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The Adsorption Equilibria of Organic Vapors on Activated Carbon at High Temperatures

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Synopsis. Nitrogen gas containing organic vapor was introduced into a column packed with activated carbon at high temperatures up to 200 °C, and the amounts of the solvents adsorbed were measured. The adsorption equilibrium data for single- and bi-component systems could be correlated by the Freundlich and extended Freundlich isotherms respectively.

The measurement of the adsorption equilibrium is very important to understanding the basic adsorption and desorption characteristics of organic vapor on activated carbon. For example, the vapor in the work environment is collected using a charcoal tube and the amount adsorbed is measured by a thermal desorption method to determine the vapor concentration, the equilibrium data at the desorption temperature are necessary to estimate the thermal desorption efficiency. Although many kinds of organic compounds are used as solvents in work places, there are very few data available on organic vapor-activated carbon systems at high temperatures, because the desorption has usually not been carried out by the thermal-desorption method, but by an extraction method using a harmful organic desorbent such as carbon disulfide.[1] In particular, we have not found out any data for a multicomponent organic vapor system, although most of the organic solvents used in work places are multicomponent ones.

In this paper, we measured the adsorption equilibria of single- and bi-component organic vapor-activated carbon systems at high temperatures up to 200 °C and correlated the data using Freundlich and extended Freundlich isotherms.

Experimental

The adsorption column is made by using a Pyrex glass tube (4 mm in inner diameter), which is inserted into a brass block heated by a band heater. Organic vapors were obtained by means of a generator developed by the authors.[2] PCB Pittsburgh activated carbon (Calgon Co., 12/30 mesh), which is commonly used for the measurement of organic vapor in a work environment, was used as the adsorbent. Before the experiments, the carbon particles were heated at 250 °C for 24 hours under a nitrogen gas flow. The column temperature was measured by the use of a thermocouple and was controlled within ±0.5 °C by means of a relay-controller and a temperature-regulator.

One hundred milligrams of activated carbon particles were put into the heated column, and then pure nitrogen gas was introduced. After steady-state conditions had been obtained, the gas was changed to nitrogen gas containing organic vapor. A part of the column outlet gas was sampled periodically by the use of an auto-gas sampler (Gasukuro Kogyo, GS-5000A), while the vapor concentrations were determined by the use of a gas chromatograph (CC, Shimadzu GC-6A) equipped with a flame-ionization detector. After carbon particles had been recognized from the breakthrough curve as being fully saturated with the solvents, the particles were put into a vial and 2 ml of carbon disulfide was added. After having been kept for about 1 hour to insure the desorption of the adsorbed solvents, a part of the solution was injected into the GC and the amount adsorbed was determined.

Results and Discussion

Single-Component System. Figure 1 shows a Freundlich plot of toluene at various temperatures. The data are expressed by the following Freundlich equation:

$$q = A\, C^{\beta} \tag{1}$$

where C is the vapor concentration, q is the adsorption capacity in equilibrium with C per unit of weight of the activated carbon (equilibrium adsorption capacity), and A and β are constants. The equilibrium adsorption capacity decreased, and the value of β increased with the increase in the temperature. These findings show that the effect of the temperature on the adsorption capacity becomes larger at lower vapor concentrations. Figure 2 shows the isotherms for benzene, toluene, *o*-xylene, and methyl isobutyl ketone (MIBK) at 200 °C. They are commonly used in work places as solvents, but their thermal-desorption efficiencies are relatively low.[3] The experimental data can also be expressed by the Freundlich isotherm.

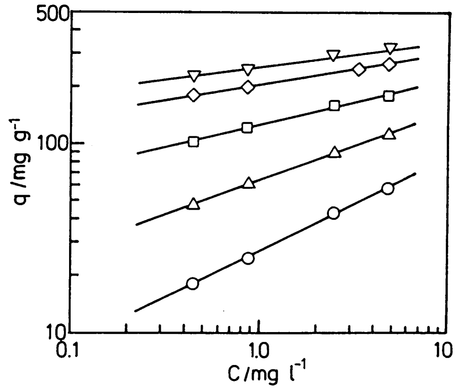

Fig. 1. Adsorption isotherm of toluene. ○: 200 °C, △: 150 °C, □: 100 °C, ◇: 50 °C, ▽: 25 °C.

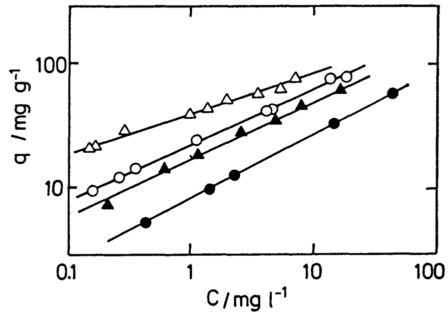

Fig. 2. Adsorption isotherm of organic solvent vapors on activated carbon at 200 °C. ○: toluene; $q=22.5C^{0.45}$, ●: benzene; $q=7.90C^{0.53}$, △: *o*-xylene; $q=42.0C^{0.35}$, ▲: MIBK; $q=17.7C^{0.47}$.

The equilibrium adsorption capacity depends on the adsorption affinity, which is itself dominated by the van der Waals force,[4] but it is difficult to obtain the quantitative relationship between the kind of material and the equilibrium adsorption capacities. In our experiment, the component which had the higher saturation vapor pressure tended to have the smaller adsorption capacity. The reason for this is that the higher vapor-pressure component is hard to condense in the pores of the adsorbent. As the saturate vapor pressure depends greatly on the temperature, the adsorption capacity may also be decreased with the temperature, as is shown in Fig. 1.

Bi-Component System. Figures 3 and 4 show the Freundlich plots of the MIBK-*o*-xylene system at 200 °C. The isotherms are shown as convex curves except when the vapor concentration of the co-adsorbed component is zero. This result indicates that the effect of the vapor concentration of the co-adsorbed component becomes larger as the vapor concentration of one component decreases. The equilibrium adsorption capacity of MIBK remarkably decreased with the increase in the *o*-xylene concentration, but the effect of MIBK on the adsorption capacity of *o*-xylene was small. The reason for this is that the MIBK which was adsorbed on activated carbon was easily desorbed and replaced by *o*-xylene because the adsorption affinity of MIBK is weaker than that of *o*-xylene, as can be predicted from the fact that the saturate vapor pressure of MIBK is larger than that of *o*-xylene.

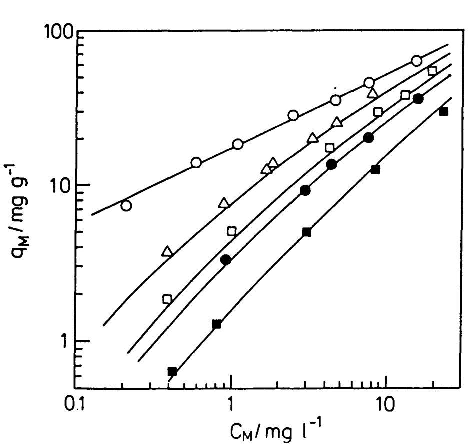

Fig. 3. Adsorption isotherm of MIBK for MIBK(M)-*o*-xylene(X) system at 200 °C. ○: *o*-xylene concentration=0.0 mg l⁻¹, △: 0.55 mg l⁻¹, □: 2.2 mg l⁻¹, ●: 3.9 mg l⁻¹, ■: 14.9 mg l⁻¹, solid line: estimated by Eq. 2 and Table 1.

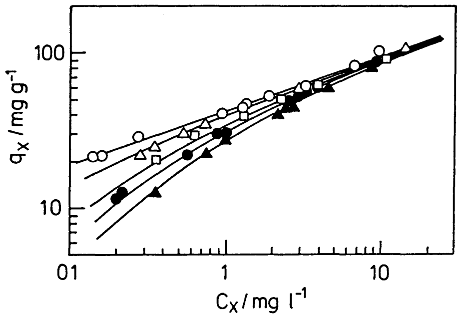

Fig. 4. Adsorption isotherm of *o*-xylene for MIBK-*o*-xylene system at 200 °C. ○: MIBK concentration=0.0 mg l⁻¹, △: 0.9 mg l⁻¹, □: 4.3 mg l⁻¹, ●: 7.0 mg l⁻¹, ▲: 12.5 mg l⁻¹, solid line: estimated by Eq. 2 and Table 1.

As the Freundlich isotherm could be applied to the adsorption equilibrium data for the single-component system, we tried to correlate the bi-component adsorption equilibrium data using the following Freundlich isotherm empirically extended.

$$q_1=\frac{A_1C_1^{\beta_1}}{C_1^{\alpha_1}+B_1C_2^{\gamma_1}}\ ,\qquad q_2=\frac{A_2C^{\beta_2}}{C_2^{\alpha_2}+B_2C_1^{\gamma_2}} \tag{2}$$

where A_i, B_i, α_i, β_i, and γ_i (i=1, 2) are constants, and where C_1 and C_2, and q_1 and q_2 are the vapor concentrations and the equilibrium adsorption capacities of Components 1 and 2 respectively. In this paper, Component 1 is the weaker-adsorption-affinity component.

The parameters in Eq. 2 could be determined by Fritz and Schlüender's method.[5] Table 1 shows the values of these parameters for several systems. The values of A_1 and A_2, and $\beta_1-\alpha_1$ and $\beta_2-\alpha_2$, are the same as those of A and β in Eq. 1 respectively. The second term of the denominator indicates the effect of the co-adsorbed component. When the vapor concentration of one component is small, the second term is neglected and Eq. 2 is reduced to Eq. 1. We can know the relative strength of the adsorption affinity from the ratio of B_1 to B_2. Usually, B_1 is larger than B_2, for the effect of C_2 on q_1 is larger than that of C_1 on q_2, but if the adsorption affinities of both components

Table 1. Parameters of the Extended Freundlich Isotherm

	B-T		T-X		M-X	
i	1	2	1	2	1	2
α_i	0.74	0.47	0.50	1.55	0.66	0.79
β_i	1.27	0.92	0.95	1.90	1.13	1.14
γ_i	0.72	0.49	0.86	1.64	0.62	0.82
A_i	7.90	22.5	22.5	42.0	17.7	42.0
B_i	1.36	0.242	1.80	0.055	1.91	0.068

B: benzene, T: *o*-toluene, X: *o*-xylene, M: MIBK.

are almost the same, B_1 may be close to B_2. The lines estimated by means of Eq. 2 and Table 1 are also shown in Figs. 3 and 4. They were in good agreement with the experimental data.

Equations 1 and 2 are empirical equations. However, as the form of these equations are simple, they can be used to estimate the thermal desorption efficiencies of organic solvents from activated carbon. These equations should thus prove useful in future investigations.

References

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