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The Adsorption Mechanism of Methanol on Alkali Halides[1)]

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The amounts of methanol adsorbed on (100) planes of the crystals of six alkali halides (LiCl, NaCl, NaBr, KCl, KBr, and KI) and the isosteric heats of their adsorption were measured. For the chloride samples, the order of magnitude of the adsorption heats at a coverage of $\theta=0.5$ was found to be LiCl>NaCl>KCl, while the order for the bromide samples was NaBr>KBr. The monolayer capacities estimated from the adsorption isotherms for KCl and NaBr were in accord with the values calculated by assuming that one methanol molecule is adsorbed on one surface anion of the crystal. In the cases of the NaCl and LiCl salts, whose lattice spacings are smaller than that of NaBr, the methanol molecule was adsorbed on the surface anion with a ratio below 1 : 1. On the other hand, for the KBr and KI samples, whose lattice spacings are larger than that of KCl, alcohol was adsorbed on the surface anion in a ratio above 1 : 1. These phenomena are reasonably interpreted in terms of a relationship between the cross-sectional area of a methanol molecule and the lattice spacing of the salt concerned. An adsorptive mechanism deduced from the isosteric heat curves was compatible with the above explanation.

In the adsorption of polar molecules on the surfaces of alkali halide particles, interaction forces between the surface anions of the salt and the adsorbates will be large. Especially, when the adsorbates form hydrogen bonds with the surface anions, the role of the anions is presumed to be very significant.[2—5)]

A methanol molecule (MeOH) has one OH group expected to form a hydrogen bond with the surface anion. Therefore, in the present paper, MeOH is used as an adsorbate for several alkali halides, and the adsorption characteristics of the samples and the role of the surface anion in MeOH adsorption are discussed.

Experimental

Materials. Samples of five alkali halides (NaCl, NaBr, KCl, KBr, and KI) were purified by two recrystallizations of special-grade reagents using distilled water. A solution of an alkali sample (*ca.* 100 ml, 20—30 wt%) was added to about a five-fold volume of ethanol cooled to -80—-90 °C with stirring. The precipitate was filtered, washed four times with absolute ethanol, and then dried under a reduced pressure of 10^{-3} mmHg. Lithium chloride was prepared by the pulverization of a special-grade reagent in a ball-mill for 10 min. The LiCl and NaBr samples, which are able to form the hydrates, were heat-treated at 350 and 450 °C respectively for 2—3 days under a reduced pressure of 10^{-6} mmHg, while the other samples were evacuated with an oil diffusion pump ($<10^{-6}$ mmHg) for 1—2 days at room temperature prior to the adsorption measurements. These samples were found by microscopy to be very small cube crystals (1—8 μm).

The methanol was purified by distillation from a reagent for the UV spectrum measurements, and then used.

Surface Area Measurement. The specific surface areas of the samples were determined by the nitrogen adsorption method at 77 K, assuming the cross-sectional area of a nitrogen molecule to be 16.2 Å^2.

Methanol Adsorption Isotherm. The adsorption isotherms of MeOH on the alkali halides at 10, 20, 30, and 40 °C were determined volumetrically by using the adsorption apparatus reported previously by the present authors.[6)]

Results and Discussion

Adsorption Isotherms. The adsorption isotherms of MeOH on alkali halides are given in Fig. 1. In the case of LiCl, it is characteristic that the amount of MeOH adsorbed increased rapidly at pressures above $p/p_0=0.14$ and that, simultaneously, the dissolution of LiCl into the adsorbed MeOH films occurred. The relative vapor pressure of a MeOH solution saturated with LiCl is about $p/p_0=0.15$ at 20 °C. The volume adsorbed at $p/p_0=0.15$ was estimated from the adsorption isotherm to be 0.28 ml STP/m^2. This volume agreed with the amount required to cover the surface of the LiCl particle with a 1.36 molecular layer of MeOH, assuming that the cross-sectional area of a MeOH molecule is 18 Å^2 [7)] (calculated from the density of liquid MeOH at 20 °C). The considerable solubility of LiCl into such a small amount of adsorbed MeOH will be explained on the basis of a strong interaction between the Li ion and the MeOH molecule. This interpretation is supported by the fact that the solubilities[8)] of lithium halides in methanol are higher than those of sodium halides in spite of the considerably larger lattice energies[9)] of the former.

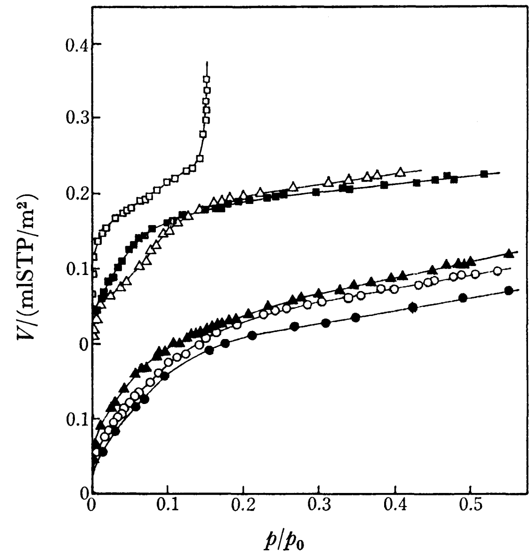

Fig. 1. Adsorption isotherms of MeOH on alkali halides at 20 °C.
—□—: LiCl, —■—: NaCl, —△—: KCl, —▲—: NaBr, —○—: KBr, —●—: KI.

TABLE 1. MONOLAYER CAPACITIES OF MeOH ADSORBED ON ALKALI HALIDES

Sample	V_{BET}(ml STP/m^2)	V_B(ml STP/m^2)	V_{cal}(ml STP/m^2)	V_B/V_{cal}
LiCl	0.23	0.17—0.18	0.282	0.62
NaCl	0.23	0.18—0.19	0.234	0.79
NaBr	0.205	0.24—0.25	0.209	1.17
KCl	0.19	0.18—0.20	0.188	1.01
KBr	0.23	0.24—0.25	0.171	1.40
KI	0.21	0.22—0.23	0.149	1.50

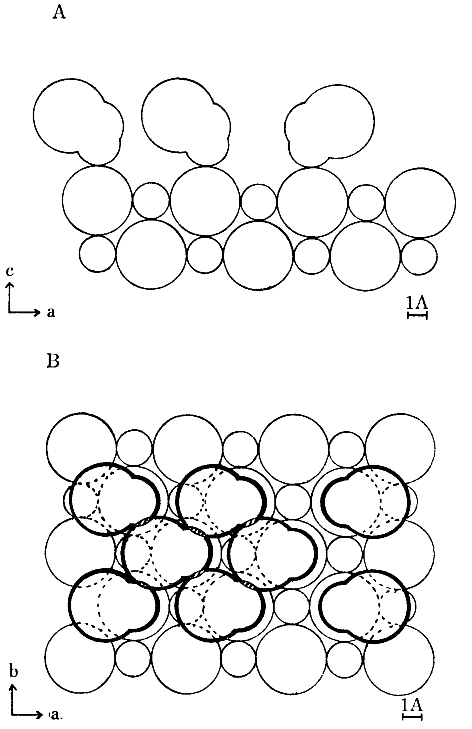

Fig. 2. Schematic diagrams of MeOH adsorption on (100) plane of NaCl.

A: Side view ⬯ : MeOH, ○: Cl$^-$, ○: Na$^+$.

B: Ground plane ⬭ : MeOH, ○: Cl$^-$, ○: Na$^+$.

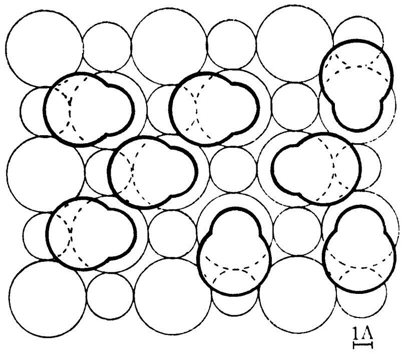

Fig. 3. Schematic diagram of MeOH adsorption on (100) plane of KBr.

○: Br$^-$, ○: K$^+$, ⬭ : MeOH.

The monolayer capacities, V_{BET} and V_B, were determined by two methods, the BET and the point B methods respectively. The values thus obtained are summarized in Table 1. As for the salt with a lattice spacing smaller than that of KCl or NaBr, V_B was less than V_{BET}. On the other hand, for the sample whose lattice spacing is larger than that of KCl or NaBr, V_B was greater than V_{BET}. These phenomena may be due to differences in the adsorption mechanisms at a coverage of $\theta=1$. This will also be discussed in the section on the mechanism of adsorption. The disagreement between V_B and V_{BET} values in each sample was within 20%.

Mechanism of Adsorption. The two assumptions introduced here to simplify the mechanism of MeOH adsorption on alkali halides are as follows: (I) all the surfaces of alkali halides particles consist of (100) planes, and (II) one MeOH molecule is adsorbed on one surface anion by an interaction such as a hydrogen bond. The former assumption for the surface structure of the salts will be reasonable in view of two experimental proofs, an electron microscopic observation of alkali halides surfaces made by Yao[2] and the fact found by Young[10] that approximately 80% of the surfaces of pulverized KCl is composed of (100) planes. The amounts of MeOH (V_{cal}) necessary for covering the unit surface area (1 m^2) were calculated for all the samples (*cf.*, Table 1). The adsorptive situation of MeOH on the surface, *i.e.*, the (100) plane of NaCl, is illustrated in Fig. 2, in which the OH axis in the molecule is perpendicular to the surface of the crystal. The van der Waals radii of the hydrogen atom, the oxygen atom, and the CH_3 group are assumed to be 1.2, 1.4, and 2.0 Å respectively.[11] In the case of NaCl, some overlaps of neighboring adsorbed MeOH molecules occur, as is shown with the shaded area in Fig. 2-B. Considering this schematic structure of MeOH adsorption, a certain degree of steric hindrance is expected to arise among the adsorbed molecules at the monolayer completion. If an OH axis of MeOH is slightly oblique to the normal surface, such steric hindrance can be avoided in the adsorption. However, since the V_B/V_{cal} value for NaCl was smaller than 1, the steric hindrance is considered to remain to some extent. On the contrary, the V_B/V_{cal} values obtained for KCl and NaBr were approximately equal to 1. Therefore, the lattice spacings of the both salts will be regarded as convenient spacings for MeOH adsorption.

In the case of the salt whose lattice spacing is smaller than that of NaCl, the steric hindrance will unavoidably be induced in the adsorbed MeOH, and the number of MeOH molecules adsorbed becomes less than that of anions on the surface. On the other hand, for KBr, whose spacing is larger than that of KCl, MeOH

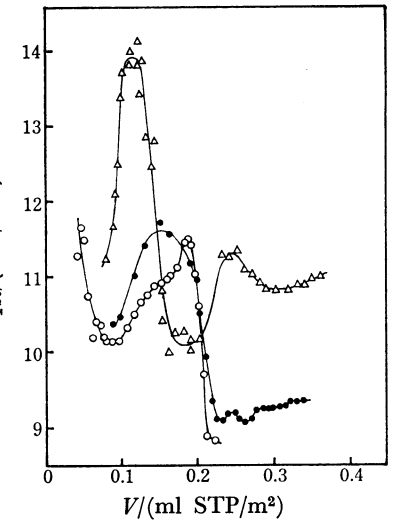

Fig. 4. Isosteric heats of adsorption of MeOH on alkali chlorides.
—△—: LiCl, —●—: NaCl, —○—: KCl.

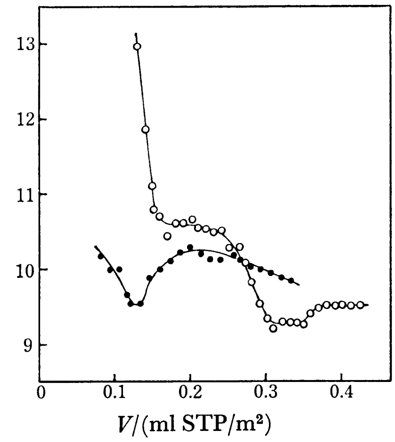

Fig. 5. Isosteric heats of adsorption of MeOH on alkali bromides.
—○—: NaBr, —●—KBr.

is adsorbed first on the surface anion in the ratio of 1 : 1. At this time, however, a vacant space is produced among the adsorbed molecules, as is shown in Fig. 3. In further adsorption, MeOH is packed more closely to diminish the vacant space. Therefore, the monolayer capacity is larger than the value to be expected from the adsorptive structure of one MeOH for one surface anion. When such a vacant space becomes larger, the amount of MeOH necessary for covering the space rises. Hence, the value of V_B/V_{cal} increases with an increase in the lattice spacing of the salt. The change in the V_B/V_{cal} values with the alteration of the samples will be explained in terms of the difference in their lattice spacings. Moreover, this explanation is supported by the discussion in the next section.

Heat of Adsorption. In Figs. 4 and 5, the isosteric heats ($-q_{st}$) of MeOH on the alkali halides are plotted against the amounts adsorbed. In the case of the chloride samples, the order of magnitude of the adsorption heats at $\theta=0.5$ ($V=0.11$ ml STP/m^2) was found to be LiCl>NaCl>KCl. For the bromide samples, the order was NaBr>KBr. The heat of MeOH adsorption rose with an increase in the ionic radius ratio, r_{anion}/r_{cation}, of the crystal. These results are consistent with the adsorptive structure described above that MeOH molecules are adsorbed on the surface anion by the hydrogen bond.

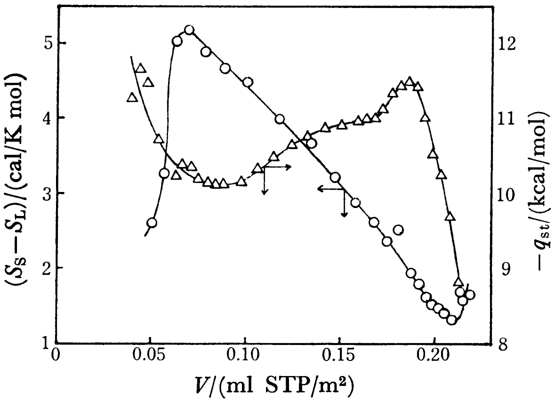

Fig. 6. Molar integral entropy of MeOH adsorbed on KCl.
S_S: Molar integral entropy of adsorbed MeOH.
S_L: Molar integral entropy of liquid MeOH at 20 °C.

The heats of adsorption for LiCl, NaCl, and KCl were noticed to have maximum values at a coverage below $\theta=1$ (<0.2 ml STP/m^2). This phenomenon is considered to be caused by a lateral interaction induced among the adsorbed molecules. The heats of adsorption for NaCl and KCl had smaller values than the liquefaction heat of MeOH at the adsorbed amounts of above $V=0.225$ and 0.21 ml STP/m^2 respectively. When a MeOH molecule is adsorbed on the surface of the (100) plane, as is shown in Fig. 2, the polar OH group in MeOH is located under the CH_3. Therefore, an interaction between MeOH and the polar groups in the formerly adsorbed molecules is expected to be depressed on the further adsorption of MeOH, *i.e.*, a two-layer adsorption, and the isosteric heat of adsorption will be small at this time. This interpretation is compatible with the molar integral entropy change in MeOH adsorbed on KCl, as is shown in Fig. 6. These entropy values were calculated from adsorption isotherms omitted in this report. At low coverages, $V<0.07$ ml STP/m^2, the entropy of adsorbed MeOH became small with a decrease in the amounts adsorbed. This entropy change suggests that the MeOH molecule is tightly adsorbed on the surface of KCl in the early stage of the adsorption.

In the case of KBr, MeOH is considered to be adsorbed first on the surface anion, as is illustrated in Fig. 3. The lateral interaction induced among the adsorbed MeOH molecules will be very weak, owing to the long lattice spacing of KBr. It will be stated, in view of such an adsorption mechanism, that the heat of adsorption decreases with the amount adsorbed until the adsorbed molecules come in contact with each other. In the vicinity of the monolayer completion, the adsorbed molecules come in touch with each other, and the lateral interaction increases to cause a peak in the isosteric heat of adsorption at $V=0.21$ ml STP/m^2. This value is approximately equal to the monolayer capacity estimated from the cross-sectional area of 18 Å^2 for a MeOH molecule. A peak caused by the lateral interaction was also observed in the curve of the adsorption heat of LiCl in the high-pressure region.

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