New Aspects of Wetting Transition Shown by the Precision Measurement of Adsorption Equilibrium Pressures: Kr and C₂H₄ on Exfoliated Graphite

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Thermodynamical properties of thick physisorbed layers have been investigated by various experimental techniques in connection with the phenomena of wetting, roughening, and melting of surface¹⁾. Of particular interest in this field is the way in which a physisorbed layer changes its two-dimensional characteristics into three-dimensional or bulk characteristics. It is believed that there are three types of growth mode in multilayer films: complete wetting, incomplete wetting, and nonwetting. The complete wetting phenomenon corresponds to the case of layer-by-layer condensation up to the infinite thickness of films. For example, multilayers of Ar, Kr, and Xe on a graphite substrate are believed to be the typical case of complete wetting in a certain temperature range. On the other hand, incomplete wetting and nonwetting phenomena correspond to the case of layer-by-layer condensation up to a finite thickness and the case of growth in which an adsorbate indicates the three-dimensional characteristics from the beginning of adsorption, respectively. The layers of Ne, He, O₂, CO₂, CH₄ and C₂H₄ on a graphite substrate are known as the systems exhibiting incomplete wetting or nonwetting. Some adsorbate-substrate systems exhibit a transition from incomplete wetting at lower temperatures to complete wetting at higher temperatures. This phenomenon is called the "wetting transition". The first experimental evidence for the wetting transition in a physisorbed film was demonstrated for C₂H₄ adsorbed on graphite²⁾. At temperatures above the bulk triple point (104 K) of C₂H₄, the equilibrium pressure p_{eq} of an adsorbed film asymptotically approaches the bulk vapor pressure p_0 as its thickness increases. On the other hand, at the lower temperatures, p_{eq} reaches p_0 at a finite

thickness: a limited number of C₂H₄ layers can adsorb before bulk condensation. This type of phase transition is known as triple-point wetting. However, the detailed behavior of p_{eq} in the vicinity of p_0 has not been clarified yet, mainly because of the difficulty in the p_0 determination.

We report here the result of adsorption equilibrium measurements for Kr and C₂H₄ films on exfoliated graphite in the pressure range very close to the saturation vapor pressure p_0 of each gas. We have been investigating the thermodynamical behavior of thick adsorbed films which are known to represent complete wetting or incomplete wetting^{3,4)}. It is one of the most promising means for this purpose to examine the adsorption isotherms and isosteres which are obtained by the precise measurement of an equilibrium pressure p_{eq} ⁵⁾. We use a double-cell system for the purpose of the precise measurement of a difference between p_{eq} and p_0 , the details of which, as well as the experimental procedures, have already been published^{3,4)}. Kr or C₂H₄ gas was adsorbed on a graphite specimen in an adsorption cell while the bulk solid or liquid of that gas was being formed on the wall of a reference cell kept precisely at the same temperature. Direct comparison between the pressures of two cells made the determination of p_{eq}/p_0 free from the errors arising from the temperature difference and the thermal transpiration effect. The temperature difference between the two cells was 2 ± 3 mK, which was estimated from the measurement of the pressure difference when both cells were filled up with bulk Kr. This temperature difference corresponds to a relative error $\Delta(p_{eq}/p_0)$ of about 5×10^{-4} or less. The adsorption cell was filled with 3.94 g of exfoliated graphite (Grafoil MAT, Union Carbide). The

Fig. 1 Adsorption isotherms of Kr on Grafoil MAT for $80\text{ K} < T < 125\text{ K}$ and $4\text{ mmol} < n < 20\text{ mmol}$. T is the temperature of the cell and n is the amount of adsorption. The measured value $\ln(p_{\text{eq}}/p_0) \sim (p_{\text{eq}} - p_0)/p_0$ is plotted against $1/T$.

Fig. 2 Adsorption isotherms of Kr on Grafoil MAT for $90\text{ K} < T < 125\text{ K}$ and $10\text{ mmol} < n < 50\text{ mmol}$.

research-grade Kr gas and C_2H_4 gas (99.999% and 99.99% of nominal purity, respectively) were further purified by several freeze-evacuation cycles in the gas handling system. The double-cell and the gas handling system were baked up to 400 K before each run to remove impurities, mainly water, which might be accumulated on Grafoil.

The adsorption isotherms of Kr on Grafoil MAT are shown in **Fig. 1** for $80\text{ K} < T < 125\text{ K}$ and $4\text{ mmol} < n < 20\text{ mmol}$ and in **Fig. 2** for $90\text{ K} < T < 125\text{ K}$ and $10\text{ mmol} < n < 50\text{ mmol}$, where $\ln(p_{\text{eq}}/p_0)$ is plotted against $1/T$ and where T is the temperature of the cell and n is the amount of ad-

sorption. **Figure 3** shows the adsorption isotherms of C_2H_4 on Grafoil MAT for $90\text{ K} < T < 120\text{ K}$ and $1\text{ mmol} < n < 28\text{ mmol}$, where $p_{0\text{liq}}$ is the bulk saturation vapor pressure in the liquid state. At temperatures below the bulk triple point T_t , the value $p_{0\text{liq}}$ was calculated by the extrapolation from the value at $T > T_t$. The solid line in the figure shows the vapor pressure of the bulk solid. The direct comparison between p_{eq} and p_0 revealed several new characteristics of thick physisorbed films.

The equilibrium pressure p_{eq} of C_2H_4 never reaches p_0 nor a certain saturated value even at a

Fig. 3 Adsorption isosteres of C_2H_4 on Grafoil MAT for $90 \text{ K} < T < 120 \text{ K}$ and $1 \text{ mmol} < n < 28 \text{ mmol}$, where p_{0liq} is the bulk saturation vapor pressure in the liquid state. The saturation vapor pressure of the bulk solid p_0 is given by the solid line.

temperature far below the bulk triple point where C_2H_4 has been believed to wet a graphite substrate incompletely. According to the original idea of triple-point wetting, an adsorbed film keeps its two-dimensional property just below T_t and changes to three-dimensional (bulk) one when the equilibrium pressure of two-dimensional or liquidlike adsorbate reaches the vapor pressure of the bulk solid. The 2d-3d transition occurs, in other words, at the intersection of the bulk solid line and the isostere line that is extrapolated from the region at $T > T_t$. However, the present result shows the bending of the isosteres at the temperatures slightly below T_t which depend on the film thickness and which are shown as the dashed line in Fig. 3. In the right side of the dashed line, p_{eq} still depends on the thickness of the film and approaches p_0 asymptotically as the thickness increases.

The slope of the adsorption isostere shown in Figs. 1-3 corresponds to the difference between the latent heat of bulk condensation and the isosteric heat of adsorption. The isosteres are almost

Fig. 4 Plot of $\ln[-\ln(p_{eq}/p_0)]$ against $\ln(n)$ for Kr on Grafoil. The dashed line shows the slope of $-3/2$.

parallel to the bulk vapor line in the right side of the dashed line in Figs. 1 and 3. In this region, the film is thought to have a bulklike structure, as the isosteric heat of adsorption is nearly equal to the bulk value. It has been believed that Kr shows no wetting transition at T_t and wets graphite completely even at a temperature below T_t . However, from the point of view of the isosteric heat of adsorption, a Kr film seems to have a bulklike structure as presented in Fig. 1. The reason why p_{eq} does not reach p_0 in such a region may be some effect of the capillary condensation.

In the adsorption isosteres, sharp discontinuities at the bulk triple point T_t and gradual changes around T_t were observed. Such discontinuities around T_t have already been noticed in the case of ethylene on graphite⁴⁾. Although the origin of the discontinuity, as well as the change in the slope of isosteres around T_t , has not been clarified yet, they may relate to the reentrant phenomena, that is, the structure change in the underlying layers⁶⁾.

For both Kr and C_2H_4 on Grafoil, the value $\Delta p_{eq}/p_0 (=1-p_{eq}/p_0)$ is smaller than 0.05 for the amount of adsorption n larger than 10 mmol (~ 10 atomic layers). However, p_{eq} never reaches p_0 and

Fig. 5 Plot of $\ln[-\ln(p_{eq}/p_0)]$ against $\ln(n)$ for C_2H_4 on Grafoil.

approaches p_0 gradually and continuously as n increases. The relation between p_{eq}/p_0 and n , namely, the manner in which an adlayer approaches the bulk state with the increase in thickness, is usually represented by the Frenkel-Halsey-Hill formula^{7,8)},

$$RT \ln \frac{p_{eq}}{p_0} \propto -n^{-x},$$

where R is the gas constant. According to the model of F-H-H for a liquidlike adlayer on a homogeneous and flat surface, the exponent x is equal to 3. Figures 4 and 5 show the plot of $\ln[-\ln(p_{eq}/p_0)]$ against $\ln(n)$ for several values of

T for Kr and C_2H_4 on Grafoil, respectively. The slope of the curves in the figures gives the exponent $-x$ in the F-H-H formula. Although the tangent of their curves is found to depend on the temperature and the film thickness, the value of x , on an average in the range of the measurement, is nearly equal to 3/2 rather than 3 in the F-H-H model. It can, however, be pointed out that the value x is nearly 3 in the range of n from 3 mmol to 10 mmol and T above 110 K for Kr on Grafoil (Fig. 4), where the layer-by-layer growth of a liquidlike film should be expected. The deviation of the exponent x from 3 should be discussed in connection with the following two factors: (1) capillary condensation, in which a relatively strong and long-range attractive force between the substrate and the Kr and C_2H_4 adsorbates can be expected because of the geometry of the exfoliated graphite, (2) the geometry of the surface of adsorbed film itself, which should be closely related to the nonwetting or surface roughening phenomena.

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