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The Physical Adsorption of Trichloroethylene on Uranium Dioxide*

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Adsorption isotherms for trichloroethylene adsorption on UO_2 were obtained gravimetrically in the range 0 to 50°C. The adsorption data were then evaluated in terms of the Freundlich, Langmuir, BET, and potential theories of adsorption. Isosteric heats of adsorption were calculated as a function of surface coverage and vary from an estimated 9.0 kcal/mole at zero coverage to 7.2 kcal/mole at a relative coverage of 1.9. The adsorption of argon on UO_2 was also measured and used to calculate the UO_2 surface area. Using the BET equation, a value of 30 $Å^2$ was calculated for the cross-sectional area of the C_2HCl_3 molecule. It was concluded that C_2HCl_3 adsorption is nonlocalized and forms continuous monolayers.

INTRODUCTION

Uranium dioxide has been used as a fuel for nuclear reactors for a number of years. During this time a great deal of effort has been expended to evaluate its physical and chemical properties. Very little, however, is known about the surface and catalytic properties of UO_2. Early adsorption studies conducted by Roberts (*1*) showed oxygen to be chemisorbed very rapidly at −183°C. More recently, the adsorption of carbon tetrachloride was investigated (*2*) in order to explain the interaction between halogenated solvents and UO_2. This type of study was necessitated by the fact that solvents are used extensively for cleaning storage containers and processing equipment. During exposure to the process environments, solvent vapors can be adsorbed on the UO_2. If an excessive amount of solvent remains adsorbed on the oxide when it is sealed in either a fuel element or storage container, serious pressurization may result at elevated temperatures.

The present study was undertaken to determine the adsorption characteristics of trichloroethylene (C_2HCl_3). The heat of adsorption of trichloroethylene on UO_2 was calculated as was the size of the adsorbed C_2HCl_3 molecule. Also included in this investigation was a measurement of the adsorption of argon on UO_2.

EXPERIMENTAL METHODS

Apparatus

Adsorption of C_2HCl_3 was measured gravimetrically using a Cahn Model RG recording microbalance. The weighing mechanism was enclosed in a metal vacuum chamber which could be evacuated into the 10^{-7} Torr range. Prior to beginning the experiments the operational characteristics of the balance were evaluated by making a number of blank runs at the adsorption temperatures. Calibration curves were then prepared to correct the adsorption data for sample buoyancy. It was found that the effects of buoyancy could be minimized by installing aluminum foil baffles in both the sample and counterbalance hangdown tubes. During adsorption of C_2HCl_3 the temperature of the sample was controlled to ±0.1°C with a constant temperature bath. Vapor pressures during the adsorption runs

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were measured with a Baratron pressure meter with an accuracy of ±0.2 Torr.

Materials

The UO_2 used for this investigation was prepared by the extended air oxidation of uranium metal at room temperature. A random sample weighing 0.7920 g was taken from this bulk supply for use in this study. Total impurity content of this sample was 540 ppm. Further examination by X-ray diffraction showed the oxide to be UO_2 with a trace of U_3O_8. During the sample pretreatment the U_3O_8 was converted to UO_2.

Reagent grade trichloroethylene containing 10–25 ppm diisopropylamine inhibitor was used for this investigation. The C_2HCl_3 was prepared for use by loading 200 ml in a stainless steel container and removing the air by a series of freezing and evacuation steps. The effectiveness of this procedure was evaluated by a mass spectrometer analysis of the C_2HCl_3 vapor. This analysis showed the solvent to be free of air and other impurities.

Procedure

The UO_2 sample was initially outgassed for 25 hr at 300°C and 5×10^{-5} Torr. Following each adsorption run the sample was again outgassed at 300°C for about 18 hr. The first adsorption measurements were made using argon as the adsorbate at −195.4°C. This information was then used to calculate the UO_2 surface area. Trichloroethylene adsorption and desorption was measured at 0.0, 15.0, 30.0, and 50.0°C. During each run the pressure was varied between 0 Torr and the saturation vapor pressure at the particular adsorption temperature. Desorption was accomplished by immersing the C_2HCl_3 reservoir in liquid nitrogen. The weight change of the sample due to adsorption or desorption was monitored continuously during the experiment.

RESULTS AND DISCUSSION

Argon Adsorption on UO_2

Argon adsorption on UO_2 at −195.4°C represents a typical physical adsorption system. The adsorption isotherm shown in Fig. 1 was completely reversible. Data from this isotherm were used to calculate the BET (*3*) surface area of the UO_2. Figure 2 shows a plot of the BET equation using the argon adsorption data. A least squares analysis of these data resulted in a value of 0.870 mg/g for $(\chi/m)_m$, the weight of argon required for monolayer coverage. Assuming a value of 13.8 Å^2 for the size of the

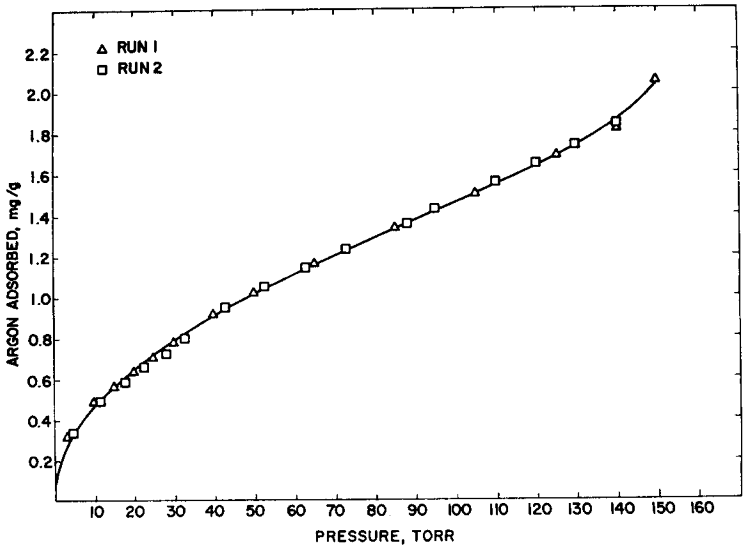

FIG. 1. Isotherm for the adsorption of argon on uranium dioxide at −195.4°C.

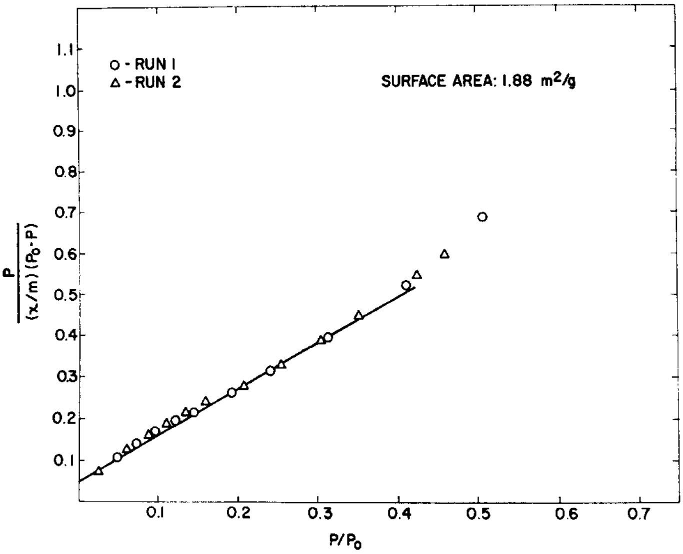

FIG. 2. BET plot for the adsorption of argon on uranium dioxide.

argon molecule (*4*), the UO_2 surface area was calculated to be 1.88 m^2/g.

Trichloroethylene Adsorption

Trichloroethylene adsorption on UO_2 was characterized by the series of Type II (*5*) isotherms shown in Fig. 3. These isotherms typify multilayer adsorption and were obtained from three or more reproducible runs. The experiments indicate there is no apparent reaction between UO_2 and C_2HCl_3 and during the adsorption process a physical type equilibrium exists.

Previous adsorption measurements on UO_2 (*2*) indicated that the oxide surface was heterogeneous. Nonlocalized adsorption on a heterogeneous surface can most simply be described by the Freundlich equation (*5*),

$$\frac{X}{m} = kp^{1/n},$$

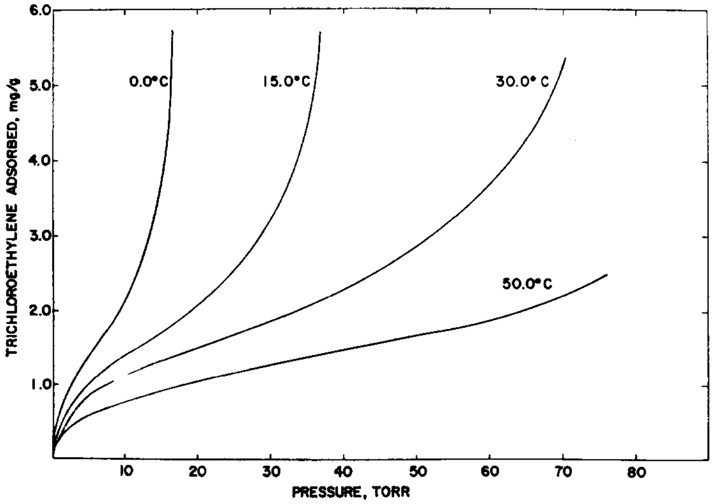

FIG. 3. Isotherms for the adsorption of trichloroethylene on uranium dioxide.

where χ/m = quantity adsorbed, p = pressure, k and n are constants. When it is obeyed it provides a concise analytical expression for the experimental facts, rather than an explanation of the mechanism of adsorption.

A log–log plot of the amount of C_2HCl_3 adsorbed versus pressure is shown in Fig. 4. The data obey the Freundlich very well until the saturation pressure is approached. Adsorption constants obtained from the Freundlich equation are shown in Table 1. The slopes, $1/n$, of the lines obtained from log–log plots are invariably less than unity (*6*). This can be explained by assuming that adsorption takes place on sites of progressively decreasing activity. The constant k is equal to the amount adsorbed at unit pressure. The decrease in k with increasing temperature is a measure of the decrease in adsorption with increasing temperature at unit pressure.

A further attempt was made to evaluate the data using the Langmuir equation (*5*),

$$\frac{P}{\chi/m} = \frac{1}{(\chi/m)_m b} + \frac{P}{(\chi/m)_m}.$$

However, since this theory is limited to monolayer adsorption on uniform surfaces it could not be expected to fully describe the adsorption observed here. When the data were substituted into this equation it was found that the theory was obeyed only at the lower pressures. The goodness of fit decreased with temperature. The deviation at higher pressures may demonstrate the inhomogeneity of the surface as well as indicate the beginning of multilayer adsorption.

TABLE 1

ADSORPTION CONSTANTS FOR TRICHLOROETHYLENE ADSORPTION ON URANIUM DIOXIDE

Temp (°C)	k	$1/n$
0.0	0.77	0.40
15.0	0.52	0.43
30.0	0.45	0.40
50.0	0.30	0.41

Molecular Area of C_2HCl_3

The foundations for describing polymolecular physical adsorption were laid by Brunauer, Emmett and Teller (*3*). Their BET isotherm equation yields two constants, $(\chi/m)_m$ and c. The first is the monolayer capacity of the adsorbent and the second is associated with the heat of adsorption. Application of this equation to the adsorption of argon was discussed earlier during the calculation of the surface area of the UO_2. The BET equation leads to reliable values of $(\chi/m)_m$ only at large values of c which are typical of low-tem-

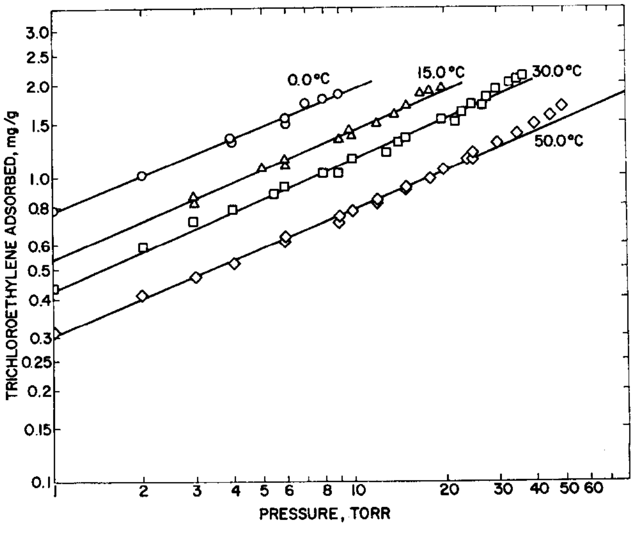

FIG. 4. Freundlich isotherms for trichloroethylene adsorption on uranium dioxide.

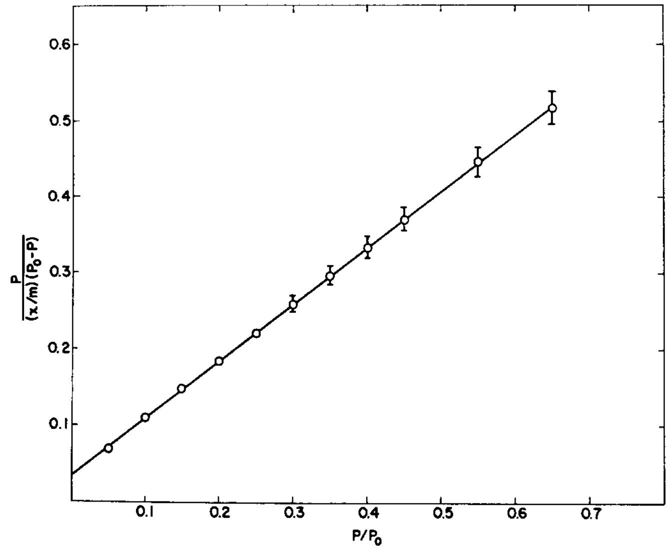

FIG. 5. A least squares fit of the trichloroethylene adsorption data at 0, 15, 30, and 50°C to the BET equation.

perature adsorption. However, this equation may also be used to describe adsorption at higher temperatures if the isotherms are Type II with well-defined "knee-bends" or plateau regions.

The Type II isotherms obtained for the C_2HCl_3 adsorption on UO_2 were further evaluated using the BET equation. Figure 5 shows a least squares fit of all the C_2HCl_3 adsorption data to the BET equation. The spread in the data at higher pressures begins primarily at relative pressures greater than 0.3 where the BET equation ceases to be applicable. For pressures less than 0.3 the data fit the BET equation very well. Table 2 summarizes the BET constants for both argon and C_2HCl_3 adsorption.

TABLE 2
BET CONSTANTS FOR ARGON AND TRICHLOROETHYLENE ADSORPTION ON UO_2

Adsorbate	Temp (°C)	$(\chi/m)_m$ (mg/g)	c (BET)
Argon	−195.4	0.87	24.3
C_2HCl_3	0.0	1.23	23.2
C_2HCl_3	15.0	1.39	24.0
C_2HCl_3	30.0	1.35	21.2
C_2HCl_3	50.0	1.39	24.0

The principal application of the BET equation is the calculation of adsorbent surface areas. Through use of a standard adsorbent, however, the molecular area, ω, of the adsorbate may be calculated. Assuming the UO_2 surface area measured by argon adsorption is correct, the apparent molecular area of adsorbed C_2HCl_3 may be calculated by the equation

$$\omega = 13.8\,\frac{(\chi/m)_m^{\mathrm{Ar}}}{(\chi/m)_m^{\mathrm{C_2HCl_3}}},$$

where $(\chi/m)_m^{\mathrm{Ar}}$ is the monolayer capacity for argon adsorbed on UO_2 and $(\chi/m)_m^{\mathrm{C_2HCl_3}}$ is the mean monolayer capacity for trichloroethylene at 0, 15, 30, and 50°C. Using this equation the value obtained for ω for C_2HCl_3 was 30 Å^2.

The validity of this number may be suspect since values for ω depend upon the nature of the adsorbent. For nonspecific adsorption ω is practically constant, while for specific adsorption molecular areas change abruptly with chemical modification of the surface. Machin (7) has suggested that CCl_4 is adsorbed in a localized manner which suggests a possible dependence of the CCl_4 molecular area on the adsorbent structure. For several different adsorbents the molecular area of CCl_4 varied from 26 to 39 Å^2. Based upon adsorption studies of C_2HCl_3 on just one adsorbent the possible variations in ω with different adsorbents could not be evaluated.

If it is assumed, however, that the molecules adsorbed on the surface have the same packing as those of the condensed phase, the value of ω is given by

$$\omega = 3.464 \times 10^{16} \left[\frac{M}{4\sqrt{2}N\delta_1} \right]^{2/3}$$

where M is the molecular weight, N is Avogadro's number, and δ_1 is the density of the liquid adsorbate (*5*). Using this equation, ω for C_2HCl_3 was calculated to be 31 Å^2. The agreement between this value and the value for ω calculated from the UO_2 surface area is very good. This indicates that there is a relatively weak localization of adsorbed C_2HCl_3 molecules corresponding to continuous monomolecular layers.

Potential Theory of Adsorption

Polanyi's theory (*5*, *8*, *9*) defines the adsorption potential at a point near the surface as the work done by the temperature independent adsorption forces in bringing a molecule from the gas phase to that point near the surface. The potential theory applies to both monomolecular and multimolecular adsorption. It is the only theory of physical adsorption that can quantitatively describe adsorption on a strongly heterogeneous surface.

The function of this theory is to determine the distribution of the volume of adsorption space, ϕ, as a function of the adsorption potential ϵ. That is,

$$\phi = f(\epsilon),$$

which is the equation of the characteristic curve. The adsorption potential is determined by the equation,

$$\epsilon = RT \ln P_0/P_x,$$

where P_x is the equilibrium pressure and P_0 is the vapor pressure. In Polanyi's concept of equipotential surfaces, the volume enclosed between the adsorbent and the equipotential surface ϵ is ϕ and is given by

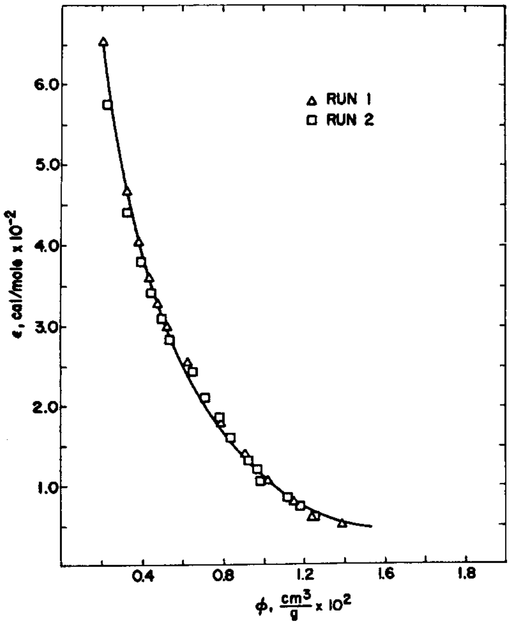

FIG. 6. Polanyi characteristic curve for the adsorption of argon on uranium dioxide at −195.4°C.

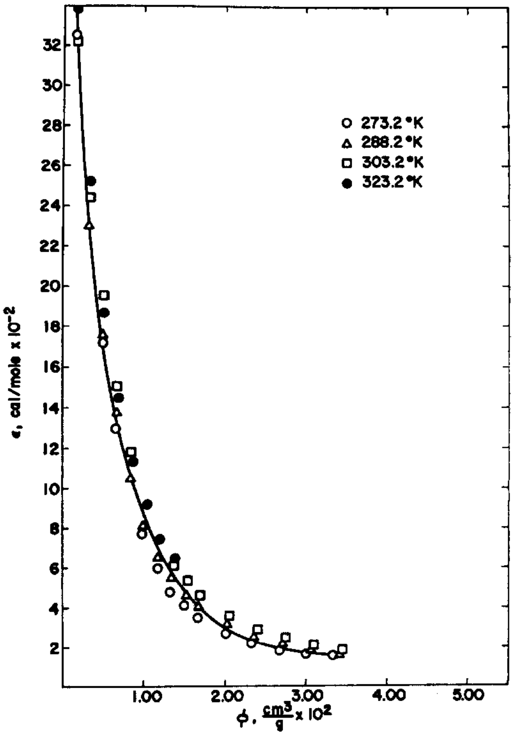

FIG. 7. Polanyi characteristic curve for trichloroethylene adsorption on uranium dioxide.

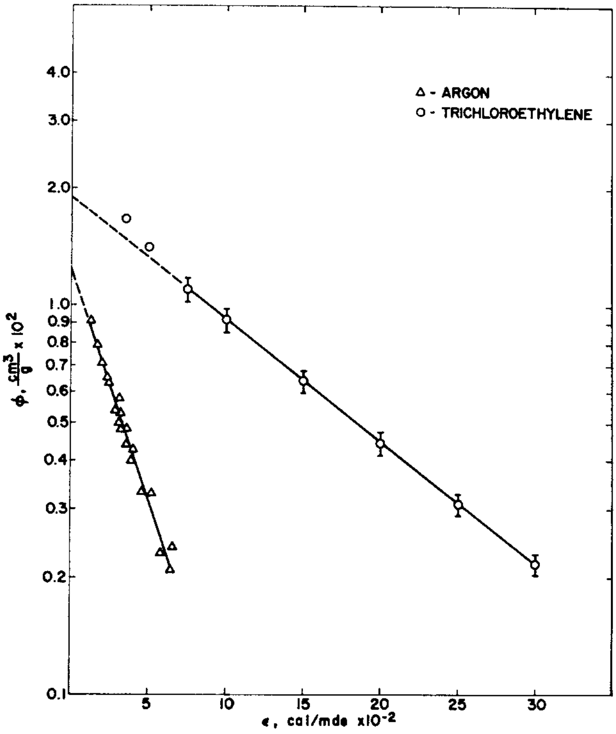

FIG. 8. Dubinin–Polanyi characteristic curve for argon and trichloroethylene adsorption on uranium dioxide.

$$\phi = \frac{\chi/m}{\delta_T}.$$

In this equation, χ/m is the weight of the adsorbed film and δ_T is the liquid density at the adsorption temperature T.

Figures 6 and 7 show the characteristic curves for the adsorption of argon and C_2HCl_3, respectively. These curves were calculated from the adsorption isotherms discussed earlier. As Fig. 7 shows, points from all four adsorption temperatures fall on the single characteristic curve.

For adsorbents which are either nonporous or contain large pores Dubinin (*10*) has shown that the equation for the characteristic curve can be written as:

$$\phi = \phi_0 e^{-m\epsilon/\beta}$$

or

$$\log \phi = \log \phi_0 - 0.434 \frac{m\epsilon}{\beta},$$

where ϕ_0 is the limiting volume of adsorption space, m a structural constant for the adsorbent, and β the affinity coefficient for the adsorbate. In this case the Dubinin–Polanyi type plot of log ϕ versus ϵ gives a straight line characteristic curve whose y-axis intercept is log ϕ_0.

A plot of the above equation is shown in Fig. 8 for both argon and C_2HCl_3 adsorption on UO_2. In this case the limit volume ϕ_0 varies from 0.012 cm^3/g for argon to 0.019 cm^3/g for C_2HCl_3.

Heat of Adsorption

The isosteric heat of adsorption of C_2HCl_3 was calculated from the adsorption isosteres using the Clausius-Clapeyron equation (*11*). These heats were found to be independent of temperature as indicated by the linear isosteres (Fig. 9). The variation in the isosteric heat of adsorption with surface coverage is shown in Fig. 10. The leveling out of the curve at about θ equal to 1.0 was probably caused by adsorption

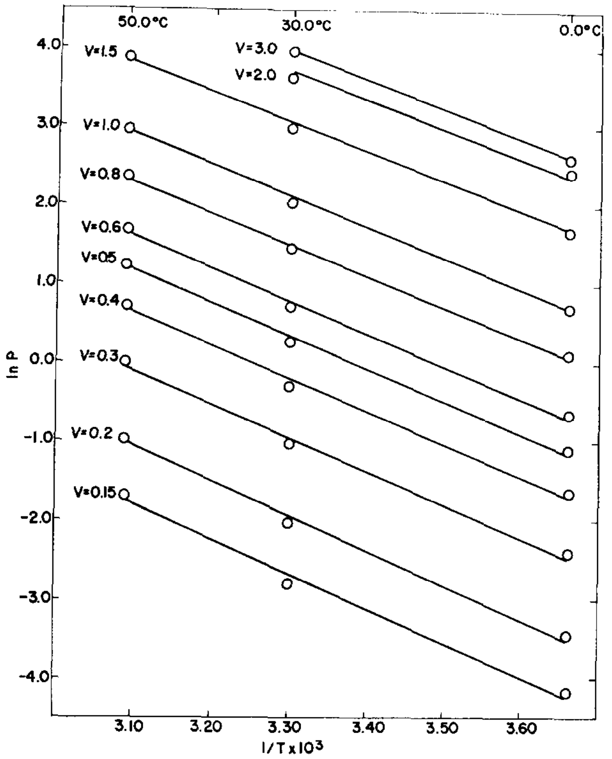

FIG. 9. Isosteres for trichloroethylene adsorption on uranium dioxide.

on less active sites and the completion of the initial monolayer. During the adsorption of the initial molecular layer the heat of adsorption decreased from an estimated 9.0 kcal/mole at zero coverage to 7.65 kcal/mole. Adsorption in the second molecular layer was most likely the reason for the further decrease in the heat of adsorption to the minimum of 7.25 kcal/mole at coverage of 1.9.

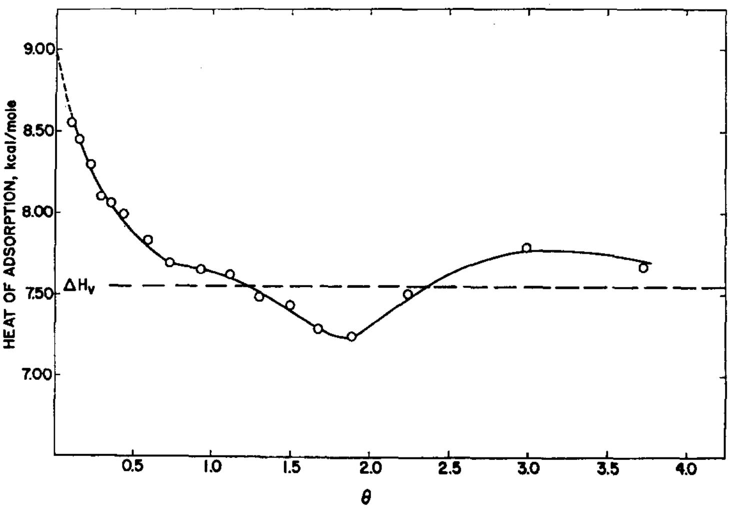

FIG. 10. Variation of the isosteric heat of adsorption with surface coverage.

CONCLUSION

The interaction between UO_2 and C_2HCl_3 was studied using a series of adsorption measurements in the temperature range 0–50°C. Adsorption was found to be physical in nature with a heat of adsorption ranging from 7 to 9 kcal/mole. The adsorption data were evaluated using the Freundlich, Langmuir, BET, and potential theories of adsorption. It was found that the best explanation of the adsorption process was given by the Freundlich, BET, and potential theories. This is consistent with the UO_2 surface being heterogeneous. Argon adsorption on UO_2 was also investigated using the BET and potential theories. The UO_2 surface area measured by argon was used to calculate the molecular area of adsorbed C_2HCl_3. The value calculated for the size of the C_2HCl_3 molecule was 30 Å^2. This compares to 31 Å^2 which is the theoretical size of the C_2HCl_3 molecule in the condensed phase. The agreement between these two values indicates C_2HCl_3 is not localized but forms a continuous molecular layer.

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