The Adsorption of Chloromethanes on KCl. The Role of the Surface Ions as Adsorption Sites

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The adsorbed amounts of chloro-substituted methanes, such as CH_2Cl_2, $CHCl_3$, and CCl_4, for KCl particles were measured by a volumetric method at various temperatures, and the isosteric heats of adsorption and differential entropies of the adsorbed molecules were estimated from the adsorption isotherms. The order of magnitude of the heats of adsorption at a coverage of $\theta=0.5$ was found to be $CH_2Cl_2>CHCl_3>CCl_4$. Moreover, a plot of the dipole moments of the three adsorbates *vs.* the adsorption heat values gave a straight line. Therefore, the differences among the adsorption heats of the three adsorbates is mainly caused by an orientation of their dissimilar dipoles to the surface. It may be concluded that the chloro-substituted methanes are adsorbed on surface anions of KCl powder.

Alkali halide crystals are used as adsorbents to investigate various adsorption phenomena, because of their simple surface structure and a regular configuration of the surface ions. Many theoretical calculations have been carried out about the heats of adsorption of nonpolar gasses on alkali halides.[1-3] On the other hand, in cases of polar substances, such heat calculations have been made for only a few systems,[4] and the subjects concerning adsorption sites, *i.e.* the role of surface ions in their adsorptions has not yet been resolved.

In the present study, the adsorbed amounts of chloro-substituted methanes, such as $CHCl_3$, CH_2Cl_2, and CCl_4, on KCl particles were measured at various temperatures, and the isosteric heats of adsorption and the differential entropies of the adsorbed molecules were calculated from the adsorption isotherms obtained. The adsorption characteristics of chloro-substituted methanes are discussed in relation to the dipole moments and the cross-sectional areas of the polar adsorbates.

Experimental

Materials. Potassium chloride was purified by twice recrystallization of special-grade reagents using distilled water. An aqueous solution of KCl was added to about a five-fold volume of ethanol cooled to −80—−90 °C with stirring. The sample thus obtained was filtered and washed four times with absolute ethanol and then dried at a reduced pressure of 1.33×10^{-1} Pa. This precipitate was found to be very small cubic crystals (≈5 μm) by electron microscopy. The sample was evacuated with an oil diffusion pump under a reduced pressure of 1.33×10^{-4} Pa for 20—30 h at room temperature prior to the adsorption measurements. The three adsorbates were purified by twice distillation of the respective special-grade reagents, and their purities were confirmed to be apporoxymatly 100% by gas chromatography.

Adsorption Measurement. The apparatus for measuring adsorbed amounts was reported previously by the present authors.[5] The equilibrium pressures of the adsorbates were determined using a mercury manometer and a reading magnifier with a resolution of 10 μm.

Surface Area Measurement. The specific surface areas of the samples were determined prior to the adsorption measurements of the chloro-substituted methanes by applying the BET equation to the nitrogen-adsorption data obtained at 77 K, assuming the cross-sectional area of a nitrogen molecule to be 16.2 Å². The obtained values were about 0.21 m²/g.

Results and Discussion

Adsorption Isotherms. The adsorption isotherms of CH_2Cl_2 on KCl are given in Fig. 1. In this case, a linear BET plot was not obtained in the BET region. On the other hand, the adsorption isotherms at adsorbed amounts above 0.13 cm³ STP/m² gave a straight line with increasing pressure, and the point "B" showing a monolayer completion was determined easily. The capacity of the monolayer adsorption was estimated to be 0.13 cm³ STP/m². This value is slightly smaller than the monolayer capacity (0.15 cm³ STP/m²) which is calculated from the cross-sectional area (24.3 Å²) of CH_2Cl_2 and the surface area obtained by N_2 adsorption, assuming that the sample surface is covered with the close-packed monolayer. The cross-sectional area is estimated from the liquid density of CH_2Cl_2 at the measurement temperature. The relative vapor pressure at the point B was higher, compared with the values determined from the adsorptions of polar substances such as CH_3OH,[6] $(CH_3)_2CO$,[7] and H_2O.[8]

The isosteric heats of CH_2Cl_2 adsorption and the differential entropies of the adsorbed molecules are shown in Fig. 2. The latter values are calculated by Eq. 1, where $\overline{S}_s$, S_γ, and S_g are the differential entropy of the adsorbed molecule on KCl, molar entropies

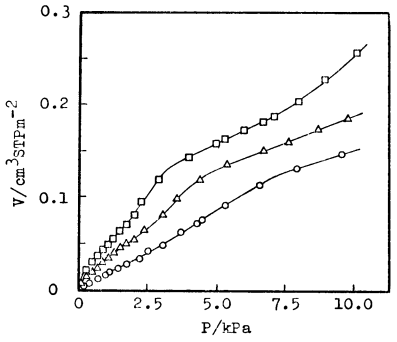

Fig. 1. Adsorption isotherms of CH_2Cl_2 on KCl. Temperature/°C: □: −6, △: 0, ○: 10,

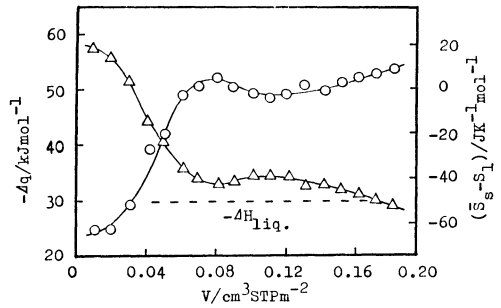

Fig. 2. Isosteric heat of CH_2Cl_2 adsorption and differential entropy of CH_2Cl_2 adsorbed on KCl. △: Isosteric heat of adsorption, ○: differential entropy.

of liquid adsorbate and vapor molecule, respectively, Λ is the heat of vaporization and x a relative vapor pressure.

$$(\bar{S}_s - S_1) = (\bar{S}_s - S_g) + \Lambda/T - R \ln x \quad (1)$$

The adsorption heat at low coverage was found to be large, but it decreased rapidly with adsorbed amounts. A peak was observed at $V=0.12$ cm³ STP/m². This value is nearly equal to the monolayer capacity described above. Therefore, the appearance of such a peak can be explained in terms of a lateral interaction among the adsorbed molecules. A slightly stepwise rise recognized in the isotherm before the monolayer completion may be also due to this lateral interaction.

On the other hand, the differential entropies obtained in the region of the adsorbed amount 0—0.06_5 cm³ STP/m² were smaller than the molar entropy of liquid CH_2Cl_2 at the measurement temperature, and at the adsorbed amounts above 0.06_5 cm³ STP/m² the entropy values were approximately equal to the molar entropy of liquid CH_2Cl_2. The former result shows that CH_2Cl_2 molecules are adsorbed strongly on the KCl surface and the mobility of the adsorbed molecules are restrained. Whereas, the latter fact indicates that the adsorbed molecules can move easily in the adsorbed layer as in liquid CH_2Cl_2. Figure 2 indicates a minimum at the monolayer completion in the entropy curve. Such change in the differential entropy corresponds to the existence of the lateral interaction described above.

Figure 3 shows the adsorption isotherms of $CHCl_3$ on KCl. The isosteric heat of $CHCl_3$ adsorption and the differential entropies of the adsorbed molecules are given in Fig. 4. The isotherms resembled in shape those obtained for the CH_2Cl_2 adsorption. A maximum was also recognized in the heat curve at about the monolayer completion ($V=0.11$ cm³ STP/m²). Therefore, it is considered that a lateral interaction will occur similarly as is shown in the case of CH_2Cl_2 adsorption. The differential entropies of adsorbed $CHCl_3$ at low coverage are larger than the molar entropy of liquid $CHCl_3$. This result is different from the case of CH_2Cl_2 adsorption.

The adsorption isotherms of CCl_4 on KCl are given

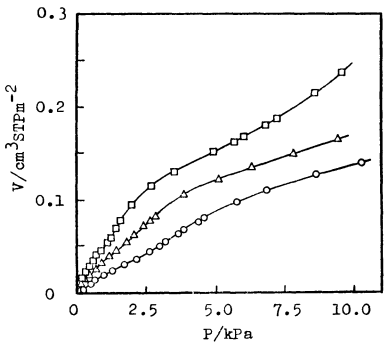

Fig. 3. Adsorption isotherms of $CHCl_3$ on KCl. Temperature/°C: □: 10, △: 20, ○: 30.

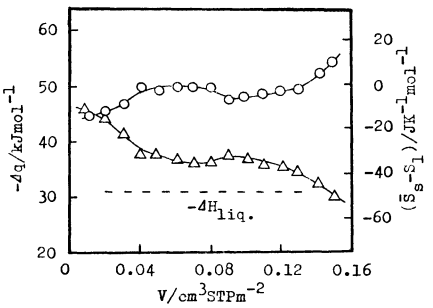

Fig. 4. Isosteric heat of $CHCl_3$ adsorption and differential entropy of $CHCl_3$ adsorbed on KCl. △: Isosteric heat of adsorption, ○: differential entropy.

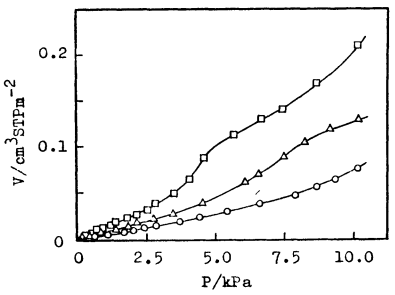

Fig. 5. Adsorption isotherms of CCl_4 on KCl. Temperature/°C: □: 20, △: 30, ○: 40.

in Fig. 5. The isotherms were classified into the BDDT III type, judging only from their profile in the early stage $V<0.1$ cm³ STP/m². However, the point B was determined at a high vapor pressure and the monolayer capacity was obtained. According to the BDDT classification, an interaction between the surface of a KCl particle and CCl_4 molecules will be weaker than those in cases of CH_2Cl_2 and $CHCl_3$ adsorptions. In Fig. 6 the isosteric heats of CCl_4 adsorption and the differential entropies of the adsorbed molecules are shown. The adsorption heats at low coverages were determined precisely in this case on account of the large equilibrium pressures. As is shown in Fig. 6, the adsorption heat value at adsorbed amounts below 0.01 cm³ STP/m² is higher than the liquefaction heat of CCl_4 vapor, but it becomes less

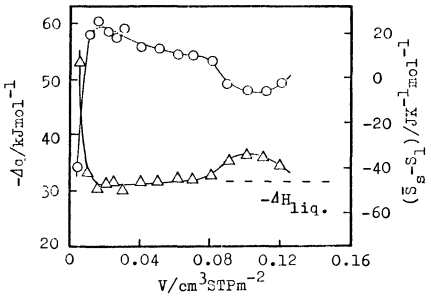

Fig. 6. Isosteric heat of CCl_4 adsorption and differential entropy of CCl_4 adsorbed on KCl.
△: Isosteric heat of adsorption, ○: differential entropy.

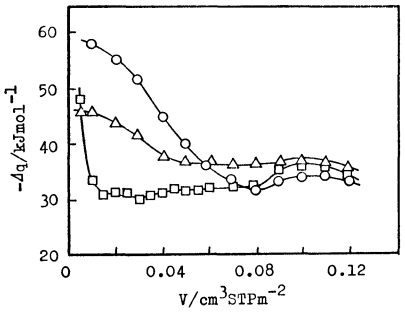

Fig. 7. Change in isosteric heat of adsorption with adsorbed amount.
○: CH_2Cl_2, △: $CHCl_3$, □: CCl_4.

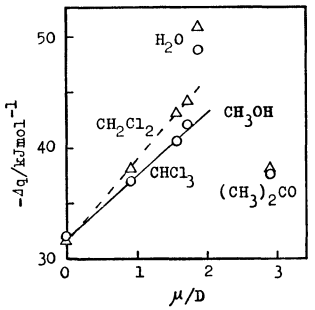

Fig. 8. Effect of dipole moment on isosteric heat of adsorption.
Coverage (θ): △: 0.4, ○: 0.5.

than the liquefaction heat at amounts above 0.01 cm^3 STP/m^2. The latter result indicates that the interaction between the KCl surface and CCl_4 molecules is weak as described above. Such estimation of the surface property is supported by the fact that the differential entropy of adsorbed CCl_4 is larger than the molar entropy of liquid CCl_4. Then the adsorption heat increased gradually with the increment of the adsorbed amount and a peak produced by the lateral interaction was observed in the heat curve at $V=0.11$ cm^3 STP/m^2. This value is equal to the monolayer capacity obtained from the isotherm. Moreover, the height of the peak was the largest among the three adsorbates. However, the differential entropy at the monolayer completion is less than the molar entropy of liquid CCl_4 and shows a minimum. From these results, the lateral interaction in CCl_4 adsorption is considered to be stronger than those of CH_2Cl_2 and $CHCl_3$ adsorptions. For the two polar adsorbates, if the molecules are adsorbed on the KCl surface orienting their dipole moments to the surface at the monolayer completion, the lateral interaction will decrease owing to the repulsive forces generated by the dipole moments which are parallel oriented. On account of this effect, the height of the peak observed in the heat curve is expected to diminish in CH_2Cl_2 and $CHCl_3$ adsorptions.

The large heat of adsorption observed in the early stage indicates the existence of active sites on the salt surface. The fraction of the active sites on the KCl surface for CCl_4 adsorption is estimated to be about 9% of the total sites. In the case of NaF prepared by the same method in the present study, Yao[9] concluded that 4% of the total surface is active from the comparison of adsorption characteristics of four polar substances he used. This fact shows that such an assessment concerning the active sites on KCl surface is reasonable.

Adsorption Mechanism. The heats of adsorption of the three adsorbates for KCl surface are, for convenience, repeatedly shown in Fig. 7. At low coverage, the adsorption heats of the chloromethanes differ considerably from each other and the value is influenced by the dipole moment of the adsorbate molecule. To clarify this point, the heats of adsorption of chloromethanes at coverages of 0.4 and 0.5 are plotted in Fig. 8 as a function of the dipole moments of the adsorbates. The other polar substances, $(CH_3)_2CO$, CH_3OH and H_2O, are also given in this figure. A linear relationship was found between the heats of adsorption and the dipole moments, expect for $(CH_3)_2CO$ and H_2O. The present authors have clarified already that one CH_3OH molecule is adsorbed on a surface anion of KCl particles,[6] whereas one $(CH_3)_2CO$ molecule is adsorbed on a surface cation conversely.[7] The adsorption heat value of CH_3OH was plotted in the straight line. However, in case of $(CH_3)_2CO$ adsorption where the mechanism is different from that of CH_3OH adsorption, the plot deviates greatly from linearity. Therefore, we conclude that the adsorption of chloromethanes on a KCl surface will occur by a similar mechanism to that proposed for CH_3OH adsorption. In other words, chloromethanes having dipole moments are adsorbed on the surface anions orienting their dipoles to the KCl surface. For H_2O adsorption one water molecule is adsorbed on two adjacent surface anions.[8] The plot of heat of H_2O adsorption also deviates from a straight line on account of the difference of the adsorptive mechanism. Considering these results, it will be concluded that the surface anions or cations play an important role in the adsorptions of polar substances on a KCl surface and that the adsorptive mechanisms largely depend on the molecular structures of the adsorbates used.

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