NOTES

BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 51 (6), 1883—1884 (1978)

Calorimetric Phenomena of Methanol Adsorption on Active Carbon

Ryoichi Tsunoda and Yoshiyuki Fukazawa
Industrial Research Institute of Kanagawa Prefecture, Showa-machi, Kanazawa-ku, Yokohama 236

(Received October 5, 1977)

Synopsis. The heats of immersion in methanol of active carbon which preadsorbed methanol from the vapor phase at a given equilibrium pressure were measured. The calorimetric phenomena of methanol adsorption on active carbon were interpreted by comparing them with the distribution of the adsorption potential of methanol on active carbon.

The adsorption of gas on active carbon is accompanied by exothermic and/or endothermic phenomena. However, the direct measurement of the calorimetric phenomena on the gas adsorption is difficult without employing a specific calorimeter for solid-gas measurements. In this study, the calorimetric phenomena of methanol adsorption on active carbon have been measured by means of a conventional calorimeter (for solid-liquid) and the observed heats of immersion have been interpreted by comparing them with the distribution of the adsorption potential of methanol on active carbon.

In a spherical Pyrex glass tube, about 12 mm in diameter, *ca.* 200 mg of commercially available Pittsburgh SGL-type active carbon, dried overnight at 110 °C, was outgassed at a pressure of 10^{-6} Torr at 30 °C for 14 h by means of a conventional adsorption apparatus, while the adsorption of methanol at a given pressure was carried out at 30 °C. After 45 min of methanol adsorption, the Pyrex glass tube was sealed. The sample was then subjected to the measurement of the heat of immersion in methanol at 30 °C by means of a twin-type calorimeter manufactured by Oyo Denki.

The adsorption isotherm,[1] the characteristic and distribution curves of the adsorption potential,[1] and the heats of immersion in methanol of active carbon which preadsorbed methanol from the vapor phase are shown in Figs. 1—3 respectively.

The net-heat of adsorption corresponding to the coverage of the monolayer was calculated from the adsorption isotherm using the BET equation:[2]

$$\frac{P/P_0}{V(1-P/P_0)}=\frac{1}{V_mC}+\frac{(C-1)P/P_0}{V_mC}, \tag{1}$$

where $C=\exp\,[(E_1-E_L)/RT]$ is the BET constant; E_1, the mean heat of adsorption in the first adsorption layer; E_L, the heat of condensation; E_1-E_L, the so-called net heat of adsorption corresponding to the coverage of the monolayer; V, the amount adsorbed at the relative pressure of P/P_0, and V_m, the monolayer capacity. The calculated parameters in the BET equation are shown

Table 1. Parameters in the BET equation

Active carbon	C[a]	E_1-E_L[b] (cal/mol)	V_m[c] (cm^3/g)
SGL	12.6	1527	0.320

a) The BET constant. b) The net-heat of adsorption corresponding to the coverage of the monolayer. c) The monolayer capacity.

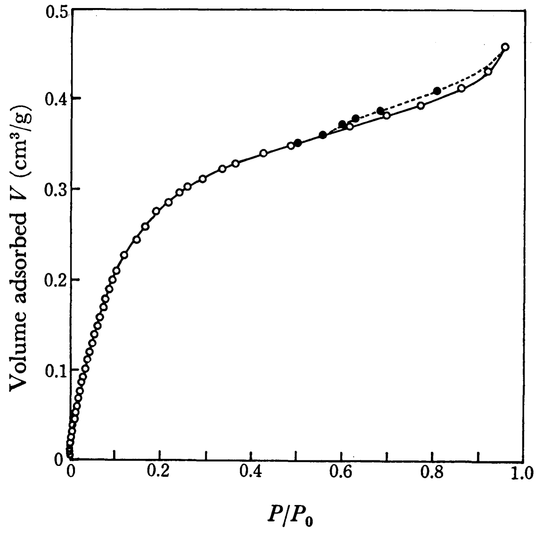

Fig. 1. Adsorption isotherm of methanol on SGL-type active carbon at 30 °C.[a)]
Filled symbols indicate desorption. a) Ref. 1.

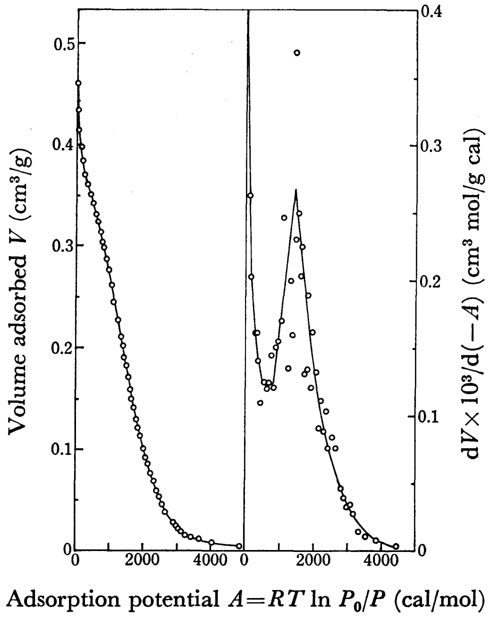

Fig. 2. Characteristic and distribution curves of adsorption potential of methanol on SGL-type active carbon at 30 °C.[a)] a) Ref. 1.

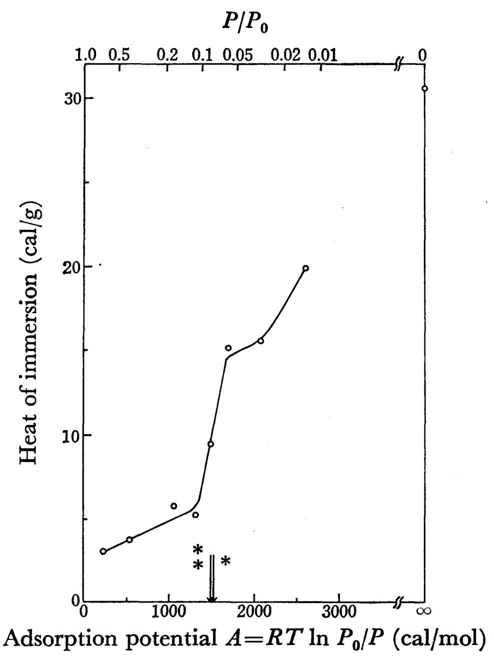

Fig. 3. Heat of immersion in methanol of SGL-type active carbon which preadsorbed methanol from the vapor phase at 30 °C.

The adsorption potential ($A=RT \ln P_0/P$) corresponds to the equilibrium partial pressure (P/P_0) at which the adsorption of methanol on active carbon was carried out at 30 °C. The heat of immersion in methanol of active carbon which preadsorbed methanol from the vapor phase was measured at 30 °C.

*: The adsorption potential corresponding to the net-heat of adsorption for the monolayer coverage.

⁑: The adsorption potential corresponding to that at $dV/d(-A)$=maximum.

in Table 1.

The observed heats of immersion showed a drastic decrease at the adsorption potential ($A=RT \ln P_0/P$) corresponding to the net-heat of adsorption (1527 cal/mol) for the monolayer coverage (see Fig. 3). However, the BET constant, C, obtained form a simple fitting of the BET equation to the adsorption isotherm reflects only the average energy parameter of adsorption sites being filled in the region of the fitting, *i.e.*, usually in $0.05<P/P_0<0.3$.[3] Therefore, the so-called net-heat of adsorption, E_1-E_L, 1527 cal/mol, calculated from the value of C may also reflect the average energy of the net-heat of adsorption.

Meanwhile, the adsorption potential at the point of the drastic decrease in the heats of immersion corresponds also to the adsorption potential (*ca.* 1470 cal/mol) at $dV/d(-A)$=maximum on the distribution curve of the adsorption potential, as is shown in Fig. 2. The adsorption potential at 1470 cal/mol is equivalent to $P/P_0=0.0872$, indicating the adsorption volume of 0.195 cm^3/g, on the adsorption isotherm in Fig. 1. The adsorption volumes corresponding to the adsorption potentials at the * and ⁑ marks in Fig. 3 are 0.181 and 0.195 cm^3/g respectively; therefore, the volume of methanol preadsorbed on active carbon, the drastic decrease of which in the heats of immersion is shown in Fig. 3, corresponds to a little more than half of the monolayer capacity of active carbon.

The observed heat of immersion in Fig. 3 corresponds to the heat of immersion of the uncovered part of the surface of the active carbon with methanol, although, strictly speaking, the observed calorimetric phenomena are accompanied by the heat of condensation of methanol adsorbed on the surface of carbon, and the decrease in the heat of immersion is proportional to the surface free-energy lowering. Moreover, taking into consideration the fact that the adsorption mechanism expressed in the relationship between $dV/d(-A)$ and A is changed at about 61% of the monolayer capacity of methanol adsorption, the observed lowering of the surface free energy seems to be due to the change in the adsorption state, *e.g.*, the change in the geometrical structure of the adsorbed methanol molecules.

References

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3) L. M. Dormant and A. W. Adamson, *J. Colloid Interface Sci.*, **38**, 285 (1972).