water, studied by Silgardo and Storrow.[8] Here, however, there appears to exist sufficient difference in polarity, mass and structure for the viscosity of the mixtures to vary significantly from additivity.

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On Physical Adsorption. V. Two-Dimensional Condensation of Ethane on Surfaces of Solids at 90°K.[1]

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The conditions for two-dimensional condensation of an adsorbed monomolecular vapor on a solid surface are postulated, and shown to be met when ethane at 90°K. is adsorbed by a solid having a large proportion of a single, unique, and uniform surface (*homotattic* surface). Previous reports of two-dimensional condensation of ethane adsorbed on cube crystals of NaCl and KCl are confirmed, using crystals of smaller dimensions prepared by sublimation. The same phenomenon is demonstrated on a sample of asbestos, described by independent investigators as having a relatively uniform surface, and on a sample of calcium fluoride. Supersaturation phenomena, and the effect of extensive supersaturation on the BET surface-area determination, are described. The value of two-dimensional condensation as a tool for the investigation of solid surfaces is pointed out.

Introduction

In previous papers of this series by Ross, *et al.*,[2-5] discontinuities in the low pressure adsorption isotherms of ethane at 90°K. on the {100} and {111} faces of sodium chloride and potassium chloride were reported, and were attributed to the condensation of a unimolecular layer of ethane from a two-dimensional gaseous phase to a two-dimensional condensed phase. Harkins, Jura and others, who had previously investigated similar discontinuities, used *n*-heptane as adsorbate and reduced silver powder,[6] ferric oxide[7] and graphite[8] as adsorbents. The failure of recent efforts to reproduce Harkins and Jura's results[9-11] may perhaps be attributable to the difficulty of finding identical surfaces of these adsorbents. We have accordingly considered it advisable, in preparation for further development of this topic, to verify the existence of the effect described, using surfaces whose nature would be independent of their history.

This paper (a) reproduces, with sodium chloride and potassium chloride prepared by sublimation, the results earlier reported for the adsorption of ethane on the same substances prepared by rapid precipitation; and (b) presents low-pressure adsorption isotherms of ethane on other surfaces deemed likely to provide conditions required to demonstrate the two-dimensional phase transition.

Apparatus and Materials

The apparatus is based on the design of Wooten and Brown[12] and, save for details of dimensions, is the same as that used by Ross and Boyd[2] for the original ethane isotherms on sodium and potassium chlorides. The authors are obliged to Dr. E. V. Ballou who first set up this apparatus in this Laboratory. Pressure measurements are made with a McLeod gage and mercury cut-offs are used to preclude the presence of stopcock grease in the adsorption portion of the apparatus. The adsorption temperature of 90°K. is maintained by a liquid oxygen bath. An oxygen gas thermometer is used to measure the temperature of the bath.

The sodium chloride (Baker and Adamson, reagent grade) and potassium chloride (Fisher Scientific Company, special buffer salt) were sublimed in a stream of prepurified nitrogen gas (Matheson Company) and collected by electrostatic discharge, as described by Craig and McIntosh.[13] The calcium fluoride (Baker and Adamson, reagent grade) was used without any further treatment than the initial desorption of air before the experiment. The ethane gas was Matheson research grade, treated by passing through Ascarite and concd. H_2SO_4 before being collected in the storage bulb. The asbestos, described as 7-R fiber, Canadian Johns-Manville Company, was furnished by courtesy of Prof. A. C. Zettlemoyer of Lehigh University. Some of its adsorption characteristics already have been published.[14]

Experimental Results

Isotherms.—The isotherms were determined volumetrically. The final equilibrium pressures were so low that the ideal gas law is valid for the unadsorbed gas. The observed pressures have not been corrected for thermal transpiration, as the existence of the discontinuity, or its relative position on the pressure axis, is not thereby affected.

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(1) Presented before the Division of Colloid Chemistry at the 125th National Meeting of the American Chemical Society, Kansas City, Mo., March 24–April 1, 1954. This paper is based on a thesis to be submitted by Werner Winkler to the faculty of Rensselaer Polytechnic Institute in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) S. Ross and G. E. Boyd, "New Observations on Two-Dimensional Condensation Phenomena," MDDC Report No. 864, 1947.

(3) S. Ross, THIS JOURNAL, **70**, 3830 (1948).

(4) S. Ross and C. H. Secoy, *J. Phys. Colloid Chem.*, **53**, 306 (1949).

(5) S. Ross, *ibid.*, **53**, 383 (1949).

(6) G. Jura, E. H. Loeser, P. R. Basford and W. D. Harkins, *J. Chem. Phys.*, **13**, 535 (1945).

(7) G. Jura, *et al.*, *ibid.*, **14**, 117 (1946).

(8) G. Jura, W. D. Harkins and E. H. Loeser, *ibid.*, **14**, 344 (1946).

(9) R. N. Smith, THIS JOURNAL, **74**, 3477 (1952).

(10) D. M. Young, R. A. Beebe and H. Bienes, *Trans. Faraday Soc.*, **49**, 1086 (1953).

(11) M. L. Corrin, THIS JOURNAL, **75**, 4623 (1953).

(12) L. A. Wooten and J. R. C. Brown, *ibid.*, **65**, 113 (1943).

(13) A. Craig and R. McIntosh, *Can. J. Chem.*, **30**, 448 (1952).

(14) A. C. Zettlemoyer, G. J. Young, J. J. Chessick and F. H. Healey, *J. Phys. Chem.*, **57**, 649 (1953).

Figure 1 reports the adsorption of ethane on cube crystals of sodium chloride. The application of the BET equation using $p_0 = 10\ \mu$, gives a surface area per gram (Σ) of 2.9 m.^{2}/g. The sample was initially freed of adsorbed gases at 90–110° for four hours. The points are adsorption points only. The diagram agrees well with one reported by Ross and Boyd,[2] for sodium chloride crystals of Σ 0.23 m.^{2}/g., determined by both adsorption and desorption points. The discontinuity is reported both for the earlier work and for the later work at 0.48 μ (uncor.).

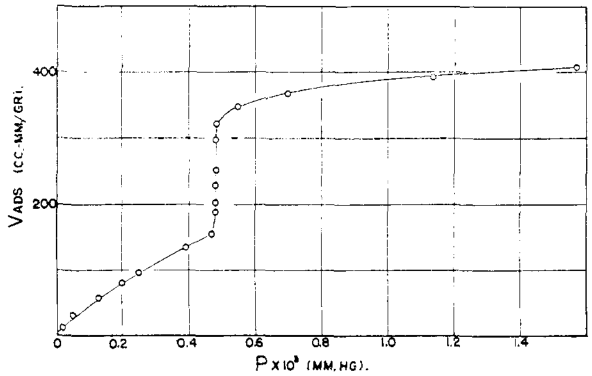

Fig. 1.—Adsorption isotherms (90°K.) of ethane on cube crystals of sodium chloride, Σ 2.9 m.^{2}/g. The amount adsorbed is calculated as cc.-mm. at 273°K. per gram of adsorbent.

Figure 2 reports the isotherm (desorption points only) of ethane on cube crystals of potassium chloride, Σ 0.34 m.^{2}/g. This first sample of KCl was prepared by rapid precipitation from a saturated aqueous solution by absolute alcohol.[15] Figure 2 also reports the isotherm (adsorption points only) of ethane on a second sample of cube crystals of potassium chloride, Σ 1.89 m.^{2}/g. This sample of KCl was prepared by the sublimation method.[13] Two isotherms are reported. For the first one determined, the preliminary desorption was at room temperature for 24 hours, and for the second it was at 90–110° for four hours. The latter treatment produced a vertical discontinuity at 0.39 μ (uncor.), the same pressure as that shown by the first sample of potassium chloride. This discontinuity is absent, and the amount of ethane adsorbed is less, when the preliminary desorption from the solid is conducted at room temperature. Residual adsorbed air is held to account for the lower isotherm and absence of discontinuity.

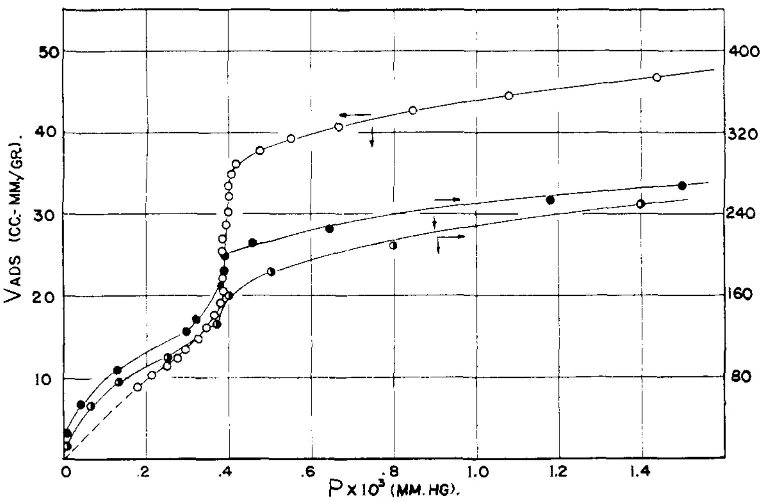

Fig. 2.—Desorption isotherm (90°K.) of ethane on cube crystals of potassium chloride, Σ 0.34 m.^{2}/g. (data of Ross and Boyd[2]). The two lower curves are adsorption isotherms (90°K.) of ethane on cube crystals of potassium chloride, Σ 1.89 m.^{2}/g. The sample was not completely freed of adsorbed air before determining the lowest isotherm.

Figure 3 reports the adsorption of ethane on commercially available calcium fluoride at 90°K., after a preliminary evacuation for several hours at 110°. The BET equation, when applied to the adsorption data at pressure higher than those shown in Fig. 3 (*i.e.*, in the usual range of validity of the equation, between 0.05 and 0.3 relative pressure), where vertical discontinuities are absent, gives Σ 24.5 m.^{2}/g.

Figure 4 shows two ethane isotherms on asbestos. The upper isotherm was obtained after keeping the solid for several hours *in vacuo* at 130–150°, the lower one after a similar treatment, but at room temperature. Nevertheless residual adsorbed air is not the cause of the difference between the isotherms; other isotherms, not reported here in further detail, determined after preliminary desorption treatment at temperatures even above 150°, are found to agree with the lower isotherm of Fig. 4.

Supersaturation Phenomena.—It will be noted that the two isotherms of Fig. 4 coincide at low pressures, but that as the pressure is increased one of them bends backwards. Similar isotherms are reported for the adsorption of nitrogen on glass spheres, and are attributed by Shereshefsky and Weir[16] to two-dimensional supersaturation of the adsorbed vapor. The vertical dotted line represents an isotherm with the two surface phases in equilibrium, but the isotherm plotted follows at first the adsorption isotherm of the supersaturated vapor. The lower isotherm shows that the supersaturation can go to large relative pressures. An attempt was made during the determination of this isotherm to induce the condensation of the two-dimensional vapor. At $p = 1.35\ \mu$, a waiting period of 12 hours was maintained without any pressure drop taking place. At a pressure of 1.60 μ the adsorbed ethane was removed from the solid by allowing it to come to room temperature and the gas was then readsorbed by lowering the temperature once more to 90°K. Eight hours later the pressure had returned to 1.60 μ and it was concluded that the adsorbed vapor was again in the supersaturated condition. Other isotherms determined

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(15) F. Marshall, *Phys. Rev.*, **58**, 642 (1940).

(16) J. L. Shereshefsky and C. E. Weir, This Journal, **58**, 2022 (1936).

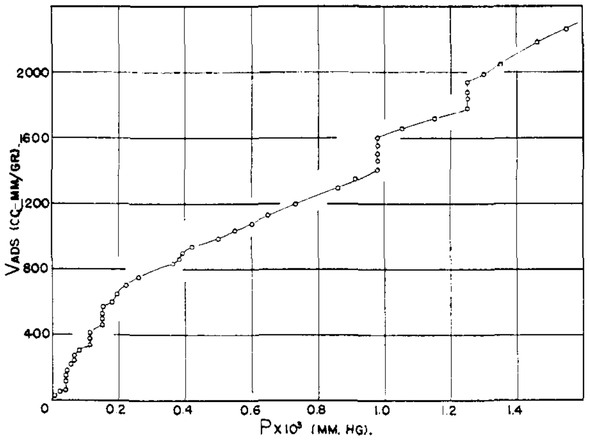

Fig. 3.—Adsorption isotherm (90°K.) of ethane on pure calcium fluoride, commercially available. The two discontinuities at highest pressures are caused by the presence of two crystallographic surfaces, and the higher energy surfaces evidenced at lower pressures are interpreted as energetically homotattic.

on this asbestos have all been of the super-saturated vapor type, though there is reason to believe that waiting for several hours at each point near the region of condensation might help to promote condensation. The removal of all the physically adsorbed moisture at 100° is also a possible factor in promoting condensation, though if the preliminary heating is carried further, to the extent of removing chemically combined water, the homotattic surface may be destroyed. X-Ray diffraction diagrams taken by Mr. J. Fisher of this Laboratory, show a broadening of the lines for samples heated to 450°, though samples heated to 100° are not changed.

Discussion of Results

The results here reported for sodium chloride and potassium chloride confirm the previous work in two respects in which it was weak. First, they show that the effect can be demonstrated with substances that are independent of their history. The alkali halides prepared by sublimation have surface areas as much as ten times those of the original samples. Second, the original results for potassium chloride were based on desorption points only. The present isotherm reaches the same equilibrium value from the opposite side, by adsorption. This method could not be followed with the necessary precision in the earlier work, because of the much smaller specific surface of the solid used.

The reproducibility of the results and the proof that the points represent true equilibria, since approached from opposite directions, is support of the interpretation of the effect as a two-dimensional phase transition. After these results had been obtained, Clark and Ross[17] discovered that the ethane–sodium chloride system shows typical critical temperature phenomena, with a two-dimensional critical temperature of 132°K. The present data have been used recently by Dr. Donald Graham to test his "equilibrium function" and to calculate the differential free energy of adsorption of ethane on

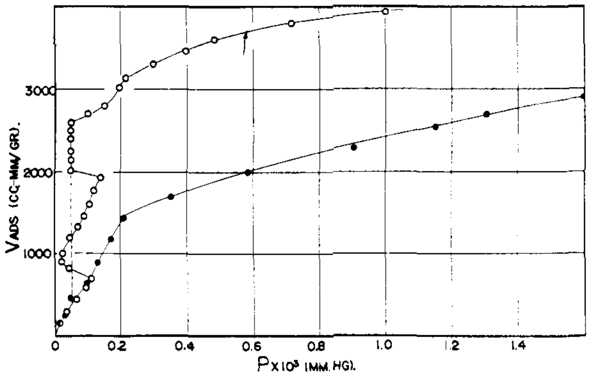

Fig. 4.—Adsorption isotherms (90°K.) of ethane on asbestos. The upper isotherm shows monolayer condensation from supersaturated two-dimensional vapor: the lower isotherm describes the supersaturated two-dimensional vapor adsorption throughout. The arrows indicate the BET monolayer point on each isotherm.

sodium chloride.[18] He has found a close agreement between the experimental facts and a theory based on a first-order two-dimensional phase transition of adsorbed ethane. These considerations go far to establish the validity of this interpretation.

Solid adsorbents in general have many surfaces where two-dimensional condensation can occur. The resulting isotherm may therefore have many vertical steps so close together that the result appears as a smooth curve. The conditions for a single vertical discontinuity in the isotherm are (1) a large proportion of the surface of the adsorbent should be a single homotattic surface[19]; (2) the surface must be free of any previously adsorbed gas; (3) the adsorbate must be a single chemical substance; (4) the temperature of the adsorption should be below the two-dimensional critical temperature of the adsorbate.[20]

Since ethane at 90°K. clearly meets conditions 3 and 4, and condition 2 is easily met experimentally for most solids, the adsorption of ethane at 90°K. ought to be useful as a means of detecting homotattic surfaces on solids. To test this supposition, solids that might be expected to have crystallographic homotattic surfaces were required. It is known that calcium fluoride is a cubic crystal that normally occurs with the {100} crystal faces, though it fractures along the octahedral or {111} planes.[21] Consequently two crystallographic homotattic surfaces would be expected to occur. The ethane adsorption isotherm (Fig. 3) shows two discontinuities at higher pressures, and also four smaller discontinuities at low pressures. This substance may have two crystallographic homotattic surfaces that behave as two or more energetically homotattic surfaces toward certain adsorbates. A similar situation is reported by Jura and Criddle[22] for argon adsorbed on graphite.

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[17] H. Clark and S. Ross, THIS JOURNAL, **75**, 6081 (1953).

[18] D. Graham, *J. Phys. Chem.*, **57**, 665 (1953), and private communication, Jan. 11, 1954.

[19] C. Sanford and S. Ross, *J. Phys. Chem.*, **58**, 288 (1954).

[20] It is not at present possible to predict the two-dimensional critical temperature, but it is usually not far from 50% of the three-dimensional critical temperature (see ref. 23).

[21] C. W. Bunn, "Chemical Crystallography," Oxford Press, New York, N. Y., 1946, p. 59.

[22] G. Jura and D. Criddle, *J. Phys. Colloid Chem.*, **55**, 163 (1951).

A sample of asbestos, described in the literature as showing evidence of relative surface uniformity,[14] was therefore obtained. The ethane adsorption isotherm showed the predicted condensation effect, but also introduced the troublesome possibility of supersaturation to relatively high pressures and the consequent non-appearance of the discontinuity. It must therefore be concluded that, while the appearance of one or more vertical breaks in the ethane isotherm demonstrates one or more homotattic surfaces on the solid, their non-appearance cannot be taken as definitive.

On the asbestos surface the pressure at which the discontinuity with adsorbed ethane appears is much lower ($p = 0.05\ \mu$) than with either sodium or potassium chlorides. Extensive supersaturation may be expected when the condensation takes place at low values of the relative pressure.[23]

Each of the two adsorption isotherms obtained for ethane on asbestos at 90°K. is described by the BET equation

$$V = \frac{CpV_m}{(p_0 - p)[1 + (C - 1)p/p_0]}$$

with the following characteristics:

	V_m(cc. at S.T.P./g.)	C	$p(\mu)$ at V_m	Σ, m.^{2}/g.
Condensed phase	4.90	204	0.58	29.6
Supersaturated vapor	3.41	48.9	1.15	20.6

Two BET straight lines can be obtained from these data. The values of Σ are calculated by the usual method, using 22.5 Å.^{2} as the area of the ethane molecule.[24] The values of V_m for the two isotherms are in a ratio of three to two. A ratio of simple whole numbers is to be expected, since adsorption sites on any homotattic surface are determined by periodic repetition. For the {100} surface of KCl two ethane molecules can be accommodated erect and one and one-third ethane molecules lying flat.[3] The three-to-one ratio is that of a completed layer of erect molecules to a completed layer of flat molecules, on a substrate similar to that of potassium chloride. For sodium chloride, with its smaller unit cell, on the {100} surface the corresponding ratio is two to one.[3]

Zettlemoyer, *et al.*,[14] have reported conflicting values for the surface area determination of this sample of asbestos by the BET method, and from heat of wetting data.[25] These effects are apparently not the result of supersaturation, as the change is in the wrong direction, *i.e.*, with water vapor adsorption the area begins to *decrease* at about 0.6 relative pressure. There is evidence of capillary structure in this solid, which could account for these findings. Several evidences of surface homogeneity are given in papers by Zettlemoyer and his group, which support the conclusions derived from the present work. This material appears to have two or more crystallographic homotattic surfaces that behave as a single energetically homotattic surface toward certain adsorbates.

Ethane adsorption in the low pressure region at 90°K. offers a useful tool for the investigation of different types of surface on a solid. The number of homotattic surfaces, the relative extent of each one and their characterization by the pressure of the discontinuity on the isotherm can all be obtained, if the conditions are satisfactory. Variation in the nature or extent of the homotattic surface by physical or chemical treatment of the solid are readily discovered. The use of ethane at 90°K. has advantages over some other vapors for which this effect has been discovered. Thus, heptane at room temperatures is far above 50% of its three-dimensional critical temperature, and hence many surfaces will probably not show condensation at so high a temperature. Heptane at lower temperatures has not yet been investigated. Argon has shown condensation on the surface of graphite,[22] but requires temperatures below that of liquid nitrogen. The advantages of ethane adsorption at 90°K. are that no cryostat is required, the low pressures can be conveniently measured with a McLeod gage, and the equilibrium is reached rapidly at the temperature of liquid oxygen. For nonpolar surfaces, where the pressure of the vertical break with ethane as adsorbate may perhaps be too low for precise measurement, a suitable system using a polar adsorbate would have to be devised.

Acknowledgment.—The present work was done with the aid of a research grant (NSF-G353) from the National Science Foundation, which the authors gratefully acknowledge.

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(23) J. H. de Boer, "The Dynamical Character of Adsorption," Clarendon Press, Oxford, 1953, pp. 222-224.

(24) H. K. Livingstone, *J. Colloid Sci.*, **4**, 447 (1949).

(25) A. C. Zettlemoyer, private communication, January 7, 1954.