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Water Vapor Affinity of Potassium Bromide Coated with Potassium Oleate(1)

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The amounts of adsorbed water and the isosteric heats for water vapor adsorption on fine crystals of KBr treated with various amounts of potassium oleate (KOl) were measured. In the adsorption isotherm of untreated KBr, a slight stepped rise of the amount adsorbed was observed, and this step is considered to be due to the two-dimensional condensation of water molecules adsorbed on the uniform surfaces of KBr particles. The monolayer capacity, determined from the adsorption isotherm of KBr by the point B method, agreed with the value calculated according to an adsorptive structure based on the two assumptions that all the surfaces of the KBr particles consist of (100) planes and that one water molecule is adsorbed per regularly distributed Br^- site.

A small amount of pre-adsorbed KOl was recognized to prevent the water vapor adsorption on KBr, and conversely, this effect disappeared with increasing KOl content while the hygroscopicity of the sample increased markedly. This abnormal increase in the adsorbed amount suggests that the adsorbed water molecules penetrate into the multilayer films of KOl on the KBr.

In order to change the surface properties of powder particles, the surface is often modified by coating with some material such as surfactants. Studies of the effect of the coating on surface properties and of the mechanism of the coating are instructive in many powder industries. In the present paper, data of the water vapor adsorption isotherms and isosteric heats of adsorption on KBr powders coated with various amounts of potassium oleate (KOl) are described, and the relationship between the water vapor affinity of KBr and the KOl concentration, the amount adsorbed on the surface per unit KBr surface area, was investigated to clarify the surface properties of the bromide. These experimental results will be available for research on the moisture-proofing and caking of powder materials.

Experimental

Materials. A potassium bromide sample was prepared by twice recrystallizing special-grade reagent KBr using distilled water. An aqueous solution of KBr (30 wt%, *ca.* 100 ml) was poured with stirring into ethyl alcohol (*ca.* 500 ml) cooled to -80—-90 °C. The bromide thus obtained was filtered and washed four times with absolute ethyl alcohol and then dried at a reduced pressure of 10^{-3} Torr. This precipitate was observed by microscopy to be very small cubic crystals (2—7 μ).

Ground powders of KBr were prepared by pulverization of the recrystallized KBr in a ball-mill for 1 h.

Potassium oleate (special-grade reagent) was purified twice with absolute ethyl alcohol and also dried at reduced pressure.

Potassium Oleate Coating. A mixed solvent of CCl_4–C_2H_5OH in a volume ratio of 5 : 1 (50 ml) including an adequate amount of KOl was stirred for 5—6 min after KBr (30 g) had been added to the solvent, and the salt thus treated was filtered and dried at reduced pressure. A standard sample was prepared by immersing KBr in a mixed solvent which was free of KOl. The amount of KOl adsorbed on the surface of KBr particles was estimated by measuring the UV absorbance at 250 mμ after the adsorptive measurement had been completed. Ethyl alcohol and carbon tetrachloride were dehydrated with metal Mg and silica-gel, respectively, and then distilled prior to use.

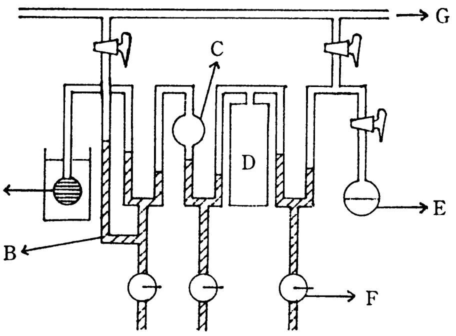

Fig. 1. Schematic diagram of apparatus for measurement of water vapor and nitrogen adsorptions.
A: Sample tube, B: mercury manometer, C, D: water vapor or nitrogen reservoir, E: water reservoir, F: greaseless cock, G: vacuum line.

Adsorption Measurement. Figure 1 shows the schematic diagram of a volumetric apparatus for water vapor and nitrogen adsorption. The equilibrium pressure of the water vapor and nitrogen were measured using a mercury manometer and a reading magnifier having a resolution of 10^{-2} mm.

Surface Area. The specific surface areas of the samples were determined 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 $Å^2$.

Results and Discussion

Water Vapor Adsorption. The specific surface area of the standard sample was estimated to be *ca.* 0.24 m^2/g, and this value agreed roughly with the surface area measured for KBr powder untreated with the above solvent. The water vapor adsorption isotherms for this standard and the ground powders of KBr are illustrated in Fig. 2. In the adsorption isotherms, slight stepped rises of the amount of adsorbed water are observed in the relative vapor pressure range of 0.075 to 0.13, excepting the case of ground KBr. More remarkable steps in the water adsorption isotherms have been observed for NaCl, KCl,(2,3) and NaBr.(4) The relative pressures, at which the steps appear in the

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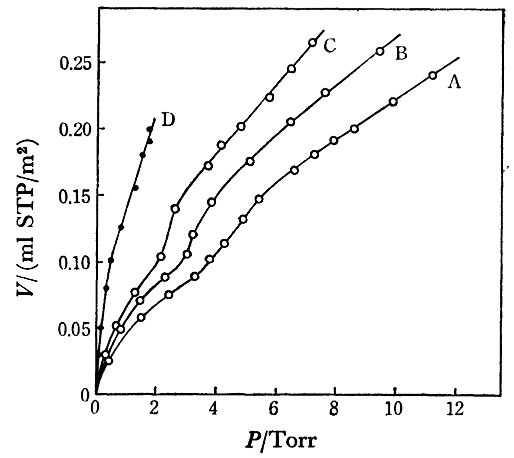

Fig. 2. Water vapor adsorption isotherms of KBr. A: at 35 °C, B: at 30 °C, C: at 25 °C, D: Ground KBr at 20 °C.

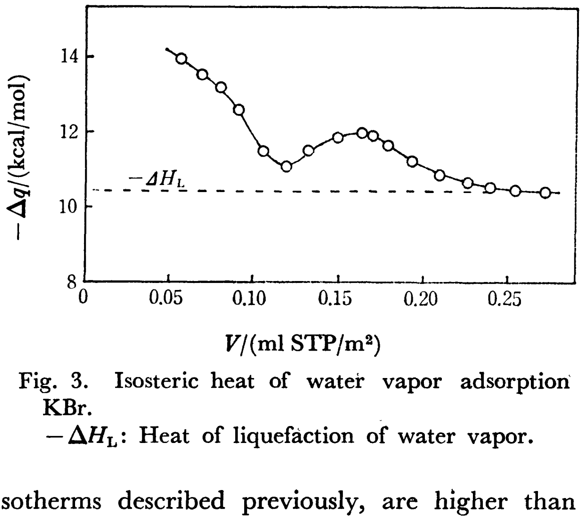

Fig. 3. Isosteric heat of water vapor adsorption on KBr.
$-\Delta H_L$: Heat of liquefaction of water vapor.

isotherms described previously, are higher than that determined for KBr. Disagreements in the relative pressures at which the step appears may be ascribable to the difference in the adsorption mechanisms of water molecules between the above salts and KBr.

Isosteric Heat of Adsorption. Figure 3 indicates the isosteric heats of adsorption calculated from the isotherms given in Fig. 2. A peak is seen in the isosteric heat curve at V=0.17 ml STP/m^2. This value corresponds closely to the monolayer capacity estimated by the point B method. On the other hand, the BET plot for the isotherm in Fig. 2 was found to be linear in the relative pressure range of 0.03 to 0.3, and it gave a monolayer capacity which is 1.3_7 times the value obtained at point B. However, no changes which are expected to suggest monolayer completion were observed in the isotherm and the isosteric heat curve at about V=$0.17 \times 1.3_7$ ml STP/m^2. If the surfaces of all KBr particles consist of (100) planes and one water molecule is adsorbed on one Br$^-$ site of the surface, the amount of monolayer adsorption is calculated to be 0.171 ml STP/m^2. This value is almost equal to that obtained by the point B method. From these results, the adsorption mechanism of water vapor on a KBr surface and the characteristics of the adsorption isotherm and isosteric heat curves will be interpreted as follows. Water molecules are adsorbed on Br$^-$ sites in a ratio of 1 : 1. An interaction force induced by hydrogenbonding among the adsorbed water molecules increases with the amount adsorbed, and reaches a maximum value at a coverage of θ=1. The peak in the isosteric heat curve appears due to the effect of hydrogenbonding. Moreover, the slight stepped rise observed in the adsorption isotherm of the recrystallized KBr is considered to be due to the two-dimensional condensation of water molecules adsorbed on the uniform surfaces of the salt, since monolayer adsorption was formed at the end of the step. On the other hand, the stepped rise disappears in the isotherm of ground KBr owing to the inhomogeneity of its surface.

Lad[5] has obtained a water vapor adsorption isotherm on cleaved NaCl crystals, and its isotherm suggests an adsorptive structure, which is a hydrogen-bonded first layer with one molecule of water for two Cl$^-$ sites. According to this result, two hydrogen atoms in a water molecule are considered to attach to two adjacent Cl$^-$ sites. Therefore, the adsorption characteristics of water vapor on an alkali halide are considerably affected by the distance between the two adjacent anions, the electronegativities and the ionic radii of the chemical elements involved. The difference between the water vapor adsorption mechanisms of NaCl and KBr may be mainly due to the differences in their lattice spacings and in the electronegativities of the elements of which the surface is composed. The distance between the two Br ions is larger than that between Cl ions, and the electronegativity of bromine is smaller than that of chlorine. Hence, the two hydrogen atoms in a water molecule do not fit onto the two adjacent Br$^-$ sites of KBr.

Effect of Potassium Oleate Coating. The effects of the concentration of the pre-adsorbed KOl on the water adsorption isotherm and the isosteric heat of adsorption are shown in Figs. 4 and 5, respectively. The slight stepped rise declined gradually with increasing KOl concentration. Moreover, no peak which was expected to appear for a coverage $\theta \doteq 1$ was observed in the heat curve of adsorption on KBr coated with KOl. Therefore, the disappearance of the step is thought to be due to increasing inhomogeneity of the component and the geometric structure of the solid surface containing adsorbed KOl. This interpretation is compatible with the result obtained using ground

Table 1. Water vapor affinities of KBr samples coated with potassium oleate

Sample[a)]	Oleate concentration (mg/m^2)	V_m (ml STP/m^2)	C	S_{H_2O}/S_{N_2}
A	0	0.236	8.46	0.69
B	0.472	0.238	6.11	0.69
C	0.576	0.225	7.36	0.65
D	0.579	0.209	9.11	0.60
E	0.597	0.231	8.58	0.67
F	1.193	0.269	9.17	0.78
H	5.25	0.35	25.6	1.0

a) The symbols are the same as those in Fig. 4.

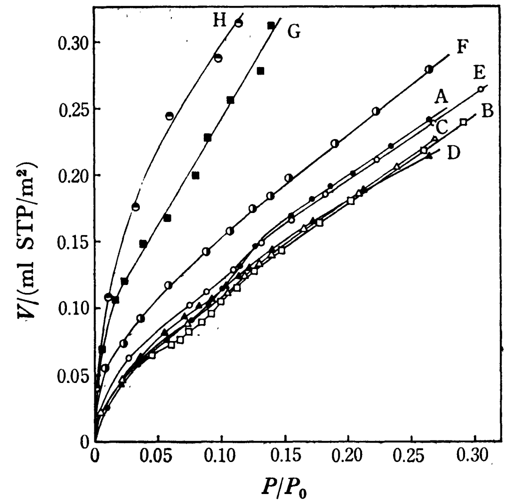

Fig. 4. Water vapor adsorption isotherms of KBr coated with KOl at 35 °C.
KOl concentration (mg/m^2): A; Zero, B; 0.463, C; 0.576, D; 0.579, E; 0.597, F; 1.19, G; 2.99, H; 5.25, G, H at 30 °C.

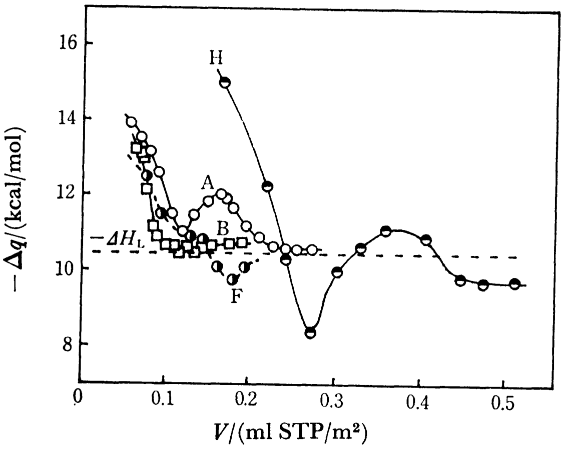

Fig. 5. Isosteric heat of water vapor adsorption on KBr coated with KOl.
KOl concentration (mg/m^2): A; Zero, B; 0.463, F; 1.19, H; 5.25.

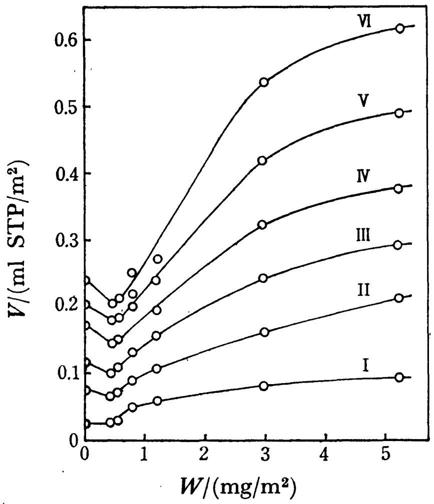

Fig. 6. Effect of KOl concentration on the amount of adsorbed water measured under fixed relative water vapor pressures.
P/P_0: I; 0.01, II; 0.05, III; 0.10, IV; 0.15, V; 0.20, VI; 0.25.

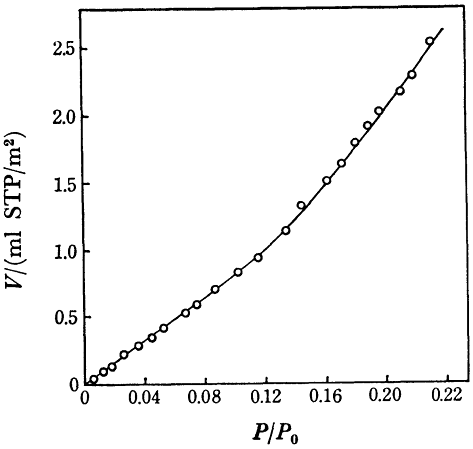

Fig. 7. Water vapor adsorption isotherm of KOl particles at 20 °C.

KBr. In addition, the pre-adsorbed KOl is believed to prevent the interaction between the adsorbed water molecules induced by the hydrophobic property of KOl and to eliminate a peak in the isosteric heat curves.

Pre-adsorption of KOl, in a certain concentration range and for a given surface coverage, weakened slightly the subsequent adsorption of water vapor, whereas at higher concentrations this trend was reversed and the amount adsorbed began to increase markedly.

Water vapor affinity, one of the surface properties of solids, is often expressed by the ratio S_{H_2O}/S_{N^2}, where S_{H_2O} and S_{N_2} are surface areas determined using H_2O and N_2 as adsorbates, respectively, assuming cross-sectional areas of 10.6 Å^2 for H_2O and 16.2 Å^2 for N_2. These values for KBr at various concentrations of pre-adsorbed KOl and C values obtained from the water vapor BET plots are summarized in Table 1. The slight effect of the pre-adsorbed KOl on the prevention of water vapor adsorption is observed for low concentrations of KOl, whereas at higher concentrations the water vapor affinity increases. The change in the isosteric heats of adsorption with increasing KOl concentration prove this tendency.

The relationship between the KOl concentration and the amount of adsorbed water at a fixed water vapor pressure is given in Fig. 6. The KOl concentration available for preventing water vapor adsorption is determined from the curve in Fig. 6 to be about 0.46 mg/m^2. If the amount of pre-adsorbed KOl required to cover the surfaces of KBr particles with a complete monolayer corresponds to a value of 0.46 mg/m^2, the resulting cross-sectional area of KOl is calculated to be 120 Å^2. However, this value is larger than the 45—50 Å^2 obtained by Adam⁶⁾ based on the structure of the liquid condensed film formed on the surface of an aqueous solution. The former value can probably be explained under the assumption that a hydrocarbon chain in the KOl molecule lies across the KBr surface. In such a case, the cross-sectional area of KOl is estimated from the molecular structure to be 130—150 Å^2. This value is close to the above-stated value (120 Å^2).

Table 1 indicates that at higher KOl concentrations the hygroscopicity of the sample increases with the KOl concentration, and this tendency seems ascribable to the penetration of water molecules into the ionic layers of KOl films adsorbed in a multilayer which may be of laminar form. A similar effect of KOl[7] has been observed in the case of adsorption on $CaCO_3$ pre-adsorbed KOl. The water-vapor adsorption isotherm on KOl powder itself is illustrated in Fig. 7. The amount of adsorbed water per unit KOl surface area is considerably larger than that estimated to be the physical adsorption of water vapor on a KOl surface. Therefore, most of the adsorbed water molecules are thought to penetrate into KOl particles. A similar observation was reported by Gross and Bauer[8] in their study of water-vapor adsorption on aluminum soaps. They concluded that water molecules penetrate into the soap crystallites and undergo hydrogen bonding at recurring Al–O linkages.[8] On the basis of these results, the abnormal increase in hygroscopicity of the sample can be reasonably explained by assuming the penetration of the adsorbed water molecules into KOl films on the surface of KBr.

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