energy value. The positive entropy value also suggests a more disordered state at the solid−solution interface during the adsorption.

Conclusions

The adsorptions of MTBE and ETBE onto F400 GAC were performed at three temperatures to investigate the thermodynamic and kinetic aspects. Analyzing the equilibrium results, the performance of the carbon is better at high temperatures for both ethers. The kinetic second-order model was the most suitable overall for both compounds. The decreasing value of free energy changes with temperature indicates that the adsorption capacity of the carbon increases at higher temperatures. The positive enthalpy changes indicate that the adsorption of ethers is an endothermic process. In addition, the values of activation energy and enthalpy confirm that the adsorption is of a physical nature. The adsorption capacity of F400 is higher for ETBE than MTBE in agreement with the literature.

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