area of the molecule in an infinitely compressed film. The limiting area per molecule before the transition is exactly twice that of the film after the transition. This finding is capable of two interpretations: (a) The monolayer is completed simultaneously with the completion of the transition, and there is no difference in the orientation of the molecules during the course of the transition. The limiting area per molecule then *apparently* drops to half its former value because the data refer to *two* molecular layers. (b) The condensed surface phase produced after the transition is still a monolayer, and is capable of further compression by adsorption of more molecules. The limiting area per molecule drops to one half its former value because the molecules erect themselves during the transition. The condensed monolayer phase is therefore composed of ethane molecules standing perpendicular to the surface.

Figure 7C, with 100% surface coverage at the end of the transition, is in accord with the first of these interpretations. Yet it is based on nothing more than the fixing of V_m by the BET equation applied to the ethane adsorption and to nitrogen adsorption data. More fundamental arguments and evidence are desirable.[24]

Ross[20] in 1948, and de Boer,[8] have favored the second interpretation. The question is still open and its answer is not only of interest to pure science; the nature of the orientation of adsorbed molecules affects the mechanism of catalytic and heterogeneous reactions.

(24) Dr. Donald Graham (E. I. du Pont de Nemours and Company. Inc.) has outlined an argument that includes more fundamental considerations. "The erection of the molecules would require lateral interaction between the adsorbed molecules sufficiently strong to overcome the energy holding the molecules flat on the surface. The activation energy for this shift would be approximately equal to the difference between the heats of adsorption of ethane and methane plus a small localization term. If this energy were available, it would still be necessary for the system with the molecules interacting from positions flat on the surface to be higher in energy than a system in which the adsorbed molecules are erect." Private communication.

TROY, NEW YORK

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, RENSSELAER POLYTECHNIC INSTITUTE]

On Physical Adsorption. VII. Two-dimensional Critical Phenomena of Diborane Adsorbed on Sodium Chloride[1]

BY SYDNEY ROSS AND HADDEN CLARK

RECEIVED MARCH 4, 1954

Diborane adsorbed on {100} surface planes of sodium chloride shows two-dimensional condensation and critical temperature phenomena at about 133°K. The isosteric heat of adsorption is reported as a function of surface coverage, and shows a large increase in the heat of adsorption after the completion of the phase transition. The effect is interpreted as a polymerization reaction in the adsorbed surface film.

Although it has been known for thirty years that unimolecular films of insoluble substances on aqueous surfaces can show phase transitions analogous to the normal condensation of vapor, there has been no convincing demonstration of the same phenomenon on solid surfaces. The reports by Jura, *et al.*, of a first-order phase transition of *n*-heptane on graphite,[2] ferric oxide[3] and reduced silver powder,[4] have not been confirmed by other independent investigators.[5–7] Certain internal peculiarities of the reported transitions had, in any case, raised doubts about them.

The present series of reports on physical adsorption is an attempt to demonstrate unequivocally that monolayer phase transitions do take place on solid surfaces. This demonstration is the more convincing the greater the variety of adsorbate vapors that are shown to exhibit the phenomenon. Xenon, methane and ethane have been shown to undergo two-dimensional condensation on the surface of sodium chloride, and to exhibit the characteristic behavior that usually describes a critical temperature for condensation.[8] The present paper reports the behavior of diborane vapor adsorbed on the same solid surface. This substance also displays a monolayer phase transition and typical critical temperature behavior.

Apparatus and Materials

The adsorption apparatus and the cryostat have been described previously.[8] The temperature of the adsorption was measured with an ethane vapor pressure thermometer, calibrated by the Antoine equation for ethane.[9] The vapor pressures of diborane were not measured directly, but obtained from the temperature by means of the vapor pressure data of Clarke, Rifkin and Johnston.[10]

The sodium chloride is the same sample that was used for the adsorption experiments with xenon, methane and ethane.[8] It has a surface area of 4.64 m.^{2}/g., determined by an application of the BET equation to the nitrogen adsorption isotherm.

The diborane gas was prepared by Mr. G. Stridde, in this Laboratory, by the method of Shapiro, *et al.*[11] The BF_3-$(C_2H_5)_2O$ was added to the ether solution of $LiAlH_4$ for convenience. Purification was by distillation at the melting point of CS_2. Infrared spectra showed no bands for ethyl ether or bands extraneous to diborane. Immediately be-

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(1) This paper is based on a portion of a Thesis submitted by Hadden Clark to the faculty of Rensselaer Polytechnic Institute, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) G. Jura, W. D. Harkins and E. H. Loeser, *J. Chem. Phys.*, **14**, 344 (1946).

(3) G. Jura, E. H. Loeser, P. R. Basford and W. D. Harkins, *ibid.*, **14**, 117 (1946).

(4) G. Jura, *et al.*, *ibid.*, **13**, 535 (1945).

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

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

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

(8) S. Ross and H. Clark, *ibid.*, **76**, 1291 (1954).

(9) "Selected Values for the Properties of Hydrocarbons," NBS Circular No. 461, U. S. Department of Commerce, Washington, D. C., 1947.

(10) J. T. Clarke, E. B. Rifkin and H. L. Johnston, THIS JOURNAL, **75**, 781 (1953).

(11) I. Shapiro, H. G. Weiss, M. Schmich, S. Skolnik and G. B. L. Smith, *ibid.*, **74**, 901 (1952).

fore use, the sample was frozen and any volatile gas present was pumped off.

Experimental Results

Adsorption isotherms of diborane on sodium chloride were determined at temperatures selected within the range of 122–139°K. The data are reported graphically in Figs. 1 and 2.

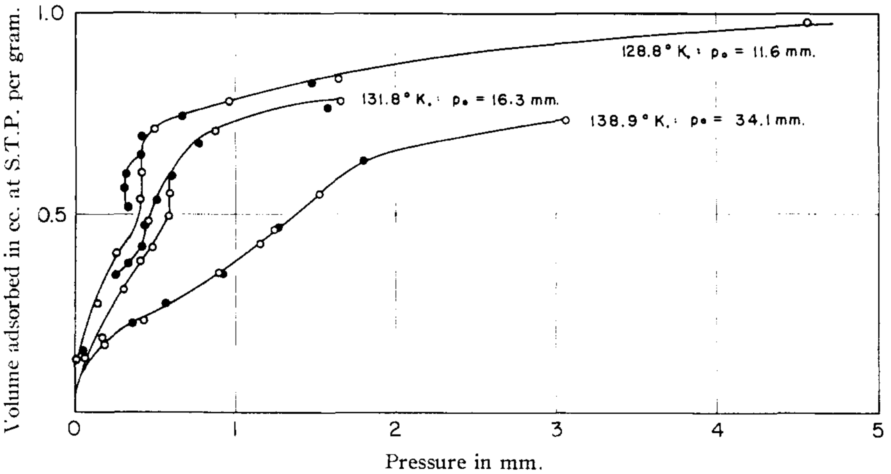

Fig. 1.—Adsorption isotherms of diborane on sodium chloride. Open circles represent adsorption and closed circles represent desorption points. Desorption hysteresis is obtained at temperatures below the two-dimensional critical temperature (133°K.).

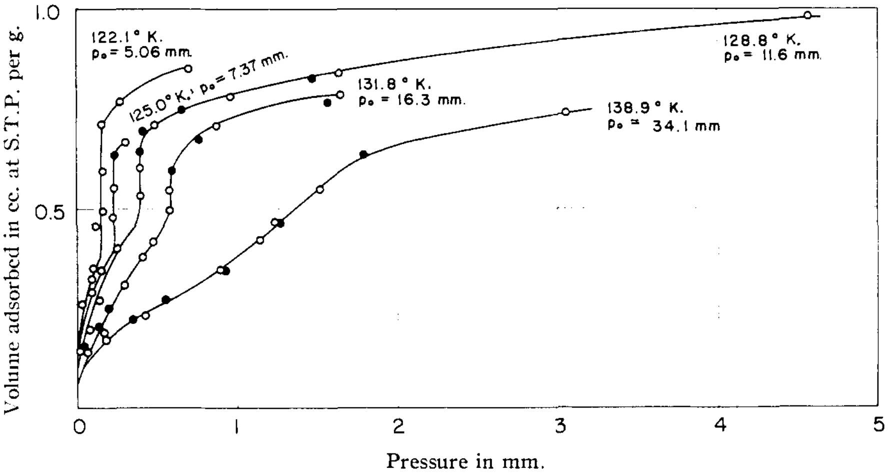

Fig. 2.—Adsorption isotherms of diborane on sodium chloride, excluding the hysteresis effects shown in Fig. 1.

Figure 1 reports a hysteresis effect on desorption of diborane that had not been observed in the same circumstances for any other adsorbate vapor on sodium chloride. The hysteresis was obtained only below the critical temperature, and even then only when the desorption had reached the stage where the condensed film would normally undergo the phase transition to the gaseous state of the adsorbed monolayer. Of the three isotherms reported in Fig. 1, the one at 138.9°K. is above the critical temperature and has a perfectly reversible adsorption–desorption equilibrium. The other two are below the critical temperature, and the curves show a desorption hysteresis beginning at the top of the vertical discontinuity. There was no evidence of hydrogen gas being evolved on this desorption.

To clarify the presentation of these data, Fig. 2 is a report of the diborane adsorption isotherms with the desorption hysteresis omitted. This diagram clearly depicts a vertical discontinuity in the adsorption isotherms at the lower temperatures, which diminishes gradually with increasing temperature and finally becomes non-existent. An extrapolation by eye sets the critical temperature at about 133°K.

Discussion of Results

1. Two-Dimensional Condensation and its Critical Temperature.—The purpose of this discussion is to marshal the evidence that supports the interpretation of the observed results as a two-dimensional condensation of the adsorbate and its disappearance at a critical temperature. The first, most direct, evidence is the general appearance of Fig. 2, which conforms to such an expectation. Second, the critical temperature of a monolayer transition is always less than the normal critical temperature of the bulk condensation of the vapor. For diborane the normal critical temperature[12] is 289.7°K. The two-dimensional critical temperature is approximately 12° lower than half the normal critical temperature. This behavior of a diborane monolayer is similar to that of monolayers of xenon, methane and ethane, all of which have a two-dimensional critical temperature several degrees less than half their normal critical temperature. An explanation has been proffered by de Boer[13] in terms of mutually oriented induced dipoles on the adsorbate molecules, arising from the ionic substrate. For isometric molecules the value of the induced dipole can be estimated.[8]

2. Integration of the Gibbs Adsorption Equation.—A third, less direct, method of testing the results is to explore the analogy between surface films on solids and insoluble films on aqueous substrates. The p–V–T data of adsorption can be transformed to π–σ–T values by an integration of Gibbs' adsorption equation.[14] The results of this

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[12] E. B. Rifkin, E. C. Kerr and H. L. Johnston, THIS JOURNAL, **75**, 785 (1953).

[13] J. H. de Boer, "The Dynamical Character of Adsorption," Clarendon Press, Oxford, 1953, p. 155.

[14] W. D. Harkins, "The Physical Chemistry of Surface Films," Reinhold Publ. Corp., New York, N. Y., 1952, pp. 112, *et seq.*

integration for the present data for the adsorption of diborane on sodium chloride are presented in Fig. 3. This diagram is again similar to the corresponding diagrams for methane and for ethane films on sodium chloride, and, like them, shows areas per molecule of reasonable value for the adsorbate. It differs markedly from them, however, in the steepness of the curves that refer to the condensed phase, showing a low compressibility for this surface film. A comparison of the shapes of the original isotherms of diborane (Fig. 2) with those of methane and ethane,[8] particularly in the region of pressures above those of the phase transition, reveals that the low compressibility shown in the π–σ–T curves (Fig. 3) depends on a real difference existing between the isotherms, and has not been introduced as an artifact during the integration. This low compressibility is of significance in the interpretation of the isosteric heat curve.

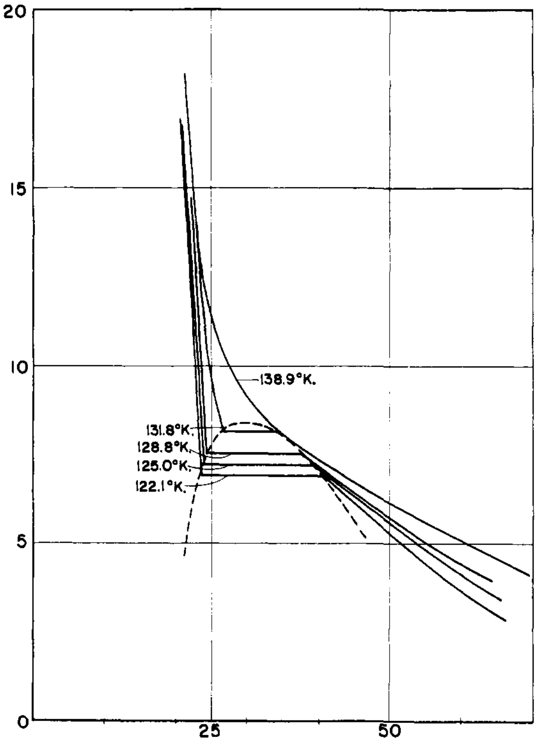
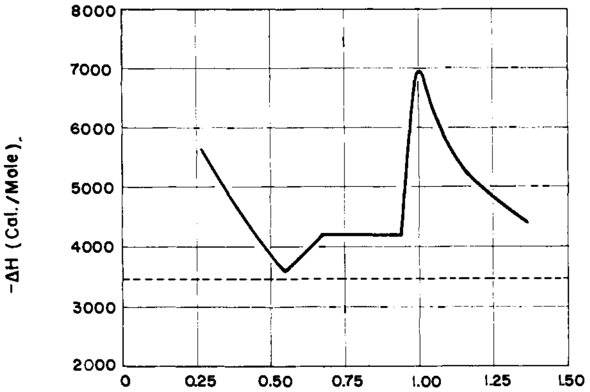


Fig. 3.—Surface pressure in dynes/cm. *vs.* area per molecule in Å.^{2}, for diborane adsorbed on sodium chloride, obtained by graphical integration of the Gibbs adsorption equation.

Figure 3 can be used to provide the fourth evidence, *viz.*, the two-dimensional heat of condensation. The positive variation of the surface pressure of the transition with temperature is proof that the monolayer condensation is exothermic. The two-dimensional heat of condensation, estimated by the Clausius–Clapeyron equation, is 900 cal./mole. The normal heat of bulk condensation of diborane in the same temperature range is 3420 cal./mole, calculated from the vapor pressures by the Clausius–Clapeyron equation. The approximation introduced by using the Clausius–Clapeyron equation for the monolayer phase, precludes the placing of much weight on these figures for purposes of interpretation, but it is satisfactory that the two-dimensional heat of condensation is only about 1 kcal./mole and that it is much less than the heat of the bulk condensation.

3. Isosteric Heats of Adsorption.—The isosteric heats of adsorption are calculated from the isotherms below the critical temperature, using the Clausius–Clapeyron equation, and an average value is reported in Fig. 4. The degree of surface coverage, $\theta = V/V_m$, is based on an average value of V_m obtained from an application of the BET equation to each diborane isotherm (V_m = 0.725 cc. of diborane at STP/g.). All the averages are close to the individual values, which have little variation within the small temperature range of the experiments.



Surface coverage.

Fig. 4.—The isosteric heat of adsorption of diborane on sodium chloride, calculated from adsorption isotherms at 122–132°K. The horizontal dotted line represents the heat of liquefaction of diborane, 3420 cal./mole, for the same temperature range.

The minimum in the isosteric heat curve, which occurs in Fig. 4 at 55% surface coverage, is apparently a characteristic of the ionic substrate, since it is found for xenon, methane, ethane and diborane on sodium chloride. It was also observed by Orr[15] for argon, nitrogen and oxygen on potassium chloride and cesium iodide. It is suggested[8] that the drop in the adsorption heat occurs because of the ability of the regular ionic array on the {100} surface planes to induce repelling dipoles on adjacent adsorbate molecules. A molecule already on the surface thereby reduces the adsorptive energies of the sites immediately adjacent. When the pressure is sufficiently large that those sites must be filled, there is a drop in the heat of adsorption, which may be more or less abrupt depending on the homogeneity of the surface and the magnitude of the repelling dipoles. On further filling of the low energy sites, however, the proximity of the adsorbed molecules brings interaction energies into play, which cause the heat of adsorption to increase, and ultimately produce condensation of the adsorbed gaseous film. During the phase transition the isosteric heat is constant, and the level of the horizontal portion of the curve above the minimum

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(15) W. J. C. Orr, *Proc. Roy. Soc. (London)*, **A173**, 349 (1939).

is approximately the magnitude of the two-dimensional heat of condensation.

When the transition is completed, the isosteric heat of adsorption of diborane shows a pronounced increase of 2700 cal./mole, between 94 and 100% surface coverage. The origin of this phenomenon is to be found in the chemistry of diborane, since it does not occur with xenon, methane or ethane on the same adsorbent. It can be interpreted as a surface reaction, such as polymerization, of the condensed surface layer, accompanied by an exothermic heat of reaction. The desorption hysteresis (Fig. 1) is evidently related to the surface reaction, since it occurs at the same degree of surface coverage. There is reversible adsorption–desorption equilibrium in the second layer (Fig. 1), which means that whatever the reaction taking place between the adsorbed molecules in the condensed surface phase of the first layer, it does not extend to the molecules of the second adsorbed layer. The same conclusion is also drawn from the decrease of the isosteric heats for second layer coverage ($\theta > 1$).

Exothermic polymerization of bulk diborane is not known, although molecular association in the liquid state has been reported.[12] It does not seem that the heat effect of molecular association would be marked. In the surface layer, however, the forces of molecular association would have better scope because of the enhanced availability of neighbors, and the heat effect magnified accordingly.

TROY, NEW YORK

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF KANSAS]

Evidence for Micelle Formation in Aqueous Solutions of Sodium Salts of Benzene Sulfonic Acids Substituted in the Ring by Methyl Groups[1]

BY HAROLD M. HUBBARD AND CHARLES A. REYNOLDS

RECEIVED MARCH 5, 1954

The effects of sodium *p*-toluenesulfonate, sodium *p*-xylenesulfonate, sodium *m*-xylenesulfonate and sodium *p*-cymenesulfonate on the polarographic reduction of nitrobenzene were studied in three different buffer systems, and, in addition, the effect of sodium *p*-xylenesulfonate on the electrocapillary curve of mercury was determined in the same buffer systems. The polarographic effects observed were very similar to those which take place in the presence of colloidal electrolytes and, on the basis of this fact, it is suggested that these simple aromatic sulfonates form micellar aggregates in much the same manner as do long chain alkyl sulfonates and the more complex aromatic sulfonates. It is believed that the phenomena observed are caused by preferential adsorption of the negatively charged micelles on the surface of the dropping mercury electrode.

The sodium salts of simple substituted aromatic sulfonic acids, such as the sodium toluenesulfonates, have not usually been considered as colloidal electrolytes, although the sodium salts of the aromatic sulfonates substituted with long chain alkyl groups have definitely shown to exhibit the behavior of micellar colloidal electrolytes.[2,3] Sodium toluenesulfonate has been included in the class of substances called hydrotropes, a term which has been applied to any substance whose presence in aqueous solution enhances the solubility of another substance in the same solution. Since it was considered likely that salts such as sodium toluenesulfonate would show micellar behavior at concentrations somewhat greater than that at which conventional micelle formers show evidence of aggregation, this study was initiated in hope of obtaining polarographic evidence of such behavior.

L. Meites and T. Meites, and Colichman have shown[4,5] that critical micelle concentrations of colloidal electrolytes can be determined with the use of the polarograph by plotting the half-wave potential or diffusion current of a simple metal ion reduction against the concentration of colloidal electrolyte in solution. The pronounced discontinuities in such plots (polarographic micelle points) were shown to be comparable to critical micelle concentrations determined from surface tension data taken by the conventional DuNouy ring method. In addition, the critical micelle concentration of a colloid was shown to be identical to the maximum suppression point, the concentration of colloid which just suppressed the polarographic maximum.

In this research, polarographic micelle points, maximum suppression points and electrocapillary curve changes were measured for the polarographic reduction of nitrobenzene in aqueous solutions of sodium *p*-toluenesulfonate, sodium *p*-xylenesulfonate, sodium *m*-xylenesulfonate and sodium *p*-cymenesulfonate. The measurements were made in well-buffered solutions at three *p*H values, and the concentration of the sulfonate salt was varied over a rather wide range while the concentration of nitrobenzene was held constant at 6×10^{-4} mole per liter.

Experimental

A Sargent Model XXI polarograph was employed for all of the polarographic measurements. All initial potential and span settings were checked with an auxiliary potentiometer circuit. The cell used was a modified H-type cell described by Lingane and Laitinen[6] with a saturated calomel half-cell anode. Oxygen was removed from the test solution by the passing of oxygen-free nitrogen. All measurements were carried out at 25 ± 0.2°. A Beckman model G *p*H meter was used for all *p*H measurements.

The commercial sulfonate salts obtained from Eastman Kodak were dissolved in distilled water, the water-insoluble impurities filtered off, and the clear solutions evaporated to dryness. These products were recrystallized twice from

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(1) Taken from the Ph.D. thesis of Harold M. Hubbard, September, 1951.

(2) R. G. Paquette, E. C. Lingafelter and H. V. Tartar, THIS JOURNAL, **65**, 686 (1943).

(3) G. R. Shuck and E. C. Lingafelter, *ibid.*, **71**, 1325 (1949).

(4) L. Meites and T. Meites, *ibid.*, **73**, 177 (1951).

(5) E. L. Colichman, *ibid.*, **72**, 4036 (1950).

(6) J. J. Lingane and H. A. Laitinen, *Ind. Eng. Chem., Anal. Ed.*, **11**, 504 (1939).