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The Adsorption of Carbon Tetrachloride on Uranium Dioxide*

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The interaction between carbon tetrachloride and uranium dioxide was investigated from a series of gravimetric adsorption measurements in the temperature range 0–50°C. All of the isotherms were Type II and completely reversible. Adsorption data could be fit to the Freundlich equation which along with the smoothness of the isotherms suggested a heterogeneous surface. The variation in the isosteric heat of adsorption, from an estimated 11.50 kcal/mole at zero coverage to 7.50 kcal/mole at a relative coverage of 1.9, further indicated the heterogeneous nature of the uranium dioxide surface. Application of the Polanyi theory produced a single characteristic curve which was independent of temperature. The surface area of the uranium dioxide was measured by argon adsorption and the cross-sectional area of the CCl_4 molecule was then calculated to be 33 Å^2 by an application of the BET equation.

INTRODUCTION

Chlorinated solvents are used extensively for cleaning nuclear materials such as plutonium and uranium. Since these materials are radioactive any trace amounts of solvent remaining on the metal or its oxide coating may be radiolytically decomposed into products which may readily react with the metal. Solvent radiolysis has even more serious ramifications in the area of oxide storage. If adsorbed contaminants such as water and hydrocarbons are not removed prior to sealing the storage container, a pressure buildup can result from the radiolysis of the contaminants (*1*). Prevention of a pressure buildup as well as possible chemical reactions originating from the presence of solvents on nuclear materials must begin with an understanding of the possible gas–solid interactions. Adsorption studies involving CCl_4 have been carried out by other workers (*2–6*). However, no work has been performed on systems consisting of nuclear materials and CCl_4.

The work described in this paper was undertaken to better understand the interactions between CCl_4 and UO_2. This investigation includes the measurement of CCl_4 adsorption on UO_2. The thermodynamic properties of the adsorbed layers were calculated from adsorption data, and the size of the CCl_4 molecule was determined experimentally by an application of the BET equation.

EXPERIMENTAL METHODS

Apparatus

The adsorption of CCl_4 was measured gravimetrically using the system described previously (*7*). A Cahn Model RG recording microbalance is the principal component of this system. The sample was contained in a quartz bucket suspended from a quartz fiber. During adsorption the temperature of the sample was controlled to ±0.1°C with a constant temperature bath. Carbon tetrachloride vapor pressures were measured with a Baratron Series 90 pressure meter in the 0–10 Torr region and with a Wallace and Tiernan pressure gauge from 10 to 140 Torr. Accuracy of the pressure measurements was ±0.01 Torr in the

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0–10 Torr region and ±0.5 Torr in the 10–140 Torr range.

Materials

The UO_2 used for this study was prepared by air oxidation of uranium metal. A random sample weighing 0.740 g was taken from the bulk supply for use in this experiment. Analysis of this oxide sample by spark source mass spectrography showed a total impurity content of 540 ppm. Further examination by X-ray diffraction showed the composition to be UO_2.

Reagent grade CCl_4 was used for this investigation. The CCl_4 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 process was evaluated by a mass spectrometer analysis of the CCl_4 vapor. This analysis showed the CCl_4 to be free of air and other contaminants.

PROCEDURE

The oxide was initially outgassed at 300°C for 18 hr at about 5×10^{-5} Torr. This outgassing step was also used after each adsorption run. Surface area measurements were made using argon adsorption at −195°C. Following the surface area measurements, CCl_4 adsorption was measured at 0.0, 15.0, 30.0, and 50.0°C. During each run the CCl_4 pressure was varied between 0 Torr and the saturation pressure of CCl_4. The weight gain of the sample due to adsorption was monitored continuously during the experiment.

RESULTS AND DISCUSSION

UO_2 Surface Area

The surface area of the UO_2 sample was measured by the BET technique (*8*) using argon adsorption. The argon adsorption isotherm was a typical Type II isotherm which was completely reversible.

Analysis of this data using the BET equation resulted in a value of 0.718 for $(x/m)_m$, the quantity of argon required for monolayer coverage. The surface area of the UO_2 sample could then be determined from $(x/m)_m$ if the size of the argon molecule were known. The most generally accepted value for the size of the argon molecule at −195°C is 13.8 Å^2 (*2*). From this value and $(x/m)_m$, the UO_2 surface area was calculated to be 1.55 m^2/g.

Carbon Tetrachloride Adsorption

Carbon tetrachloride adsorption on UO_2 was characterized by a series of Type II isotherms typical of multimolecular layer adsorption (Fig. 1). Adsorption at all four temperatures was reversible and reproducible. These experiments indicate that there is no apparent chemical reaction between UO_2 and CCl_4 and that a physical type equilibrium exists between the adsorbed CCl_4 and the CCl_4 in the gas phase.

An examination of the adsorption isotherms in Fig. 1 showed that they were smooth over the entire pressure range. This absence of steps is indicative of a heterogeneous surface (*9, 10*). Nonlocalized adsorption on a heterogeneous surface can be most simply described by the Freundlich equation (*9*),

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

where x/m = quantity adsorbed, p = pressure, and k and n are constants.

A log–log plot of the amount of CCl_4 adsorbed versus pressure is shown in Fig. 2. These data obey the Freundlich equation over the entire adsorption region. Adsorption constants obtained from the Freundlich equation are shown in Table 1.

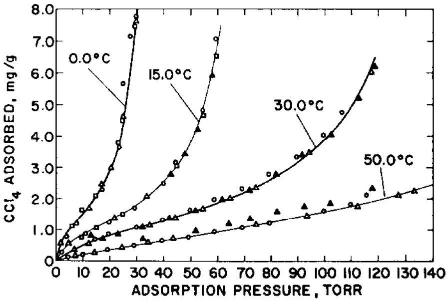

FIG. 1. Type II isotherms for the adsorption of carbon tetrachloride on uranium dioxide. Symbols denote multiple adsorption runs.

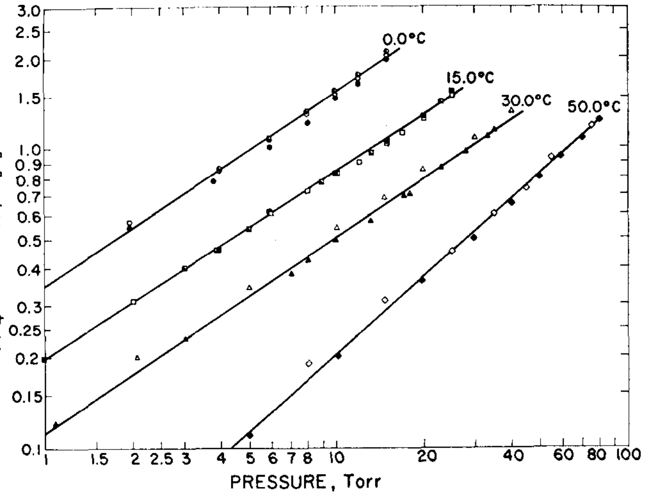

FIG. 2. Freundlich plot for carbon tetrachloride adsorption on uranium dioxide. Symbols denote multiple adsorption runs.

Deviations in the slope, $1/n$, from the theoretically expected unity can be explained on the assumption that adsorption takes place on sites of decreasing activity (*9*).

The CCl_4 adsorption data were further evaluated using the BET adsorption equation. The volume of CCl_4 required for a monomolecular layer was calculated from the BET plots shown in Fig. 3. For the three temperatures, 0.0, 15.0, and 30.0°C, $(x/m)_m$ varied from 1.14 to 1.19 mg/g. This agreement was not nearly as good for the 50.0°C isotherm since the higher temperature created more pressure variation and considerable scatter in the BET plot.

The previously reported molecular cross-sectional area for CCl_4 is 37 Å^2 (*2*). Assuming the UO_2 surface measured by argon adsorption is accurate, the apparent molecular area of CCl_4 was calculated from the $(x/m)_m$ value obtained from the CCl_4 adsorption data. The value obtained for the molecular area of CCl_4 was 33 Å^2. This value is in reasonably good agreement with the theoretical value of 37 Å^2. Machin (*11*) has suggested that CCl_4 is adsorbed in a localized manner which would indicate a possible dependence of the CCl_4 molecular area on the adsorbent structure. Such a dependence was found for several adsorb-

TABLE 1
ADSORPTION CONSTANTS FOR CARBON TETRACHLORIDE ADSORBED ON URANIUM DIOXIDE

Temp (°C)	k	$1/n$
0.0	0.35	0.64
15.0	0.20	0.63
30.0	0.115	0.65
50.0	0.029	0.87

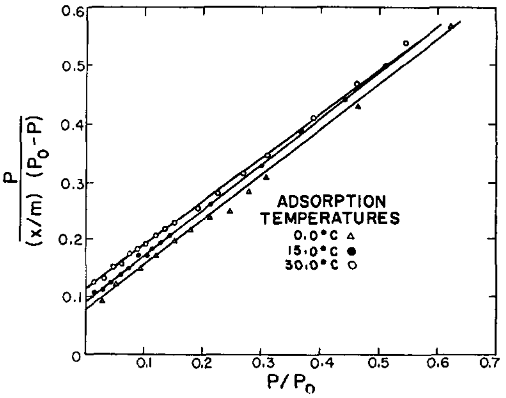

FIG. 3. BET plot for the adsorption of carbon tetrachloride on uranium dioxide at 0.0, 15.0, and 30.0°C.

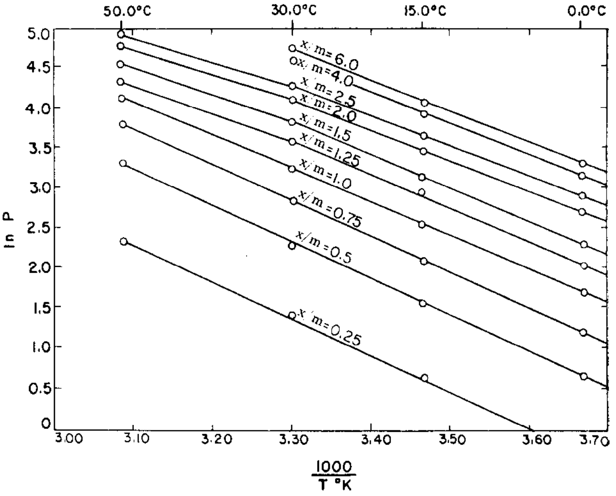

FIG. 4. Carbon tetrachloride adsorption isosteres.

ents with "unit cell areas" ranging from 40 to 44 Å^2. In this case the apparent molecular area of CCl_4 varied from 26 to 39 Å^2 (*11*). This type of dependence may partially explain the somewhat low value of 33 Å^2 calculated for the molecular area of CCl_4 adsorbed on UO_2.

Adsorption Thermodynamics

The thermodynamic properties, ΔG, ΔS, and q_{st} were calculated from the CCl_4 adsorption data (*12*). Isosteric heats of adsorption were calculated from adsorption isosteres using the Clausius-Clapeyron equation. These heats were found to be independent of temperature up to a monolayer coverage as indicated by the linear isosteres (Fig. 4). Adsorption in the multimolecular layer region resulted in heats of adsorption that were more temperature dependent. Figure 5 shows the isosteric heat curve for CCl_4 adsorbed on UO_2. The steep initial slope of the heat curve is indicative of adsorption on a heterogeneous surface. Molecules adsorbed first were adsorbed preferentially on the most active sites. The leveling out of the heat curve at about θ equal to 1.0 was probably due to adsorption on less active sites and the completion of the monolayer. During the adsorption of the monolayer the heat of adsorption decreased from about 11.50 to 8.45 kcal/mole. Subsequent adsorption in the second molecular layer was most likely the reason for the further decrease in the heat of adsorption to 7.50 kcal/mole at a coverage of 1.9.

A compilation of all the thermodynamic properties calculated for CCl_4 adsorption on UO_2 is given in Table 2. Both the free energy and the isosteric heat of adsorption decreased with surface coverage. The isosteric differential entropy was most negative when the surface coverage was equal to 1 and 3 molecular layers. This type of behavior is generally attributed to a more ordered type of adsorption (*9*).

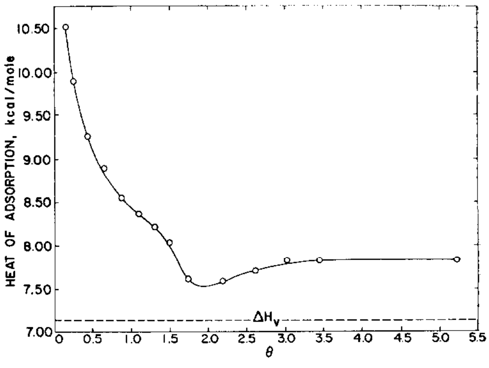

FIG. 5. Isosteric heats of adsorption for carbon tetrachloride adsorbed on uranium dioxide.

TABLE 2

THERMODYNAMIC DATA FOR CARBON TETRACHLORIDE ADSORPTION ON URANIUM DIOXIDE

θ	T (°K)	P (Torr)	$-\Delta S$ (cal/mole deg)	q_{st} (kcal/mole)	$-\Delta G$ (kcal/mole)
0.22	273.2	0.65	22.18	9.89	3.83
	288.2	1.70	22.21		3.49
	303.2	4.30	22.33		3.12
	323.2	11.5	22.28		2.69
0.43	273.2	1.90	22.00	9.26	3.25
	288.2	4.75	22.03		2.91
	303.2	10.00	21.93		2.61
	323.2	28.0	22.09		2.12
0.65	273.2	3.25	21.67	8.88	2.96
	288.2	8.30	21.83		2.59
	303.2	17.5	21.80		2.27
	323.2	45.0	21.84		1.82
0.86	273.2	5.25	21.38	8.54	2.70
	288.2	13.5	21.62		2.31
	303.2	26.3	21.47		2.03
	323.2	61.5	21.44		1.61
1.08	273.2	7.50	21.38	8.35	2.51
	288.2	19.0	21.65		2.11
	303.2	36.6	21.50		1.83
	323.2	78.5	21.32		1.46
1.29	273.2	10.0	21.41	8.20	2.35
	288.2	24.3	21.62		1.97
	303.2	46.5	21.50		1.68
	323.2	94.0	21.23		1.34
1.51	273.2	12.3	21.17	8.02	2.24
	288.2	29.0	21.34		1.87
	303.2	55.5	21.24		1.58
	323.2	109.0	20.95		1.25
1.72	273.2	14.5	19.88	7.58	2.15
	288.2	33.0	20.06		1.80
	303.2	62.5	20.02		1.51
	323.2	122.5	19.83		1.17
2.16	273.2	17.7	20.28	7.58	2.04
	288.2	40.0	20.44		1.69
	303.2	75.5	20.42		1.39
	323.2	140.0	20.08		1.09
2.59	273.2	20.0	20.97	7.70	1.97
	288.2	45.0	21.10		1.62
	303.2	86.5	21.08		1.31
3.02	273.2	22.2	21.60	7.82	1.92
	288.2	48.5	21.65		1.58
	303.2	95.5	21.67		1.25
3.45	273.2	23.7	21.73	7.82	1.88
5.17	273.2	27.7	22.15	7.85	1.80

Potential Theory of Adsorption

Polanyi's theory (*13–15*) defines the adsorption potential at a point near the surface as the work done by the adsorption forces in bringing a molecule from the gas phase to that point. 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. However, since the theory does not attempt to formulate an isotherm equation the scope of information obtainable is limited.

The adsorption potential ϵ of a gas near the adsorbent is the work done in compressing one mole of vapor from the equilibrium pressure P_x to the vapor pressure P_0, and is given by

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

In Polanyi's concept of equipotential surfaces the volume enclosed between the adsorbent and the equipotential surface ϵ is φ. The value of φ corresponding to any given ϵ is

$$\varphi = \frac{x}{\partial_T},$$

where x is the weight of the adsorbed film and ∂_T is the liquid density at the adsorption temperature T. The potential theory assumes the adsorption potential does not change with temperature. Therefore, the curve representing the potential distribution, i.e., $\epsilon = f(\varphi)$, is the same for all temperatures. This curve is called the "characteristic curve" for the particular adsorption system.

Figure 6 shows the characteristic curve for the adsorption of CCl_4 on UO_2 as derived from the adsorption data. Adsorption data from the four temperatures studied fall on this curve as demanded by the Polanyi theory.

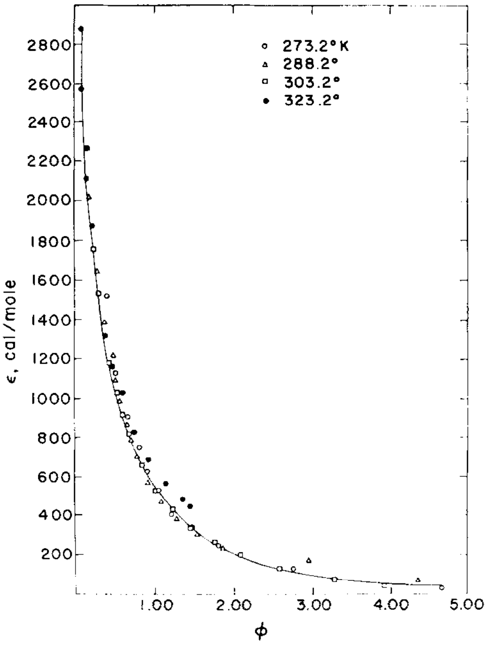

FIG. 6. Characteristic curve for the adsorption of carbon tetrachloride on uranium dioxide.

CONCLUSION

Carbon tetrachloride adsorption on UO_2 was measured from 0 to 50°C and over the CCl_4 vapor pressure range 0–120 Torr. Adsorption was found to be physical in nature involving van der Waals type forces. The data could not be fit to the Langmuir adsorption equation which required that the adsorbent be homogeneous. However, a good fit was obtained using the Freundlich equation. The data could also be explained using the Polanyi theory. These observations indicate that the UO_2 surface is heterogeneous. The surface area of the absorbent was measured using argon adsorption. This value was then used to calculate the cross-sectional area of CCl_4 using the BET equation. The calculated value of 33 Å^2 compared favorably with the reported value of 37 Å^2 and provided a check on the internal accuracy and consistency of the adsorption measurements.

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