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MEASURING THE EQUILIBRIUM PRESSURE OF SUPPORTED AND UNSUPPORTED ADSORBENTS

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A simple experimental technique for measuring the equilibrium (vapor) pressures of unsupported and supported adsorbents was employed to determine the vapor pressure data for the lithium chloride-water-Torvex system at 32° C., for impregnation of 3% anhydrous salt by weight, and for the lithium chloridewater system at several temperatures.

N ATTEMPT was made to select and develop a simple technique to measure low vapor pressure of hygroscopic salts accurately for both supported and unsupported adsorbent systems.

The static method was used. The hydrate and supporter were placed in a sample flask and the system was allowed to reach equilibrium. The vapor pressure was measured by a cathetometer and the composition determined by measuring the displacements of a calibrated spring.

A schematic diagram of the apparatus is shown in Figure 1. The apparatus consists of a sample tube housing a spring holder, a calibrated spring with a hook, and a sample block; an isothermal bath (Bailey Instrument Co., Model 136) capable of maintaining the temperature within $\pm 0.01^{\circ}$ C. between -10° and 150° C.; manometers; a vacuum pump with a trap; and a cathetometer.

Apparatus and Procedure

Determination of Equilibrium Pressure of Supported Hygroscopic Salts. The system, lithium chloride impregnated on a solid supporter (Torvex), was chosen for the investigation because lithium chloride is widely used commercially in drying; its potential application in air conditioning has been recognized; and its desirable properties include a high drying rate, high moisture capacity, high efficiency, easy regenerability, chemical stability, and low relative humidity.

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Torvex, produced in alumina and mullite compositions, was selected for its large peripheral surface area, low resistance to flow, and inertness to chemicals.

First the spring constants were determined for weight ranges of interest at various temperatures. Then a cylindrical Torvex block 2 inches in diameter and 1 inch in length was preconditioned in an oven at 300° F. for 12 hours or more, weighed, and dipped into the lithium chloride salt solution.

The sample block was hooked to the calibrated spring inside the sample tube. The tube was immersed in the isothermal bath at a specified temperature and connected to the system. The spring displacements and the vapor pressures were measured with the cathetometer after enough time was allowed for the system to attain equilibrium. Then the system was evacuated from 3 seconds to several hours to reduce the adsorbate content in the adsorbent. Because the evaporation of moisture cools the block and because of the poor heat transfer in the low-pressure system, several hours were generally required for the system to equilibrate thermally. The process may be repeated at different isothermal bath temperatures and for other samples with varying degrees of salt impregnation. The accuracies of the reported measurements are: temperature control $\pm 0.01^{\circ}$ C., vapor pressure reading ± 0.01 mm. of water, and weight ± 0.1 mg.

The vapor pressure data thus obtained for the lithium chloride-water-Torvex system as a function of the water concentration in lithium chloride at 32° C. with salt impregnation of 3% anhydrous lithium chloride by weight are shown in Figure 2. This figure compares the vapor pressure of the

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Figure 2. Vapor pressure-composition diagram for LiCl impregnated on Torvex

Temperature 32° C. Salt impregnation 3.0 weight % LiCl — Unsupported O Supported on Torvex

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lithium chloride-water-Torvex system with that of an unsupported system—lithium chloride-water alone. Torvex does not change the vapor pressure.

Determination of Equilibrium Pressure of Unsupported Hygroscopic Salts. The sample flask is first dried in the oven, cooled, greased, and weighed accurately. About 2 to 5 grams of lithium chloride salt is introduced into the flask. Depending upon the region in which the vapor pressures are to be measured, an estimated amount of water is added to the salt with a syringe.

After the whole system, excluding the sample flask, is evacuated, the lithium chloride-water is deaerated by repeated heating and freezing of the sample, then connected to the manometer for measurements of vapor pressure. The readings are taken when steady state is reached.

The temperature of the bath is raised or lowered to the next desired level without further evacuation. After all the measurements are taken at various temperatures, the sample flask is taken out, cleaned, and weighed. The salt in the flask and the solution is titrated to find the mole fraction of lithium chloride.



Figure 3. Vapor pressure-temperature diagram for LiCl-H $_2O$ system

The variation of the vapor pressure with the temperature for the lithium chloride salt is shown in Figure 3. This figure shows the aqueous pressure of monohydrate in equilibrium with the anhydrous salt and with the saturated solution. These data lie on a straight line on a $\log P - 1/T$ plot in accordance with the familiar Clausius-Clapeyron equation.

Figure 3 compares the present data for the lithium chloride salt with the data available in the literature. The authors' data for the equilibrium between the anhydrous salt and monohydrate agree well with those of Slonim and Huttig (1929). Present data corresponding to the equilibrium between the monohydrate and the saturated solution show good agreement with those of Foote (1965). Many other investigators have also reported the vapor pressure data of saturated solutions. At high temperatures, Gokcen's data (1951), measured with a dynamic method, do not agree with the present data as well as with those of Foote. This is not

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thium water npregshown of the surprising because, generally, data measured by dynamic methods are higher than those determined by static methods.

The values for the heat of adsorption and the entropy of lithium chloride salt for the transition from anhydrous to monohydrate were calculated as detailed by Thakker et al. (1967, 1968). The heat of adsorption of LiCl·H₂O given by Slonim and Huttig as 1465 B.t.u. per pound of water agreed with our calculated value of 1490. The calculated entropy change was 6.361 B.t.u. per pound of water per degree Rankine. The calculated free energy change was 1924 B.t.u. per pound of water.

Conclusions

The vapor pressures of several hygroscopic salts were measured using the method described. An experimental method for the determination of the transition point for the hydrates has also been established. These and other details are given by Thakker et al. (1968) and Chi (1968).

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DETERMINATION OF THE MICROSCOPIC SURFACE AREA **NF** POLYETHYLENE FILM

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An apparatus for measuring the surface area of plastic film by the krypton adsorption method has been developed. The surface area of a polyethylene film was measured and its roughness factor shown to be about unity.

N CONNECTION with the reactions on the surface of polymeric material, we were interested to know the microscopic surface area of a polyethylene film. It is known that the microscopic surface area of solids may be considerably larger than that calculated from their macroscopic dimensions: the ratio of the microscopic to the macroscopic surface is termed the roughness factor. Since polyethylene can be looked upon as a very viscous liquid, the roughness factor was expected to be not much greater than unity. The problem was therefore to determine the microscopic surface area of a substance with a very low specific surface area.

For this purpose Beebe, Beckwith, and Honig have suggested (1945) determining the BET adsorption isotherms with krypton at 78° K. (boiling point of nitrogen). In the usual experimental arrangement the adsorption vessel is connected through a capillary tube with the pressure gage at room temperature. The vessel is immersed up to a mark on the capillary tube in boiling nitrogen. In that case the volumes at 78° K. and room temperature are sufficiently well defined. Such an arrangement is suitable for powders which can be introduced through the capillary tube. As polyethylene film could not be introduced in such a way, it was necessary to use a relatively wide tube to connect the cold and warm sections; this had the further advantage of avoiding pressure drops due to thermal transpiration (Knudsen effect). On the other hand, a special method had to be developed to reduce the uncertainty in defining the cold and warm zones.

Procedure

The adsorption vessel used (Figure 1) was about 10 mm. in diameter and 150 mm. long; at its upper end it was connected through a conical ground joint to a storage vessel, a vacuum line, and a Pirani vacuum gage. A measured amount of polyethylene film was crumpled and introduced into the lower portion, A, of the adsorption vessel. Adhesion to the wall was avoided by a small number of protrusions.

Two thermocouples, B and C, were glued with epoxy resin to the outer wall above the lower portion of the adsorption vessel, at a vertical distance of 4 mm. from each other. Over the upper thermocouple, C, a heating wire was wound and connected to a variable power source, D. A vacuum flask with liquid nitrogen was jacked up until the surface of the boiling nitrogen reached the upper thermocouple and the current through the heating wire was adjusted until the upper thermocouple showed room temperature. The nitrogen level was kept such that the lower thermocouple indicated the boiling point of nitrogen. The surface, E, bisecting the distance between the two thermocouples was taken as the dividing line between the volume at 78° and 300° K. (thermostated room temperature). The volumes were determined in the usual way by weighing with water.

Results

Before determining the surface area of polyethylene film, the apparatus was tried out on γ -alumina powder. The sur-