

ADSORPTION OF HCN AND H₂O VAPOR MIXTURES BY ACTIVATED AND IMPREGNATED CARBONS

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Introduction

Isotherms for HCN on BPL activated and ASC whetlerite carbons¹ and for H₂O on the same carbons² have been measured and characteristic parameters for these adsorbate-adsorbent combinations have been noted. Under non-laboratory conditions, adsorption usually takes place in the presence of water vapor. It is therefore of interest to investigate the adsorption properties of the BPL activated and ASC whetlerite carbons with respect to HCN in the presence of water vapor at about 80% humidity. The data from the single vapor isotherms are used as a basis for interpreting the results of a binary mixture adsorption study.

Experimental

The experimental technique employed for single vapor isotherm measurement and the carbons investigated have been described previously.³ Binary vapor isotherms were measured by three different procedures: 1) the carbon sample was allowed to equilibrate with H₂O vapor and then an HCN isotherm was measured while maintaining the initial amount of H₂O in the system; 2) the carbon sample was allowed to equilibrate with HCN vapor and then an H₂O isotherm was measured while maintaining the initial amount of HCN in the system; 3) a mixed gas consisting of H₂O and HCN was introduced into the system. In the first procedure, two gas storage flasks were used; one to store pure HCN gas and the other for cold trapping the binary mixture. After allowing the carbon sample to equilibrate with H₂O vapor, a valve (V6) isolated the adsorption chamber from both gas storage flasks. A liquid nitrogen cold trap was employed to trap the H₂O vapor not in equilibrium with the carbon behind a second valve (V7), which was then closed, HCN was next allowed to enter the system in a region between valves V6 and V7. V7 was opened after the H₂O had evaporated, and the two vapors were allowed to mix and reach room temperature before V6 was opened to the adsorption chamber. This procedure kept the partial pressure of H₂O constant and allowed the HCN partial pressure to be increased in controlled steps. The sample mass was allowed to stabilize as in the single gas isotherm, determinations and the data recorded. Subsequent amounts of HCN were introduced in the same manner by cold trapping the H₂O/HCN mixture after V6 had been again closed to prevent the adsorbate pressure from changing in the adsorption chamber. The second procedure was similar with the roles of H₂O and HCN reversed.

In the third procedure, a carbon sample was first allowed to come into equilibrium with a particular pressure of H₂O vapor and then the water vapor was collected in one of the gas storage flasks and allowed to mix with a controlled amount of HCN. The mixture was then treated in the same manner as a single vapor to determine an isotherm.

Care was taken to have each isotherm pass through a point where the partial pressure of water was ~0.8 of its saturation vapor pressure and the partial pressure of HCN was ~0.15 of its saturation vapor pressure.

After every isotherm, the carbon sample was heated to 400°C (BPL activated) or 150°C (ASC Whetlerite) for several hours at ~10⁻⁶ torr and the sample mass was recorded. Any increase over the initial dry sample mass was ascribed to chemisorption of the adsorbates.

Results and Discussion

Figure 1 is a conventional isotherm showing the volume of HCN adsorbed per gram of BPL activated carbon as a function of relative pressure (P/P_0) of the HCN adsorbate. P is the equilibrium isotherm pressure and P_0 the saturated vapor pressure of adsorbate. This data may also be plotted according to the Dubinin-Polanyi adsorption isotherm equation:⁴ $\log W = \log W_0 - k\epsilon^2$, where W is the volume of adsorbate, W_0 is the volume of adsorbate at saturation, k is a parameter which characterizes the adsorbate-adsorbent interaction, and ϵ , the adsorption potential, is equal to $RT \ln(P_0/P)$, where R is the gas constant and T the absolute temperature. W_0 and k values of 0.42 c.c./gm and 14.9×10^{-8} cal.²/mole.² were obtained for the BPL carbon and a W_0 value of 0.35 c.c./gm. was obtained for ASC Whetlerite. After exposure to HCN the BPL samples could be completely regenerated and did not, within our accuracy, show any significant chemisorption effects. The ASC Whetlerite did chemisorb > 0.04 c.c./gm., which lowered the adsorptive capacity of those samples for future isotherm measurements.¹

Figure 2 is a conventional isotherm showing the volume of H₂O adsorbed per gram of BPL activated carbon as a function of relative pressure of the H₂O adsorbate. Plotting this data according to the Dubinin-Polanyi adsorption isotherm equation yielded W_0 values of 0.40 c.c./gm. and 0.36 c.c./gm. for the BPL activated and the ASC impregnated carbons respectively. No chemisorption effects were observed. As shown in Fig. 2, there is a great deal of hysteresis exhibited, which persists at all relative pressures between 0.002 and 1.²

Figure 3 shows conventional isotherms for the three modes of binary vapor adsorption. The adsorption is expressed as mass adsorbed per gram of adsorbent in all three cases. The top curve shows the adsorption of HCN as a function of HCN relative partial pressure for a BPL carbon sample in equilibrium with H₂O at a relative partial pressure of 0.84 and an initial adsorption equal to 0.374 gm. of H₂O per gm. of carbon. Additional adsorption of HCN occurs which, with the H₂O already adsorbed, exceeds the amount of HCN or the amount of H₂O absorbed in a single vapor isotherm run. The HCN adsorption

considered alone, however, is only about half that observed for HCN in a single vapor isotherm.

The middle curve shows the adsorption of H₂O as a function of H₂O relative partial pressure for a BPL carbon sample in equilibrium with HCN at a relative pressure of 0.19 and an initial adsorption equal to 0.301 gm. of HCN per gm. of carbon. There is very little additional adsorption of water (~0.003 gm. of H₂O per gm. of BPL carbon) in the presence of HCN even up to relative water vapor pressures ~1.

The lowest curve is the adsorption of an H₂O/HCN mixture as a function of the ratio of the total pressure of the H₂O/HCN mixture to the sum of their saturation vapor pressures. The adsorption noted in this phase of the experiment was substantially less than that observed in the other two modes of adsorption.

It is instructive to note that each of the isotherms shown contain points which reflect HCN relative pressures up to 0.2 and H₂O relative pressures up to 0.8.

It would appear that the HCN gas is soluble in water and goes into solution with the adsorbed (liquid) phase present on the carbon which has been pre-exposed to water vapor relative pressures of about 0.8. This adsorption probably does not reflect the adsorptivity of the carbon, but rather the affinity of the H₂O adsorbed (liquid) phase for HCN.

When the carbon is pre-exposed to HCN and then to H₂O, the total adsorption seems to be almost entirely due to HCN with only a very small adsorption of H₂O. This implies that while HCN is soluble in water, under the conditions of adsorption, the reverse is not true.

The adsorption of the mixture, without any pre-exposure, results in less adsorption than would be expected for either vapor separately. This may be interpreted as a competitive process which is not conducive to mutual adsorption.

In all cases, the BPL activated carbon samples showed very small chemisorption effects entirely consistent with the limits of experimental precision. The ASC Whetlerite carbons showed chemisorption effects similar to those exhibited in the adsorption of HCN alone.

Acknowledgments

This research was supported by the Department of the Army through Edgewood Arsenal Contract No. DAAA15-74-C-0163.

References

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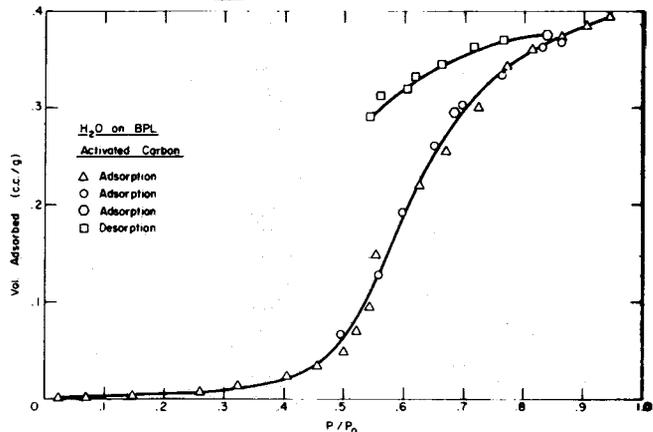


Figure 2. H₂O on BPL Activated Carbon

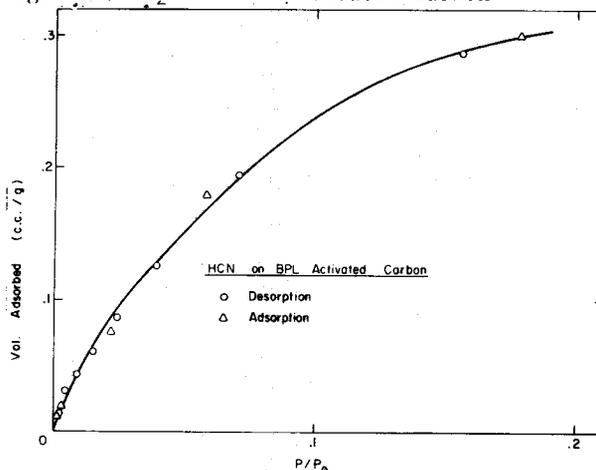


Figure 1. HCN on BPL Activated Carbon

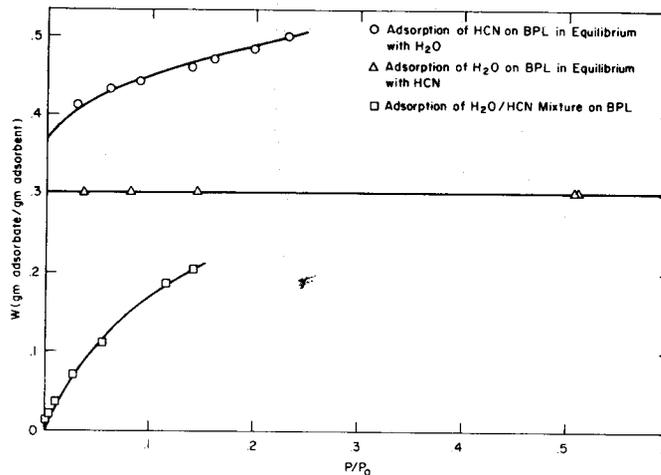


Figure 3. Mixed Vapor Isotherms on BPL Activated Carbon