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Adsorption Equilibrium of Solvent Vapors on Activated Carbons

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Abstract−Adsorption amounts of solvent vapors such as n-hexane, toluene, and MEK on two commercial activated carbons (SLG-2PS and X-7000) were measured experimentally using a quartz spring balance connected with a high vacuum system. Single-species equilibrium data show typical type II isotherms, which are most frequently encountered in separation processes. Equilibrium data obtained at relative vapor pressures less than 0.3 were fitted to four well-known isotherms such as Langmuir, Freundlich, Sips, and Dubinin-Astakov (D-A) equations. All isotherm equations were found to describe experimental equilibrium data satisfactorily. Only the Langmuir equation was not proper to fit the equilibrium data of solvent vapors on SLG-2PS. In order to evaluate the adsorption energy distribution of the solvent vapors on activated carbons, a simple model based on the condensation approximation (CA) approach was applied. According to the result, it was proven that two carbons have energetically heterogeneous surfaces.

Key words: Recovery of Solvent Vapors, Activated Carbons, Isothermal Adsorption, Adsorption Equilibrium, Surface Heterogeneity

INTRODUCTION

Solvents have been used as dissolving and cleaning agents in many industrial processes such as printing, film coating, and manufacturing of magnetic tapes and electronic chips. The emission of solvent vapors from these industrial processes caused not only severe air pollution but also a great loss of valuable chemicals. Therefore, the proper recovery of volatile solvent vapors from industrial effluents has multiple purposes such as reduction of production cost, energy saving, and environmental protection [Mukhopadhyay et al., 1993; Yun et al., 1997]. There are three major methods to recover volatile solvents: condensation, absorption, and adsorption [Ruddy et al., 1993]. Mixed solvent vapors can be condensed by lowering temperature below their boiling points. However, this method has a drawback which requires relatively higher concentration to improve its recovery efficiency. On the other hand, the absorption method, which employs an absorbing liquid, has been known as an efficient recovery process even at low concentration levels, but it requires an additional unit to separate the solvent from the absorption mixture, resulting in high operation cost. Nevertheless, the adsorption method would be an efficient and economic technique for recovering solvent vapors from their mixtures which contain 1,000-3,000 ppm of volatile solvents, once a proper adsorbent is found [Manes, 1984]. In Korea, more that 1,000 tons of various solvents are used in a year in many industrial processes such as polyethylene coating and cleaning agents. The emissions from some industries contain BTX (benzene, toluene, and xylene), MEK (methyl ethyl ketone), and chlorinated hydrocarbons [Chihara et al., 2000] etc. which should be recovered to reduce production cost and air contamination. Therefore, the solvent recovery stands for a "two birds with one stone" technique. In this work, three major solvents, n-hexane, toluene, and MEK, which are mainly used in many industries, were chosen and two pelletized activated carbons were used as adsorbents for solvent recovery. Since the solvent recovery process requires adsorbents with good hardness, pelletized carbons are better than granular types. Adsorption amount of each solvent vapor was measured accurately by a quartz spring balance which is connected with a high vacuum system. Single-species adsorption data were fitted to well-known isotherms such as Langmuir, Freundlich, Sips, and D-A equations. The adsorption energy distribution was also calculated by using a simple method based on the condensation approximation approach to obtain the surface character of activated carbons. Such results can be applied in simulating the column dynamics in future studies.

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EXPERIEMNTAL

Adsorbents used in this study are pelletized activated carbons, X-7000 manufactured by Dakeda (Japan) and SLG-2PS by a domestic (Korean) company. The arithmetic average particle diameter was determined by sieving a number of particles with a set of standard sieve trays. Various densities of carbons were measured by weighing the sample and by displacing the void fraction with carbon tetra-chloride in a picnometer. Other properties such as pore size distribution, pore volume, and specific surface area were measured by N_2 adsorption in a BET system. Prior to use, the carbon particles were leached with boiling water for 48 h to remove impurities from internal pores of the particles. The particles were then dried in an oven maintained at 378.15 K.

Solvents are n-hexane (Duksan, GR, 97%), toluene (Duksan, GR, 99%), and MEK (Osaka, GR, 99%) which have been used in many industries. All chemicals were used as received without any further treatment. Their physical properties are listed in Table 1. The vapor of each solvent was generated in a small chamber that was maintained at a constant temperature. The adsorption amount of each

Table 1. Properties of adsorbates used at 308.15 K

Adsorbate	M.W. mol/g	Critical pressure atm	Saturated vapor pressure at 308.15 K atm	Critical temperature K	Boiling temperature K
n-Hexane	86.18	30.1	0.3019	507.5	341.9
M.E.K	72.17	42.1	0.1876	536.8	352.7
Toluene	92.14	41.0	0.0614	591.8	384.8

solvent vapor was measured by a quartz spring balance, which was placed in a closed glass system. A given amount of carbon particles were placed on the dish that was attached to the end of quartz spring and the system was vacuumed for 4 h at 10^{-5} mmHg and 573.15 K to remove volatile impurities from the carbon particles. The system pressure was measured by a pressure sensor, and the variation of weight was converted by a digital voltmeter, which is connected with the spring sensor. Equilibrium experiments were carried out at three different temperatures, 298.15, 308.15, and 318.15 K. Desorption experiments were also carried out according to a reversed way of adsorption.

RESULTS AND DISCUSSION

1. Adsorbent Characterization

In designing an adsorption column, the characterization of adsorbents should be done prior to experiments. In particular, one should know not only the specific surface area but also the pore size distribution of the adsorbent in order to confirm that it would be proper for a given purpose. The surface area and pore volume of carbons measured by the BET analysis are listed in Table 2. The surface area of X-7000 was determined to be 900 m^2/g, which is much smaller than that of SLG-2PS, 1,221 m^2/g. The average pore diameter of X-7000 is 1.81 nm, while that of SLG-2PS is 2.58 nm.

Table 2. Physical properties of activated carbons, SLG-2PS and X-7000

Property	SLG-2PS	X -7000	Unit
Particle size	1.67	1.3-1.6	mm
Particle density	800	920	g/ml
Packing density	322	436	g/ml
Surface area	1220	900	m^2/g
Mean pore diameter	25.8	18.1	Å

2. Adsorption Equilibrium

As mentioned previously, the adsorption amounts of three solvent vapors on two different pelletized activated carbons were measured by a quartz spring balance at three temperatures. Figs. 1-6 show experimental data in terms of temperature and concentration. They

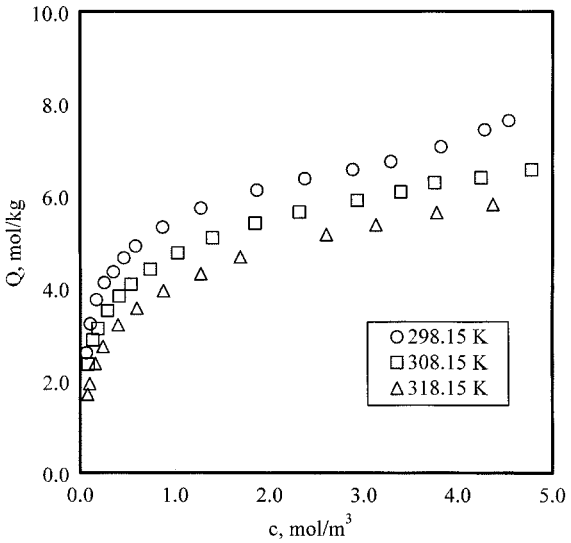

Fig. 2. Adsorption equilibrium curves of MEK on SLG-2PS.

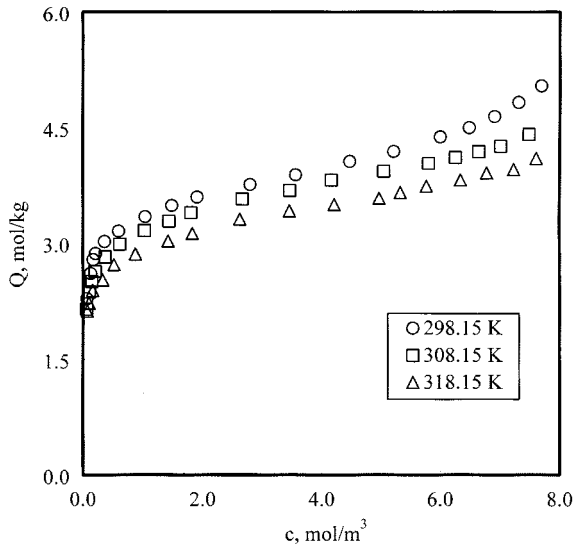

Fig. 1. Adsorption equilibrium curves of n-hexane on SLG-2PS.

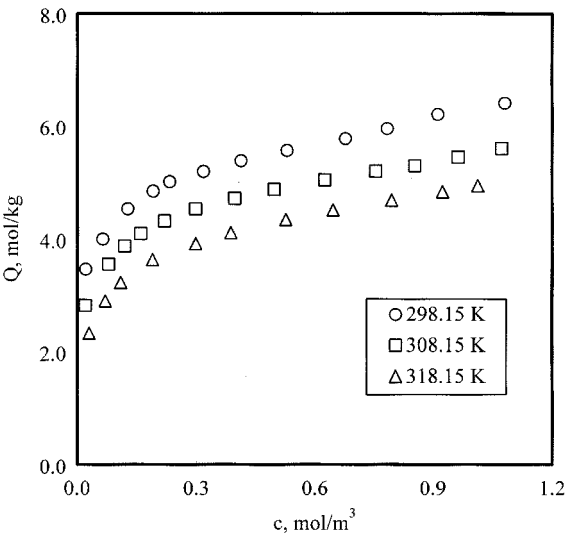

Fig. 3. Adsorption equilibrium curves of toluene on SLG-2PS.

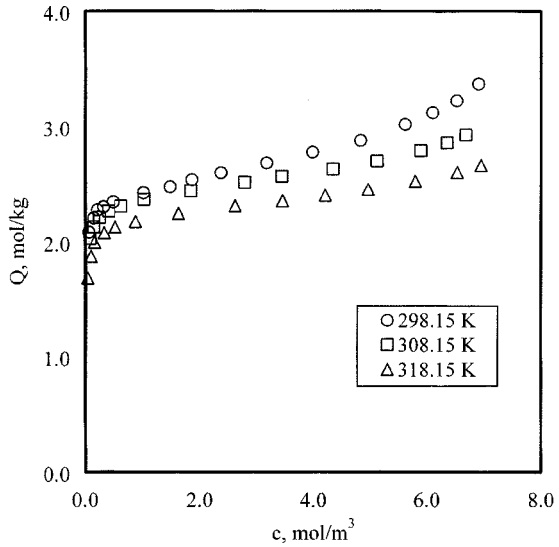

Fig. 4. Adsorption equilibrium curves of n-hexane on X-7000.

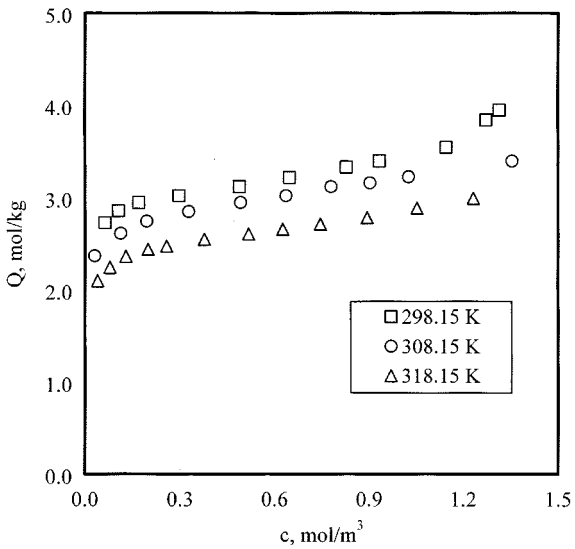

Fig. 6. Adsorption equilibrium curves of toluene on X-7000.

are typical type II isotherms, which are frequently encountered in many separation processes, according to the BDDT classification [Yang, 1987]. The amount adsorbed decreases with temperature, as expected, since adsorption is an exothermic process. Fig. 1 shows the adsorption amounts of n-hexane on SLG-2PS at three temperatures, while Fig. 4 shows those of n-hexane on X-7000. According to experimental results, the adsorption capacity of SLG-2PS is larger than that of X-7000. For other solvent vapors, similar results were obtained. This implies that SLG-2PS has a larger adsorption capacity for the three solvent vapors encountered here than X-7000 since it has a higher specific surface area. However, one cannot conclude that one with larger adsorption capacity is better than the other since the performance of adsorbents should be assessed by their working or reversible capacities, particularly in the solvent recovery process, which employs a cyclic operation, for example, adsorption, desorption, and washing [Takeuchi and Shigeta, 1991]. The adsorption amount on SLG-2PS is in the order of toluene, MEK,

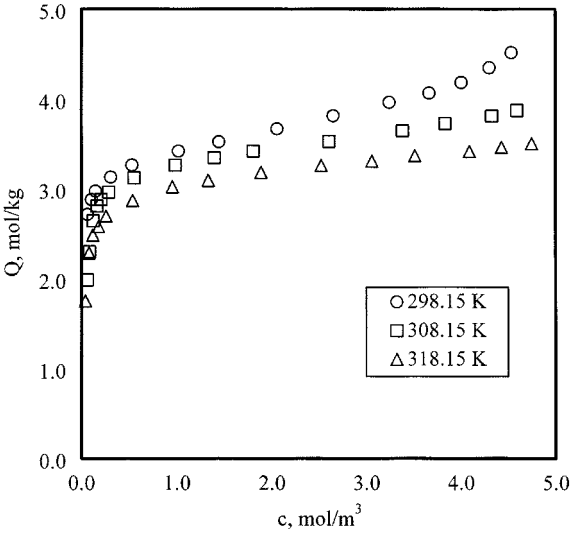

Fig. 5. Adsorption equilibrium curves of MEK on X-7000.

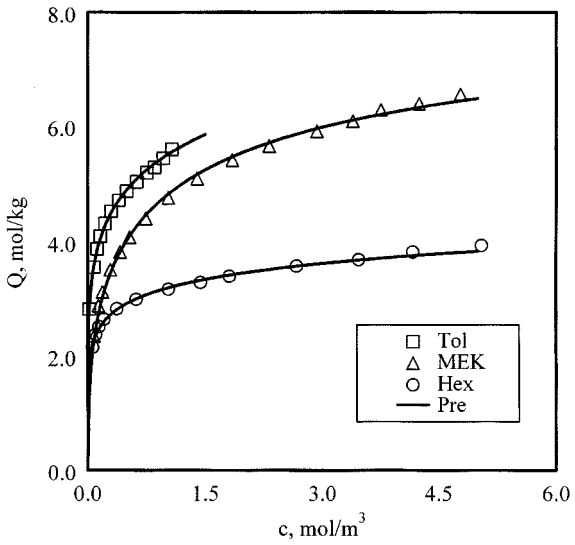

Fig. 7. Experimental and Freundlich isotherms of three solvent vapors on SLG-2PS at 308.15 K.

and n-hexane, while the amounts of MEK and toluene on X-7000 are similar and they are larger than that of n-hexane. Such a result could be explained by the mutual interaction between adsorbent and adsorbate such as adsorption energy distribution. Figs. 7 and 8 show experimental equilibrium data of three solvent vapors on two activated carbons at 308.15 K and corresponding amounts fitted with the Freundlich isotherm. Only the part of equilibrium data measured at relative vapor pressures less than 0.3 were used in determining their isotherms since simple equations cannot fit all experimental data of the type II system well. This will not create any trouble in applying them to real adsorption systems because the concentrations of solvent vapors are relatively low in real situations. Here, single-species equilibrium data were fitted to four common isotherms, namely Langmuir, Freundlich, Sips, and D-A equations.

Langmuir equation: $$Q = \frac{Q_m bc}{1+bc} \quad (1)$$

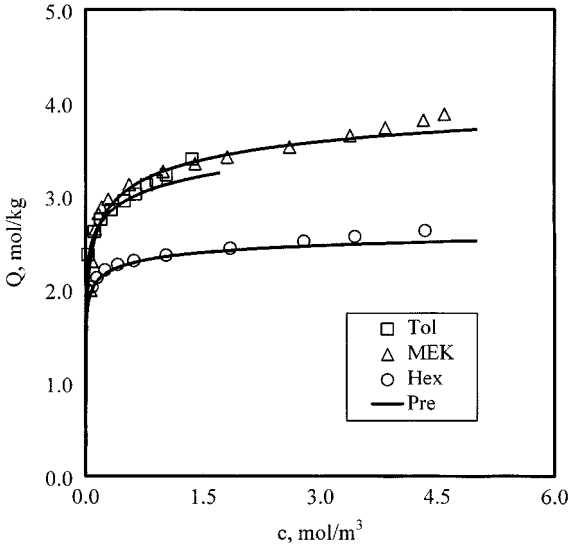

Fig. 8. Experimental and Freundlich isotherms of three solvent vapors on X-7000 at 308.15 K.

Freundlich equation: $$Q = Kc^{1/n} \quad (2)$$

Sips equation: $$Q = \frac{Q_m bc^{1/n}}{1+bc^{1/n}} \quad (3)$$

D-A equation: $$W = W_0 \exp\left[-\left(\frac{A}{E}\right)^r\right] \quad (4)$$

Here, Q_m is the monolayer adsorption amount and A is defined as

$$A = RT \ln\left(\frac{P_s}{P}\right) \quad (5)$$

Other parameters, b, K, n, W_0, E, and r, are empirical isotherm parameters which can be obtained from experimental equilibrium data by minimizing the object function. The object function, E(%), represents the average percent deviation between experimental and fitted (or calculated) results as follows:

$$E(\%) = \frac{1}{N}\sum_{k=1}^{N}\left[\frac{|Q_{exp} - Q_{cal}|}{Q_{exp}}\right]_k \quad (6)$$

All isotherm parameters and E(%) are listed in Table 3. According to the results, the Sips, D-A, and Freundlich equations represent the experimental data fairly well, while the Langmuir equation somewhat shows deviations in the case of SLG-2PS. This fact implies that activated carbons used here are energetically heterogeneous unlike polymeric adsorbents, which show homogeneous surface characteristics [Lee et al., 1997].

In solvent recovery processes, the desorption step would be very important as well as the adsorption step since it requires a great deal of energy. In general, steam has been used in regenerating spent activated carbons, which were loaded with organic solvents because most activated carbons are hydrophobic. However, the reuse of recovered solvents requires one more step to separate solvents from mixtures with water. Therefore, the regeneration technique using inert gases, namely nitrogen, has been considered as an efficient and economic process for this purpose, instead of the steam regeneration [Yun et al., 2000]. Figs. 9 and 10 show adsorption and desorption loops of n-hexane on SLG-2PS and X-7000, respectively. The desorption data appear slightly higher than the adsorption data at the same vapor concentration. This phenomenon, which is called "hysteresis," resulted from differences in adsorption and desorption rates. According to the classification by de Boer, they are the second-type hysteresis. This result implies that activated carbons used here have inkbottle type pores or slit pores [de Boer, 1958]. On the other hand, one may see that most adsorption amount is reversible from adsorption and desorption curves of n-hexane on two activated carbons as shown in Figs. 9 and 10, considering that the desorption was performed by reducing only the vapor pressure in the system. This implies that physical adsorption prevails and working capacities are similar to actual adsorption equilibrium amounts. However, the removal efficiency of an activated carbon for a solvent vapor should be related to its kinetic characteristics such as film and intraparticle mass transfer coefficients. Therefore, kinetic

Table 3. Adsorption equilibrium isotherms of solvents at 308.15 K

	SLG-2PS				X-7000		
Equations	Parameters	n-Hexane	M.E.K	Toluene	Parameters	n-Hexane	M.E.K	Toluene
Langmuir	Q_m	3.15	4.56	5.02	Q_m	2.47	3.49	2.97
	b	45.9	32.6	57.4	b	47.8	23.0	118.
	E(%)	7.30	18.3	7.8	E(%)	3.07	1.9	3.2
Freundlich	k	3.17	4.62	5.51	k	2.39	3.24	3.20
	n	7.72	4.02	5.92	n	15.2	8.41	11.0
	E(%)	1.06	2.06	0.90	E(%)	1.25	4.02	1.12
Sips	Q_m	3.89	24.0	24.5	Q_m	2.57	3.63	3.40
	b	5.51	0.243	0.288	b	22.8	11.9	26.6
	n	1.67	3.60	4.90	n	1.06	1.33	1.04
	E(%)	2.96	1.87	0.77	E(%)	3.79	2.17	6.84
D-A	r	1.31	1.70	1.57	r	2.08	2.72	1.56
	Wo	0.530E-3	0.588E-3	0.588E-3	Wo	0.336E-3	0.343E-3	0.335E-3
	$(1/E)^r$	2.399E-5	0.114E-6	0.258E-5	$(1/E)^r$	0.664E-4	0.375E-6	0.136E-5
	E(%)	0.88	1.22	1.07	E(%)	1.13	3.07	0.85

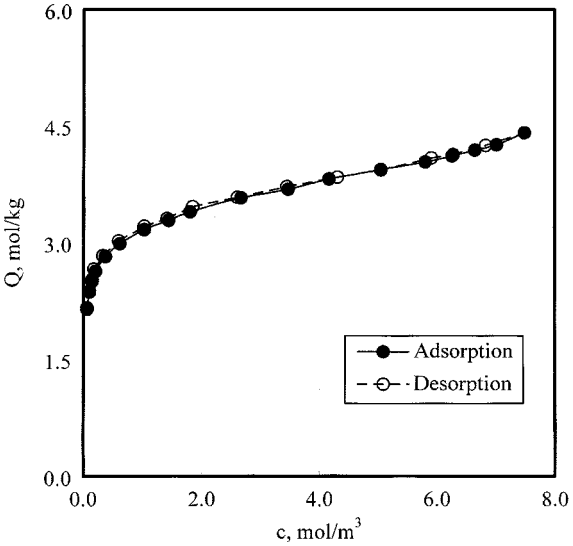

Fig. 9. Adsorption and desorption curves of n-hexane on SLG-2PS at 308.15 K.

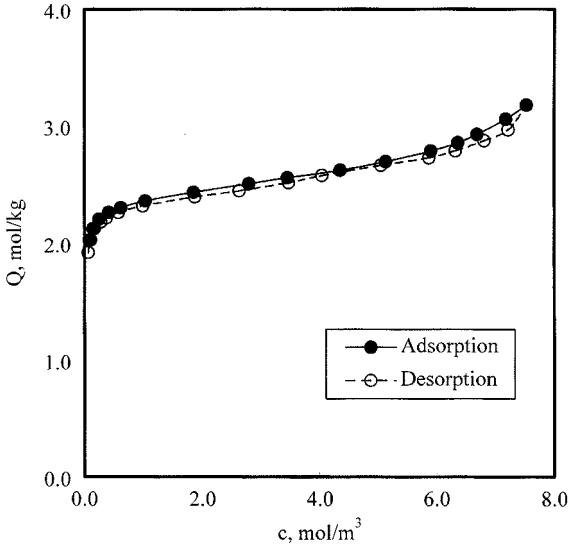

Fig. 10. Adsorption and desorption curves of n-hexane on X-7000 at 308.15 K.

experiments are required to get sufficient information for simulating and designing an adsorption column properly.

3. Adsorption Energy Distribution

In general, many researchers have assumed that the surfaces of adsorbents are energetically homogeneous in analyzing their adsorption data as a matter of convenience. However, this assumption cannot be true for real adsorbents. Since Langmuir [1918] himself suggested the surface heterogeneity, many studies have been done in order to obtain the adsorption energy distribution [Moon and Tien, 1988]. To get information on surface (namely energetical) heterogeneity of an adsorbent, one might use a distribution function and a local isotherm as well as adsorption equilibrium data. If the adsorption energy (ε) is distributed in the range of [0~∞], the overall adsorption isotherm can be obtained from [Rudzinski and Everett, 1994]

Table 4. Energy distribution parameters of solvents on SLG-2PS and X-7000

Adsorbent	Adsorbate	r	E(kJ/mol)
SLG-2PS	n-Hexane	1.31	20.0
	M.E.K	1.70	11.8
	Toluene	1.57	9.39
X-7000	n-Hexane	2.08	25.1
	M.E.K	2.72	17.8
	Toluene	1.56	29.6

$$\theta_T(T,P) = \int_0^\infty \theta_l(T,P,\varepsilon)\chi(\varepsilon)d\varepsilon \tag{7}$$

where $\theta_l(T, P, \varepsilon)$ is the local isotherm with an adsorption energy, ε, and $\chi(\varepsilon)$ is the adsorption energy distribution. When the local isotherm is represented by the D-A equation, the adsorption energy distribution can be obtained as a Gaussian type based on the condensation approximation approach [Rudzinski and Everett, 1994]. All parameters for the adsorption energy distributions are listed in Table 4.

$$\chi(\varepsilon) = \frac{r(\varepsilon-\varepsilon_0)^{r-1}}{E^r}\exp\left[-\left(\frac{\varepsilon-\varepsilon_0}{E}\right)^r\right] \tag{8}$$

Here E and r are the characteristic energy and exponent of the D-A equation. If the exponent is unity, the D-A equation stands for the Freundlich equation while r=2 means the Dubinin-Radushkevich (D-R) equation [Jaroniec and Madey, 1988]. In general, activated carbons with various pores have the value of r between 1 and 2. However some microporous carbons and zeolites have very large values of r, about 5 or 6. When the D-A equation is applied, the exponent represents the interaction between adsorbates and surface or the effect of pore structures on adsorption. As r increases, the adsorption energy distribution becomes uniform, which means energetically more homogeneous surfaces for a given adsorbate. According to the results in Table 4, X-7000 is likely to be energetically more homogeneous than SLG-2PS. Also one can see that SLG-

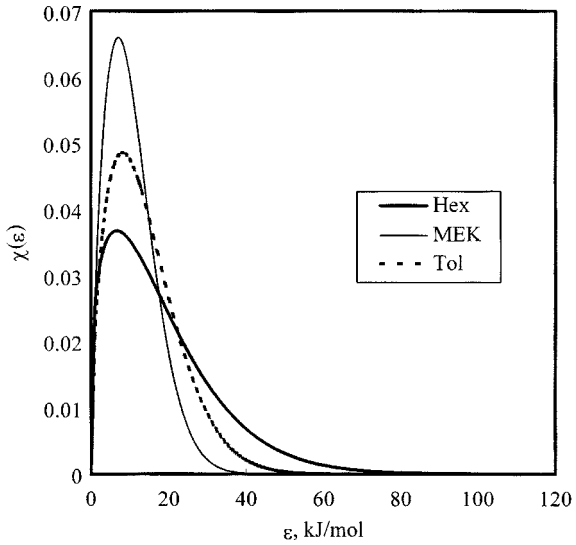

Fig. 11. Adsorption energy distribution for solvents on SLG-2PS at 308.15 K.

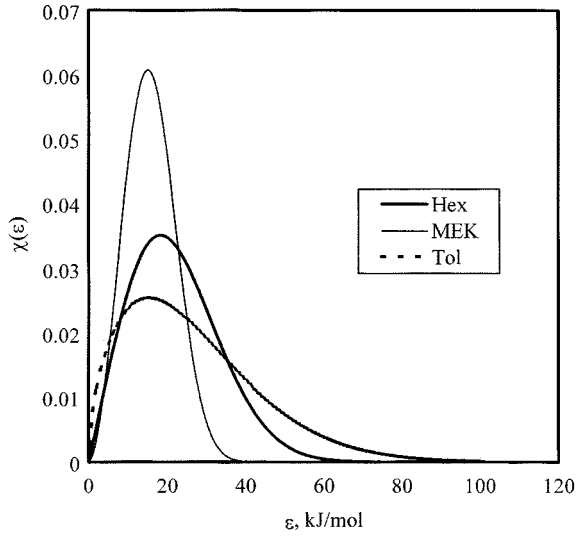

Fig. 12. Adsorption energy distribution for solvents on X-7000 at 308.15 K.

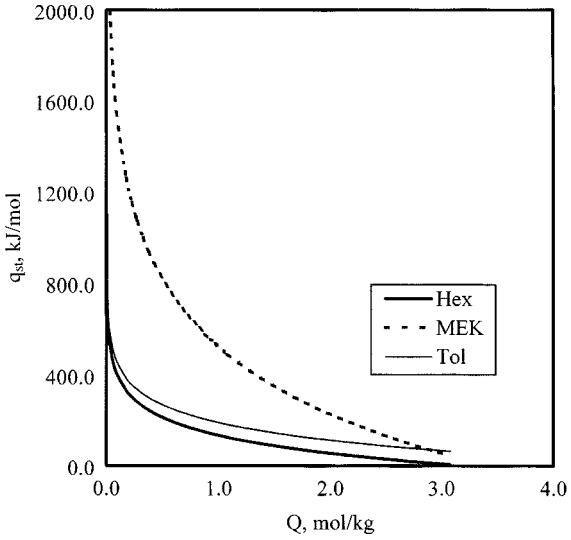

Fig. 14. Isosteric heat of adsorption for solvents on X-7000.

2PS has smaller adsorption energies but more skewed energy distributions than X-7000 for three solvents as shown in Figs. 11 and 12. This result may be related to their pore size distributions. It should be noted that even the Langmuir equation can fit equilibrium data of all solvent vapors on X-7000 reasonably well as shown in Table 3.

4. Heat of Adsorption

When an adsorbent adsorbs one or more adsorbates, adsorption heat is usually generated since all adsorption processes are exothermic. Eventually, the heat evolved affects the adsorption performance considerably. If the adsorption system was very ideal following the Langmuir isotherm, the heat of adsorption would be independent of the amount adsorbed. However, it would not be true for most adsorption processes because adsorbents have energetically heterogeneous surfaces as mentioned in the previous section. The isosteric heat of adsorption may be evaluated simply by applying the Clausius-Clapeyron equation if one has a good set of adsorption equilibrium data obtained at several temperatures [Ruthven, 1984].

$$\frac{q_{st}}{RT^2} = \left.\frac{\partial \ln\left(\frac{P}{P_S}\right)}{\partial T}\right|_Q \tag{9}$$

The isosteric heats of adsorption for three solvent vapors on X-7000 and SLG-2PS are shown in Figs. 13 and 14. Regardless of adsorbates, the heat of adsorption decreases almost exponentially with the adsorption amount since the Freundlich equation was used as the single-species isotherm. This result is quite natural since the adsorption occurs primarily on sites with higher energy. In Fig. 13, the magnitude of q_{st} is the order of toluene<n-hexane<MEK at lower concentrations but it becomes n-hexane<toluene<MEK at higher concentrations. The isosteric heats of adsorption on X-7000 are also shown in Fig. 14. Such reversal of q_{st} in terms of the amount adsorbed as shown in Fig. 13 will affect the adsorption dynamics of mixture adsorption.

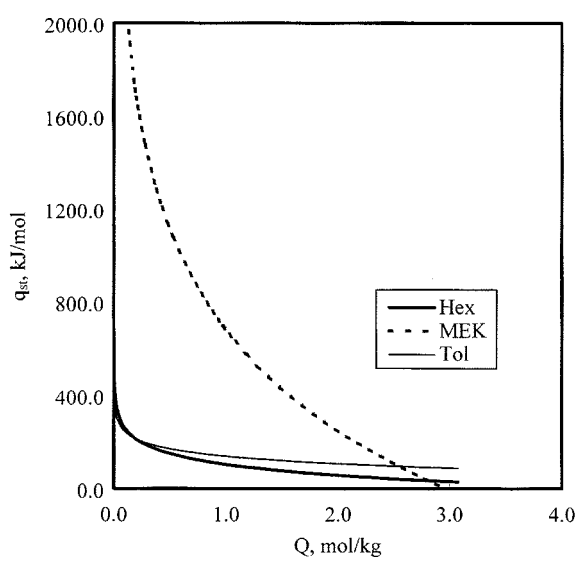

Fig. 13. Isosteric heat of adsorption for solvents on SLG-2PS.

CONCLUSIONS

The adsorption of three major solvent vapors such as n-hexane, toluene, and MEK, on two pelletized commercial activated carbons was measured by using a quartz spring balance equipped in a high vacuum system in order to assess those carbons for recovering solvent vapors from industrial effluents. Single-species adsorption data show typical type II isotherms. Equilibrium data measured at low relative pressures were fitted to four well-known isotherms. All experimental data were reasonably fitted with Freundlich, Sips, and D-A equations well. However, the Langmuir equation does not give good results for SLG-2PS since the activated carbon has energetically more heterogeneous surfaces. According to adsorption-desorption experiments, the activated carbons show the second-type hysteresis, implying that they have inkbottle or slit type pores.

The adsorption energy distribution of each solvent vapor on the carbons was evaluated from the D-A equation based on the condensation approximation approach. The exponent of the D-A equation varied from 1.31 to 2.72, showing the typical character of ac-

tivated carbon with various pores. However, the exponent values on X-7000 are larger than those on SLG-2PS. From this result, one may conclude that X-7000 is more homogeneous than SLG-2PS. Considering that the solvent recovery employs a cyclic adsorption-desorption operation, X-7000 with homogeneous adsorption energy seems to be more plausible than SLG-2PS even if the adsorption capacity is somewhat low. In future studies, the working capacity should be measured in a packed-bed adsorber to confirm this conclusion. Furthermore, the isosteric heat of adsorption was also evaluated from the Freundlich equation using the Clausius-Clapyron equation. Therefore, the heat of adsorption exponentially decreases with the amount adsorbed, regardless of adsorbates and carbons. It should be noted that the isosteric heats of adsorption of three solvent vapors were reversed at a certain amount adsorbed. This phenomenon can give important clues for surface heterogeneity and adsorbate-adsorbate interaction relating to adsorption. This result will be rigorously applied in simulating the adsorption dynamics in the future.

ACKNOWLEDGEMENT

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NOMENCLATURE

A : defined in Eq. (5)
b : isotherm parameter in Langmuir and Sips equations [m^3/mol, $(m^3/mol)^{1/n}$]
c : vapor-phase concentration [mol/m^3]
E : characteristic energy in D-A equation [J]
E(%) : object function or average deviation defined in Eq. (6)
K : isotherm parameter in Freundlich equation [$(m^3/mol)^{1/n}$]
N : number of components
n : exponent parameter in Freundlich and Sips equations
P : gas pressure [mmHg]
P_s : saturated pressure [mmHg]
Q : amount adsorbed [mol/kg]
Q_{cal} : calculated amount adsorbed [mol/kg]
Q_{exp} : experimental amount adsorbed [mol/kg]
Q_m : monolayer amount adsorbed [mol/kg]
q_{st} : isosteric heat of adsorption [J/mol]
R : gas constant [J/K mol]
r : exponent in D-A equation
T : absolute temperature [K]
W : adsorbed volume [m^3]
W_0 : parameter in D-A equation [m^3]

Greek Letters

ε : adsorption energy [J/mol]
ε_0 : reference adsorption energy [J/mol]
χ : adsorption energy distribution
q_l : local adsorption isotherm
θ_T : overall adsorption isotherm

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