The adsorption of benzene and methylethylketone onto activated carbon: thermodynamic aspects

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Abstract

The adsorption of volatile organic compounds (VOCs), exemplified by benzene and methylethylketone (MEK), onto seven different types of activated carbon was investigated. Results show that for benzene adsorption the adsorption characteristic energy, enthalpy, free energy and entropy are in the range 17.12–36.86, –20.8 to –44.7, –11.89 to –16.22 kJ/mole and –29.4 to –85.3 J/mole/K, respectively. For the adsorption of MEK, the adsorption characteristic energy, enthalpy, free energy and entropy are in the range 14.47–32.34, –18.3 to –40.8, –10.78 to –15.56 kJ/mole and –24.8 to –60.3 J/mole/K, respectively. The adsorption enthalpy can be calculated indirectly from statistical thermodynamic method and directly from the immersion enthalpy method. The adsorption characteristic energy is calculated by the Dubinin–Astokhov equation. The free energy is calculated by the measured equilibrium adsorption constant. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Activated carbon is a porous carbonaceous material and has been extensively used in many industrial applications (Koresh and Sofer, 1983; Hassan et al., 1987; Ruthven et al., 1987; Grunewald and Drago, 1990). It has found common uses in air purification, volatile solvent recovery, deodorization, and drinking water treatment (McDowell, 1961; Cheremisinoff and Ellerbush, 1978). Activated carbon has also been used as a catalyst and catalyst support by the chemical industry (Trapnell, 1955).

Better understanding of the thermodynamic aspects of the adsorption reaction can aid in the design of ac-

tivated carbon adsorption process. As far as adsorption of volatile organic compounds (VOCs) at the activated carbon–water interface is concerned, much has been reported on the determination of free energy of adsorption. However, very little is known about the entropy and the enthalpy of adsorption between VOCs and activated carbon. Moreover, the distribution energy on the activated carbon surface remains a subject of little attention.

Dubinin et al. (1991) by applying the Dubinin–Raduskevich equation, i.e., theory of micropore volume filling (TVFM), have determined the adsorption energy of ethylene, benzene, carbon tetrachloride on activated carbon. Based on the Dubinin theory, Stoeckli and Kraehenbueh (1981) have established the relationship between the enthalpy of immersion and some parameters of TVFM for the adsorption of benzene, *n*-heptane and water onto activated carbon. However the TVFM theory can not distinctly determine the free energy and

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entropy of adsorption. Afzal et al. (1993) have used the adsorption data and a virial isotherm to calculate the enthalpy, entropy and free energy of the adsorption of methanol, acetone, methyl formate and acetaldehyde by activated carbon. However, they have not succeeded in determining the relevant thermodynamic parameters. This study is to determine the thermodynamic properties and the energy distribution function of the adsorption of VOCs by activated carbon exemplified by benzene and methylethylketone (MEK). Both immersion enthalpy method and statistical thermodynamic method (for entropy calculation) were used.

2. Theoretical aspects

2.1. Immersion enthalpy method

According to Dubinin, the net heat of adsorption (q^{net}) is the difference between the isotheric heat of adsorption (q^{st}) and the heat of condensation (ΔH_{con}), that is,

$$q^{\text{net}} = q^{\text{st}} - \Delta H_{\text{con}}. \quad (1)$$

The adsorption isotheric heat can be estimated by the following equation (Smisek and Cerny, 1970; Gregg and Sing, 1982)

$$q^{\text{net}} = RT^2 \left(\frac{\partial \ln x}{\partial T} \right)_a, \quad (2)$$

where x is the relative pressure, p/p_0 , and is related to the Gibbs equation, that is,

$$\Delta G = -RT \ln x = -RT \ln \frac{p}{p_0}, \quad (2a)$$

where p_0 is the saturation vapor pressure and p is the equilibrium vapor pressure.

By definition,

$$a\bar{v} = W, \quad (3)$$

where W is the volume of adsorption space, a is the number of moles adsorbed and $\bar{v}$ is the molar volume of adsorbed material.

According to the potential theory, W is a function of T and x , that is,

$$W = f(T; \ln x) = a\bar{v}. \quad (4)$$

Taking a total differentiation of Eq. (4), one has

$$d(a\bar{v}) = \left(\frac{\partial a\bar{v}}{\partial T} \right)_{\ln x} dT + \left(\frac{\partial a\bar{v}}{\partial \ln x} \right)_T d \ln x. \quad (5)$$

Diving all terms in Eq. (5) by T at equilibrium and since $d(a\bar{v}) = 0$, one has

$$\left(\frac{\partial a\bar{v}}{\partial T} \right)_{\ln x} = -\bar{v} \left(\frac{\partial a}{\partial \ln x} \right)_T \left(\frac{\partial \ln x}{\partial T} \right)_{a\bar{v}} \quad (6a)$$

or

$$\left(\frac{\partial a\bar{v}}{\partial T} \right)_{\ln x} = -\bar{v} \left(\frac{\partial \bar{v}}{\partial \ln x} \right)_T \left(\frac{\partial \ln x}{\partial T} \right)_{a\bar{v}}. \quad (6b)$$

The coefficient $(\partial a\bar{v}/\partial T)_{\ln x}$ can also be expressed as

$$\left(\frac{\partial a\bar{v}}{\partial T} \right)_{\ln x} = a \left(\frac{\partial \bar{v}}{\partial T} \right)_{\ln x} + \bar{v} \left(\frac{\partial a}{\partial T} \right)_{\ln x}. \quad (7)$$

By defining α as the thermal coefficient of volume expansion and α is equal to $1/\bar{v}(\partial \bar{v}/\partial T)_{\ln x}$. Eq. (7) becomes

$$\left(\frac{\partial a\bar{v}}{\partial T} \right)_{\ln x} = a\alpha\bar{v} + \bar{v} \left(\frac{\partial a}{\partial T} \right)_{\ln x}. \quad (8)$$

Combining Eqs. (6b) and (8) yields the following expression

$$a\alpha\bar{v} + \bar{v} \left(\frac{\partial a}{\partial T} \right)_{\ln x} = -\bar{v} \left(\frac{\partial a}{\partial \ln x} \right)_T \left(\frac{\partial \ln x}{\partial T} \right)_{a\bar{v}}. \quad (9a)$$

Rearranging Eq. (9a) one has

$$\left(\frac{\partial a}{\partial T} \right)_{\ln x} = - \left(\frac{\partial a}{\partial \ln x} \right)_T \left(\frac{\partial \ln x}{\partial T} \right)_{a\bar{v}} - a\alpha. \quad (9b)$$

According to the potential theory, ΔG is independent of the temperature, so we can have following relationship

$$\left(\frac{\partial \Delta G}{\partial T} \right)_{a\bar{v}} = -RT \ln x - R \left(\frac{\partial T \ln x}{\partial T} \right)_{a\bar{v}} = 0 \quad (10a)$$

or

$$\left(\frac{\partial \ln x}{\partial T} \right)_{a\bar{v}} = - \frac{\ln x}{T}. \quad (10b)$$

By substituting Eq (10b) into Eq. (9b), it yields

$$\left(\frac{\partial a}{\partial T} \right)_{\ln x} = \left(\frac{\partial \ln a}{\partial \ln x} \right)_T \frac{\ln x}{T} - a\alpha. \quad (11)$$

Expressing a as a function of T and $\ln(x)$, one has

$$da = \left(\frac{\partial a}{\partial T} \right)_{\ln x} dT + \left(\frac{\partial a}{\partial \ln x} \right)_T d \ln x = 0. \quad (12a)$$

Rearranging Eq. (12a) yields

$$\left(\frac{\partial a}{\partial T} \right)_{\ln x} = - \left(\frac{\partial a}{\partial \ln x} \right)_T \left(\frac{\partial \ln x}{\partial T} \right)_a = 0. \quad (12b)$$

By substituting Eq. (12b) into Eq. (11), one has

$$-\left(\frac{\partial a}{\partial \ln x}\right)_T \left(\frac{\partial \ln x}{\partial T}\right)_a = \left(\frac{\partial a}{\partial \ln x}\right)_T \frac{\ln x}{T} - \alpha a. \quad (13a)$$

Rearranging Eq. (13a) yields

$$\left(\frac{\partial \ln x}{\partial T}\right)_a = -\frac{\ln x}{T} + \alpha \left(\frac{\partial \ln x}{\partial \ln a}\right)_T. \quad (13b)$$

By substituting Eq. (13b) into Eq. (2), and after rearrangement, one has

$$q^{\text{net}} = RT^2 \left[\alpha \left(\frac{\partial \ln x}{\partial \ln a}\right)_T - \frac{\ln x}{T} \right]. \quad (14)$$

The terms, $(\ln x)$ and $(\partial \ln x / \partial \ln a)$, can be further expressed as follow (Dubinin et al., 1991)

$$\ln x = -\frac{\beta E_0}{RT} \left[\ln \left(\frac{W_0}{a\bar{v}} \right) \right]^{1/n}. \quad (15)$$

Taking partial differentiation of x by a , one has

$$\frac{\partial \ln x}{\partial \ln a} = \frac{\beta E_0}{RTn} \left[\ln \left(\frac{W_0}{a\bar{v}} \right) \right]^{(1/n)-1}. \quad (16)$$

By substituting Eqs. (15) and (16) into Eq. (14), it yields the following expression

$$q^{\text{net}} = \beta E_0 \left\{ \frac{\alpha T}{n} \left[\ln \left(\frac{W_0}{a\bar{v}} \right) \right]^{(1/n)-1} + \left[\ln \left(\frac{W_0}{a\bar{v}} \right) \right]^{1/n} \right\}, \quad (17)$$

where θ is the filling degree of the micropore, that is, $W_0/a\bar{v} = \theta$, ΔH_{con} is the enthalpy of condensation, α is the thermal expansion coefficient, a is the number of moles adsorbed and $\bar{v}$ is the molar volume of adsorbed material.

Note that W_0 is the total micropore volume and is related to W by the Dubinin–Astokhov equation

$$W = W_0 \exp \left[- \left(\frac{\Delta G}{\beta E_0} \right)^n \right], \quad (18)$$

where W is the volume of adsorption space, ΔG the adsorption energy, β is the affinity coefficient and E_0 is the adsorption characteristic energy, it characterizes the sorption properties (distribution function for the adsorption potential, $f(W)$) of the adsorbent (Poniec et al., 1974); n is the constant.

By substituting $(W_0/a\bar{v} = \theta)$ into Eq. (17) one has the following expression

$$q^{\text{net}}(T; \theta) = \beta E_0 \left[\left(\ln \frac{1}{\theta} \right)^{1/n} + \frac{\alpha T}{n} \left(\ln \frac{1}{\theta} \right)^{(1/n)-1} \right]. \quad (19)$$

The enthalpy of immersion (ΔH_i) of a surface such as activated carbon in organic liquids can be described by the following equation (Poniec et al., 1974; Stoeckli and Kraehenbueh, 1981):

$$-\Delta H_i(T) = \int_0^1 q^{\text{st}}(T; \theta) d\theta - \Delta H_{\text{con}}(T). \quad (20)$$

By combining Eqs. (1) and (20), one has

$$-\Delta H_i(T) = \int_0^1 q^{\text{net}}(T; \theta) d\theta. \quad (21)$$

By substituting Eq. (19) into Eq. (21) and upon integration of the final equation, one has

$$-\Delta H_i = \beta E_0 \Gamma \left(\frac{1}{n} + 1 \right) + \frac{\beta E_0 \alpha T}{n} \Gamma \left(\frac{1}{n} \right), \quad (22)$$

where

$$\Gamma \left(\frac{1}{n} \right), \Gamma \left(\frac{1}{n} + 1 \right) : \text{the Gamma function.}$$

In the case of activated carbon, $n = 2$ (Marsh and Rand, 1970; Stoeckli and Houriet, 1976; Stoeckli et al., 1980; Barton, 1987; Jankowska et al., 1991) and the following molar enthalpy of immersion is obtained

$$\Delta H_i = \frac{\beta E_0 \sqrt{\pi} (1 + \alpha T)}{2}. \quad (23)$$

According to the potential theory, the adsorbate conduces in the adsorption space and immerses the adsorbent (Smisek and Cerny, 1970). The potential theory further assumes that, the enthalpy of adsorption, ΔH , is equal to the enthalpy of immersion, ΔH_i , that is $\Delta H \cong \Delta H_i$. With known free energy and enthalpy of adsorption, the entropy (ΔS) of adsorption can be readily obtained by the following equation

$$\Delta S = \frac{\Delta H_i - \Delta G}{T}. \quad (24)$$

2.2. Statistical thermodynamic method

Based on statistical thermodynamics, it is possible to estimate the change of total entropy of adsorption. The differential entropy change, i.e., when one mole of gas at 1 atm pressure is adsorbed by a given amount of activated carbon surface with a surface coverage of q , involves several possible partition functions such as total translational and vibrational. Initially, the total specific translational partition function (Q_{tot}) (Stoeckli et al., 1980) is

$$Q_{\text{tot}} = \frac{1}{a} \left[\left(\frac{2\pi M k T}{h^2} \right)^{3/2} \tilde{V} \right]^a, \quad (25)$$

where M is the molecular weight, k is the Boltzmann constant, h is the Planck constant, $\tilde{V}$ is the specific volume of gas and a is the mole of molecules adsorbed.

According to the Sterling's approximation and replacing $\tilde{V}/N$ by kT/P , one has the Sackur–Tetrode equation (Stoeckli et al., 1980)

$$S_{\text{trans}}^g = R \ln \left(\frac{T^{5/2} M^{3/2}}{P} \right) - 2.30. \quad (26)$$

If the adsorption site is regarded as a two-dimensional potential box, as implied by the kinetic derivation given above, the corresponding translational entropy (S_{trans}^s) must be evaluated. The total partition function for n molecules is merely $(2\pi M kT/h^2)\sigma^0)^n$, and the normal operation yield is (Adamson, 1982)

$$S_{\text{trans}}^s = R \ln (MT\sigma^0) + 63.8, \quad (27)$$

where σ^0 is the molecular cross-sectional area.

The localized adsorption is attributed to the adsorption bond. Per degree of vibrational freedom (S_{vib}^s) can be obtained as follows:

$$\begin{aligned} S_{\text{vib}}^s &= R \left[\frac{h\nu^0/kT}{e^{h\nu^0/kT} - 1} - \ln \left(1 - e^{-h\nu^0/kT} \right) \right], \\ &\cong R [1 - \ln (h\nu^0/kT)], \end{aligned} \quad (28)$$

where $1/\nu^0(\tau^0)$ is the time of molecule staying on the solid surface (ν^0 is taken to be 10^{12} s^{-1}).

However, in order to be consistent with the kinetic derivation of the Langmuir equation, it is necessary to assume that there is a potential box and a weak adsorption bond of ν^0 corresponding to $1/\tau^0$. Under these above assumptions, one has

$$\Delta S_{\text{local}}^{\text{ads}} = -R \ln \left(\frac{\theta}{1-\theta} \right) + S_{\text{trans}}^s + S_{\text{vib}}^s - S_{\text{trans}}^g. \quad (29)$$

The values of the entropy of “localized” adsorption can be widespread depending on whether the site is viewed as equivalent to a strong adsorption bond of negligible entropy or as a potential box with a weak bond. By combining Eq. (2a) (for ΔG) and Eq. (29) (for ΔS), and then substituting into Eq. (24), the adsorption enthalpy can be obtained

$$\begin{aligned} \Delta H &= -RT \ln x + \left(-R \ln \left(\frac{\theta}{1-\theta} \right) \right. \\ &\quad \left. + S_{\text{trans}}^s + S_{\text{vib}}^s - S_{\text{trans}}^g \right) T. \end{aligned} \quad (30)$$

2.3. Adsorption energy distribution

In order to understand the adsorption energy distribution, the following procedures are followed. The overall adsorption isotherms, θ_t , can be calculated from given isotherm, θ_1 , and adsorption energy distribution function, (Cerofolini, 1974), i.e., $\chi(\epsilon)$

$$\theta_t(T; P) = \int_0^\infty \theta_1(T; P; \epsilon) \chi_c(\epsilon) d\epsilon. \quad (31)$$

Cerofolini (1974) has modified the above equation as the following

$$\theta_t(T; P) = \int_0^\infty \chi_c(\epsilon) d\epsilon. \quad (32)$$

Furthermore in order to solve the above energy distribution equation analytically, the following assumption are made:

1. Adsorption isotherms follow the Dubinin–Astakhov equation, that is

$$\theta_t = \frac{W}{W_0} = \exp \left[- \left(\frac{\Delta G}{\beta E_0} \right)^n \right].$$

2. Local adsorption isotherms correlate with the Langmuir type without the lateral effect, that is, $\Gamma_e = \Gamma_m K C_f / (1 + K C_f)$, where C_f , K , Γ_e , and Γ_m are equilibrium concentration of adsorbate, equilibrium constant, adsorption density and saturation adsorption density, respectively.

3. The condensation pressure (p_m) is equal to the saturation vapor pressure (p_0), that is, $p_m = p_0$.

4. The e_0 value is the condensation heat at critical point (Eq. (34)), that is,

$$\Delta G = \epsilon - \epsilon_0 = RT \ln \left(\frac{p_0}{p} \right). \quad (33)$$

In addition, ϵ_0 can also be estimated by the Riedel equation (Perry and Green, 1984)

$$\epsilon_0 = \Delta H_{\text{vap}} = 1.093 RT_c \left(T_b \frac{\ln(p_c - 1)}{0.930 - T_b} \right), \quad (34)$$

where T_c is the critical point, T_b is the boiling point and p_c is the critical pressure.

Based on the above assumptions, and the fact that the adsorption isotherms are consistent with the Dubinin–Astakhov equation, the adsorption energy distribution can be rearranged as follows

$$\begin{aligned} \chi_c(\epsilon) &= - \frac{\partial \theta_t}{\partial \epsilon} \\ &= n \frac{(\epsilon - \epsilon_0)^{n-1}}{(\beta E_0)^n} \exp \{ - [(\epsilon - \epsilon_0)/\beta E_0]^n \}. \end{aligned} \quad (35)$$

Table 1 summaries the relevant equations needed for the calculation of thermodynamic properties of the adsorption of VOCs by activated carbon.

3. Experimental

3.1. Adsorbents and adsorbates

Activated carbon (8×30 mesh) was provided by Kowa Cosmos Company, Japan. Before experiments, the activated carbon was stored in an oven at 105°C for 48 h. Activated carbon was pretreated before adsorption experiments. To each of the five 2-l polyethylene bottles,

Table 1

List of analysis methods for the calculation of thermodynamic parameters

Analysis methods	Thermodynamic parameters		
	ΔH	ΔG	ΔS
Immersion enthalpy method	$\Delta H \cong \Delta H_i = \frac{\beta E_0 \sqrt{\pi}(1 + \alpha T)}{2}$ (Eq. (23))	$\Delta G = -RT \ln x$ (Eq. (2a))	$\Delta S = \frac{H_i - \Delta G}{T}$ (Eq. (24))
Statistical thermodynamic method	$\Delta H = \Delta G + T\Delta S$ (Rearranging from Eq. (24))	$\Delta G = -RT \ln x$ (Eq. (2a))	$\Delta S_{\text{local}}^{\text{ads}} = -R \cdot \ln \left(\frac{\theta}{1 - \theta} \right) + S_{\text{trans}}^s + S_{\text{vib}}^s - S_{\text{trans}}^g$ (Eq. (29))

it was added 500 g activated carbon. Added 1 l NaOH solutions to each bottle to attain various NaOH concentrations from 1 to 5 M. The bottles containing the activated carbon sample were then placed in a rotating vibrator and mixed for 24 h. The activated carbons, after separation from the solution by sedimentation, were dried in an oven at 105°C for another 48 h. NaOH-treated activated carbon samples (250 g) were treated further with ozone at a concentration 40 mg/l and flow rate of 2.5 l/min (or 100 mg/min) for 30 min. A water tank was used to control the reaction temperature during treatment to below the combustion point of the activated carbon. Activated carbon samples were washed with distilled water until the concentration of sodium ion in the rinse water reached that of the distilled water. The activated carbon was then separated from the solution, filtered, dried at room temperature, and placed in a vacuum oven at 105°C for 48 h. The temperature was then decreased to 30°C and the activated carbon was purged with nitrogen gas for three more hours. The activated carbon samples treated were divided into the following categories: untreated, ozone only, 1N NaOH and ozone, 2N NaOH and ozone, 3N NaOH and ozone, 4N NaOH and ozone, 5N NaOH and ozone. These activated carbon samples were designated as: AC, AC(O₃), AC(1N-O₃), AC(2N-O₃), AC(3N-O₃), AC(4N-O₃) and AC(5N-O₃), respectively.

3.2. Sorption experiments

Diffusion tubes filled with liquid benzene or MEK were placed inside a temperature control tank as to generate the VOCs needed for this study. The temperature was maintained within $\pm 0.5^\circ\text{C}$. The concentration of VOCs in the nitrogen stream was determined by gas chromatography equipped with a flame ionization detector (HP, Model 5890 II).

The activated carbon adsorbent was then dried in a vacuum oven for 24 h at 105°C and 10^{-2} – 10^{-3} mm Hg. Adsorption experiments were conducted According to the following experimental procedures place activated

carbon (50 mg) sample in the electrical balance that was connected to a data Acquisition system. A flow of nitrogen gas carrying the adsorbate was then purged through the activated carbon to allow adsorption reaction to take place. The influent concentrations of benzene ranged from 372 to 2486 ppm and those of MEK from 500 to 1470 ppm. The inflow rate of benzene and MEK vapor was maintained at 2.0 l/min. In order to obtain the thermodynamic constants, three adsorbents including AC, AC(O₃), AC(2N-O₃) were selected to perform the benzene and MEK adsorption experiments at 30°C, 70°C and 120°C. The adsorption tests were repeated four times for all adsorbate concentrations.

4. Results and discussion

4.1. Thermodynamic characteristics of benzene adsorption

Table 2 summarizes the adsorption characteristic energy and enthalpy of benzene at 30°C for the seven activated carbons studied. The adsorption characteristic energy, E_0 , immersion enthalpies, ΔH_i , adsorption free energy, ΔG , and adsorption entropy, ΔS , are between 17.12 and 36.86, –20.8 and –44.7, –11.89 and –16.22 kJ/mole, and –29.4 and –94.0 J/mole/K, respectively. The adsorption characteristics energy, E_0 , follows the order: AC(1N-O₃) > AC > AC(3N-O₃) > AC(4N-O₃) > AC(O₃) > AC(5N-O₃) > AC(2N-O₃). The immersion enthalpy, Δ_i , free energy of adsorption, ΔG , and entropy of adsorption, ΔS follow the order: AC(2N-O₃) > AC(5N-O₃) > AC(O₃) > AC(4N-O₃) > AC(3N-O₃) > AC > AC(1N-O₃).

According to the volume filling of micropores theory, the smaller the E_0 the easier is for the adsorbates to adsorb onto the adsorbent (Poniec et al., 1974). Hu and Vansant (1995) used elutrilite-producing carbon to adsorb benzene, and reported on adsorption characteristic energy in the range 9.8–25.9 kJ/mole. The pore structure of the activated carbon changes upon NaOH-ozone treatment. As a results benzene easily becomes adsorbed onto the NaOH-ozone activated carbons.

Table 2
Adsorption energy of benzene ($N = 4$)

Adsorbents	E_0 (kJ/mole) ^a	E_0/T (kJ/mole-K) ^b	ΔH_i (kJ/mole) ^c	Δh_i (J/ml-adsorbate) ^d	Γ_m (mole/Kg) ^e	K (m ³ /mole) ^f	ΔG (kJ/mole) ^g	ΔS (J/mole-K) ^h
AC	34.45	113.7	-41.8	-464.9	2.90	562.5	-15.95	-85.3
AC(O ₃)	26.04	85.9	-31.6	-351.5	2.69	312.4	-14.47	-56.5
AC(1N-O ₃)	36.86	121.7	-44.7	-497.5	2.91	625.9	-16.22	-94.0
AC(2N-O ₃)	17.12	56.5	-20.8	-231.1	2.99	112.2	-11.89	-29.4
AC(3N-O ₃)	31.44	103.7	-38.2	-424.3	2.84	467.0	-15.48	-75.0
AC(4N-O ₃)	30.06	99.2	-36.5	-405.7	2.81	427.2	-15.26	-70.1
AC(5N-O ₃)	17.88	59.0	-21.7	-241.3	2.91	129.2	-12.25	

^a $W = W_0 \exp\{-(A/\beta E_0)^n\}$, $n = 2$.

^b a/T .

^c $\Delta H_i = \beta E_0 \sqrt{\pi}(1 + \alpha T)/2$.

^d $\Delta h_i = \Delta H_i$ /molar volume, the molar volume of benzene is 90.0 ml/mole at 1 atm and 303 K.

^e Γ_m = saturation adsorption capacity.

^f K = equilibrium constant.

^g $\Delta G = -RT \ln K$, $R = 8.314$ J/g-mole/K, $T = 303$ K.

^h $\Delta S = \Delta H_i - \Delta G/T$.

Table 3
Adsorption energy of MEK ($N = 4$)

Adsorbents	E_0 (kJ/mole) ^a	E_0/T (kJ/mole-K) ^b	ΔH_i (kJ/mole) ^c	Δh_i (J/ml-adsorbate) ^d	Γ_m (mole/Kg) ^e	K (m ³ /mole) ^f	ΔG (kJ/mole) ^g	ΔS (J/mole-K) ^h
AC	23.54	77.7	-29.7	-327.2	3.07	241.3	-13.82	-52.4
AC(O ₃)	14.47	47.8	-18.3	-201.2	3.64	72.1	-10.78	-24.8
AC(1N-O ₃)	27.74	91.6	-35.0	-385.6	3.27	322.9	-14.55	-67.5
AC(2N-O ₃)	32.34	106.7	-40.8	-449.4	3.00	481.7	-15.56	-83.3
AC(3N-O ₃)	19.05	62.9	-24.0	-264.8	3.30	143.6	-12.51	-37.9
AC(4N-O ₃)	27.18	89.7	-34.3	-377.8	3.01	333.2	-14.63	-58.3
AC(5N-O ₃)	15.90	85.5	-32.7	-360.0	2.99	306.8	-14.42	-60.3

^a $W = W_0 \exp\{-(A/\beta E_0)^n\}$.

^b a/T .

^c $\Delta H_i = \beta E_0 \sqrt{\pi}(1 + \alpha T)/2$.

^d $\Delta h_i = \Delta H_i$ /molar volume, the molar volume of benzene is 90.8 ml/mole at 1 atm and 303 K.

^e Γ_m = saturation adsorption capacity.

^f K = equilibrium constant.

^g $\Delta G = -RT \ln K$, $R = 8.314$ J/g-mole/K, $T = 303$ K.

^h $\Delta S = \Delta H_i - \Delta G/T$.

4.2. Thermodynamic characteristics of MEK adsorption

Table 3 summarizes the MEK adsorption characteristic energy, immersion enthalpy, free energy of adsorption and entropy of adsorption for seven activated carbons. The adsorption characteristic energy, E_0 , immersion enthalpy, ΔH_i , free energy of adsorption, ΔG , and entropy of adsorption, ΔS , are between 32.24 and 14.47, –40.8 and –18.3, –15.56 and –10.78 kJ/mole and –83.3 and –24.8 J/mole/K, respectively. The adsorption characteristic energy, E_0 , follows the order: $\text{AC}(2\text{N}-\text{O}_3) > \text{AC}(1\text{N}-\text{O}_3) > \text{AC}(4\text{N}-\text{O}_3) > \text{AC} > \text{AC}(3\text{N}-\text{O}_3) > \text{AC}(5\text{N}-\text{O}_3) > \text{AC}(\text{O}_3)$. The immersion enthalpy, ΔH_i , adsorption free energy ΔG , and adsorption entropy, ΔS , follow the order: $\text{AC}(\text{O}_3) > \text{AC}(5\text{N}-\text{O}_3) > \text{AC}(3\text{N}-\text{O}_3) > \text{AC} > \text{AC}(4\text{N}-\text{O}_3) > \text{AC}(1\text{N}-\text{O}_3) > \text{AC}(2\text{N}-\text{O}_3)$. Results indicate that the adsorption energies of benzene were greater than those of MEK for the same activated carbon adsorbent which implies that MEK is more adsorbable than benzene by activated carbon. This can be attributed in part to the polar-nature of the both the activated carbon and the MEK. Apparently specific chemical energy plays the most important role on VOC adsorption.

4.3. The distribution of adsorption energy

Fig. 1 displays the distribution of adsorption energy of benzene. Note that the data points are experimentally

obtained. The adsorption energy of $\text{AC}(2\text{N}-\text{O}_3)$ and $\text{AC}(5\text{N}-\text{O}_3)$ are identical and mostly in the range between 10 and 50 kJ/mole. AC , $\text{AC}(\text{O}_3)$, $\text{AC}(1\text{N}-\text{O}_3)$, $\text{AC}(3\text{N}-\text{O}_3)$, and $\text{AC}(4\text{N}-\text{O}_3)$ exhibit larger adsorption energy with a broad energy distribution profile. The smaller the adsorption energy is, the sharper the energy distribution.

4.4. Comparison of method for the determination of desorption energies

Three adsorbents (AC , $\text{AC}(\text{O}_3)$ and $\text{AC}(2\text{N}-\text{O}_3)$), two adsorbates (benzene and MEK) and three adsorption temperatures (30°C, 70 °C, and 120°C were selected in the experiments. The thermodynamic information regarding the adsorption of VOCs was calculated by two different methods as described above (Table 3). Table 4 summarizes the results of thermodynamic calculations.

4.4.1. The immersion enthalpy method

According to the premise of the immersion enthalpy method, it is assumed that the enthalpy is equal to the heat of immersion. When the adsorption temperature increases from 30°C to 120°C, the benzene immersion enthalpy decreases from –35.0 to –30.3, –39.8 to –34.4 kJ/mole for $\text{AC}(\text{O}_3)$, and –40.6 to –35.1 kJ/mole for $\text{AC}(2\text{N}-\text{O}_3)$, respectively. The MEK immersion enthalpy decrease from –44.4 to –38.2 kJ/mole for AC ,

Fig. 1. Adsorption energy distribution of benzene is adsorbed on AC , $\text{AC}(\text{O}_3)$, $\text{AC}(1\text{N}-\text{O}_3)$, $\text{AC}(2\text{N}-\text{O}_3)$, $\text{AC}(3\text{N}-\text{O}_3)$, $\text{AC}(4\text{N}-\text{O}_3)$, and $\text{AC}(5\text{N}-\text{O}_3)$. The points are experimental data. The lines are fitted by Eq. (35).

Table 4
Thermodynamic parameters of benzene and MEK adsorption

Adsorbents	Temperature (°C)	Benzene				MEK			
		ΔH (kJ/mole)		ΔG (kJ/mole)		ΔH (kJ/mole)		ΔG (kJ/mole)	
		IE	ST	IE	ST	IE	ST	IE	ST
AC	30	-30.3	-42.6	-16.0	-16.0	-38.2	-37.5	-13.9	-80.2
	70	-31.9	-33.9	-11.4	-11.4	-40.5	-32.2	-9.4	-90.7
	120	-35.0	-33.2	-8.7	-8.7	-44.4	-38.2	-13.6	-78.4
AC(O ₃)	30	-34.4	-37.0	-14.4	-14.4	-39.9	-33.0	-10.8	-96.0
	70	-36.3	-32.8	-10.2	-10.2	-42.3	-33.3	-11.1	-91.0
	120	-39.8	-34.0	-9.3	-9.3	-46.3	-36.6	-12.4	-86.2
AC(2N-O ₃)	30	-35.1	-35.2	-11.9	-11.9	-37.8	-38.8	-15.5	-65.0
	70	-37.0	-32.8	-10.3	-10.3	-40.1	-32.8	-10.9	-85.1
	120	-40.6	-35.5	-10.6	-10.6	-43.9	-37.3	-13.1	-78.4

IE and ST designate as immersion enthalpy method and statistical thermodynamic method, respectively.

-46.3 to -39.9 kJ/mole for AC(O₃) and -43.9 to -37.8 kJ/mole for AC, (2N-O₃), respectively.

Gibbs free energy of adsorption for benzene are between -16.0 and -8.7 kJ/mole for AC, -14.4 and -9.3 kJ/mole for AC(O₃), and -11.9 and -10.6 kJ/mole for AC(2N-O₃), respectively. Gibbs free energy of adsorption for MEK are between -13.9 and -9.4, -12.4 and -10.8, and -15.5 to -10.9 kJ/mole for AC, AC(O₃), and AC(2N-O₃), respectively.

The adsorption entropy for benzene is in the range from -66.8 to -47.2 J/mole/K for AC, -77.6 to -66.0 J/mole/K for AC(O₃) and -76.3 to -77.8 J/mole/K for AC(2N-O₃), respectively. MEK adsorption entropy is between -90.7 and -78.4 J/mole/K for AC, -96.0 to -86.2 J/mole/K for AC(O₃), and -85.1 to -65.0 J/mole/K for AC(2N-O₃).

The condensation heat of benzene and MEK at normal boiling point is -30.8 and -31.2 kJ/mole, respectively (Gallant and Yaws, 1993). Heat of benzene adsorbed on mercury is -42.7 kJ/mole (Poniec et al., 1974). According to the above literatures, it is noted that the adsorption energy is governed by both the VOCs and the adsorbent. The constancy of entropy of condensation at normal boiling point for benzene and MEK are -87.0 and -88.7 J/mole/K, individually (Schwarzenbach et al., 1992). Kistiakowsky utilized the Clapeyron equation and the ideal gas law to calculate the entropy of both benzene and MEK and reported a value of -85.4 J/mole/K at normal boiling point (Schwarzenbach et al., 1992). Our results are consistent with those reported in the literature. The immersion heat of MEK is higher than that of benzene. This can be attributed to the fact that MEK has methyl and carbonyl as the major functional groups. That is, MEK is a polar species whereas benzene is non-polar. Therefore, the MEK can immerse in both the polar and non-polar sites of adsorbents and subsequently generate stronger chemical reactions than that of the benzene.

4.4.2. Statistical thermodynamic method

According to the principle of the statistical thermodynamic method, the major factors controlling the entropy of adsorption are the ratio of adsorption site as occupied by adsorbate, the transport of adsorbate and the vibration of the adsorbate. The vapor pressure and boiling point of benzene and MEK are close, therefore it is expected that their entropy of adsorption would be almost identical.

The enthalpy of adsorption for benzene ranges between -42.6 and -33.2 kJ/mole for AC, -37.0 and -32.8 kJ/mole for AC(O₃), and -38.2 to -32.2 kJ/mole for AC(2N-O₃), respectively. The enthalpy of adsorption for MEK is in the range between -38.2 and -32.2 kJ/mole for AC -36.6 and -33.0 kJ/mole for AC(O₃), and -38.8 and -32.8 kJ/mole for AC(2N-O₃), respectively.

Fig. 2. The thermodynamic characteristics of benzene adsorption at differential temperatures.

Gibbs free energy of adsorption is measured by the immersion enthalpy method. The entropy of adsorption for benzene is in the range between -87.6 and -62.3 J/mole/K for AC, -74.3 and -63.0 J/mole/K for $AC(O_3)$ and -77.0 and -63.5 J/mole/K for $AC(2N-O_3)$, respectively. The entropy of adsorption for MEK is between -77.9 and -62.4 J/mole/K for AC, -75.2 and -61.4 J/mole/K for $AC(O_3)$ and -76.8 and -61.7 J/mole/K for $AC(2N-O_3)$, respectively.

Adsorption entropy and enthalpy of benzene and MEK were measured by the statistical thermodynamic method. The data are in the same range as those reported in the literatures [28–30]. Generally, the statistical thermodynamic method only deals with the physical characteristics of the adsorbate and the adsorbent. It does not consider the chemical reaction between the adsorbate and the adsorbent. This is attributed in part to the differences of the immersion enthalpy method and statistical thermodynamic method.

Figs. 2 and 3 show the variation of ΔG , ΔS and ΔH at different temperatures. Our data are comparable with those reported by Yeh who studied the adsorption of benzene onto granular activated carbon (Everett and Ottewill, 1969). Yeh reported an adsorption enthalpy

Fig. 3. The thermodynamic characteristics of MEK adsorption at differential temperatures.

between -48.1 and -29.3 kJ/mole (Everett and Ottewill, 1969). There is no significant difference among all thermodynamic parameters obtained by the above methods. Results clearly indicate the both methods can be used to estimate the thermodynamic parameters of VOC adsorption with equal degree of consistency.

5. Conclusions

This study deals with the thermodynamic parameters of the adsorption of benzene and MEK onto seven activated carbon samples. Results indicate that the adsorption energy of benzene are greater than that of MEK for the same adsorbent. Based on the energy distribution of benzene adsorption, it is concluded that the lower the adsorption energy the sharper is the energy distribution. That is, benzene is easily adsorbed by activated carbon than MEK. Both the immersion enthalpy and statistical thermodynamic methods can be used to calculate the thermodynamic parameters of adsorption at least for benzene and MEK.

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