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Adsorption of 1,1,1-Trichloroethane and Tetrachloroethylene on Silica Gel

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Adsorption studies of 1,1,1-trichloroethane and tetrachloroethylene on silica gel were carried out at 288, 293, and 298 K. Experimental data provided type I isotherms and were correlated by the Langmuir equation, the model of Hines et al., and the vacancy solution model developed on the basis of the Flory–Huggins activity coefficient model. The absolute errors between the values calculated by these models and the experimental data were below 5%. The surface area occupied by each adsorbate was calculated by using the BET equation.

Introduction

Two common indoor air pollutants that appear in most homes are 1,1,1-trichloroethane and tetrachloroethylene. The chlorinated hydrocarbon, 1,1,1-trichloroethane, comes into the home with aerosol sprays and is considered to be responsible for dizziness and irregular breathing. Tetrachloroethylene finds its way into homes in the form of dry cleaning fluids or fumes on clothes and may pose damage to human nerves, livers, and kidneys.

Although indoor air pollution has drawn considerable attention from researchers in recent years (*1–3*), relatively few studies have been made in which the pollutants were removed from the air. An adsorption study using silica gel as an adsorbent for indoor air pollutants was made by Kuo and Hines (*3*).

This study is an extension of the previous investigation and contains equilibrium isotherms for 1,1,1-trichloroethane and tetrachloroethylene on silica gel at 288, 293, and 298 K from low pressure up to saturation.

Experimental Section

The adsorbent used in this study was type PA 40, 80–100 mesh silica gel supplied by Davison Chemical Co. The 1,1,1-trichloroethane was obtained from J. T. Baker Chemical Co. and had a purity of 99.8%. The tetrachloroethylene was obtained from Eastman Kodak Co. with a purity of 99.5%.

The experimental adsorption studies were carried out gravimetrically using a Cahn C-2000 electrobalance, which has a sensitivity of 0.1 μg. The adsorption apparatus was housed in a vacuum bottle assembly and was designed so that either gases or vapors could be studied. A refrigerated–heated bath and circulator with a temperature control of ±0.1 K was used to control the adsorption temperature. A vacuum system consisting of two vacuum pumps, a sorption trap, and a diffusion pump was used to obtain a vacuum of 1×10^{-4} mmHg for the adsorption system during regeneration. The leak rate of the complete system was approximately 0.005 mmHg/h. Two thermistor gauges were used to monitor the pressure when the system was evacuated and during the adsorption runs. Pressures up to 760 mmHg were measured with a Wallace and Tiernan absolute pressure gauge with an accuracy of ±0.02 mmHg. The error of the weight measurements was estimated to be ±10 μg.

The adsorbent was regenerated by evacuating the system and applying heat at 423 K to the sample hang-down tube. Heating was continued until a constant sample weight was obtained, which typically required from 4 to 10 h. After regeneration, the adsorbent was cooled to the adsorption temperature and the adsorbate, which was degassed, was introduced into the system. When equilibrium was reached, as indicated by a constant sample weight, the pressure and weight were recorded. Equilibrium adsorption data were collected from very low pressures up to saturation. Following adsorption, desorption measurements were made by reducing the system pressure.

Buoyancy tests were conducted to determine the effects of the gas on the weight readings, other than the effect of actual gas adsorption. The procedure followed was exactly like the one used in collecting data, except that glass beads were placed in the sample pan rather than the adsorbent. The maximum error introduced by the buoyancy effect upon the measured adsorbed weight was estimated to be less than 0.5% for each adsorbate.

Results and Discussion

Equilibrium Data. Adsorption isotherms were obtained for 1,1,1-trichloroethane and tetrachloroethylene on silica gel at 288, 293, and 298 K after overnight regeneration of the adsorbent at 423 K in vacuo. The experimental equilibrium data are presented in Table I. The weight of the sample was measured to within 10 μg. Since the regenerated sample weight was 0.0856 g, the error in the weight measurement was 0.012%. Pressures were measured with an accuracy of ±0.1 mmHg. Except for the lowest pressures, the maximum error in the pressure measurements was less than 0.5%. The average error over the entire adsorption range was estimated to be less than 1%. Several of the data points were reproduced with differences no greater than 1%.

The adsorption data for both 1,1,1-trichloroethane and tetrachloroethylene on silica gel were type I, according to the Brunauer (*4*) classification, and showed no apparent hysteresis when either one was desorbed. The absence of capillary condensation, as shown by the equilibrium data, implies that silica gel contains mostly micropores. The amount of adsorbate removed by the silica gel is shown in Table I. The fact that the maximum uptake of both adsorbates by the silica gel was in the range of 0.444–0.472 g of adsorbate/(g of silica gel) suggests that silica gel is an effective adsorbent for removing either of the chlorinated hydrocarbons. It is important to note that if water vapor is present along with the chlorinated hydrocarbons, their uptake would be decreased significantly.

Data Correlation. The isosteric heats of adsorption were calculated at constant adsorbent loading from the relationship

$$q = -R\left[\frac{\partial(\ln P)}{\partial(1/T)}\right]_N \qquad (1)$$

The heterogeneity of the adsorbent surface is usually caused

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Table I. Adsorption Isotherm Data for 1,1,1-Trichloroethane and Tetrachloroethylene on Silica Gel

288 K		293 K		298 K	
P/mmHg	N/(mmol g^{-1})	P/mmHg	N/(mmol g^{-1})	P/mmHg	N/(mmol g^{-1})
		1,1,1-trichloroethane			
1.2	1.61	0.9	1.20	0.8	0.88
3.4	2.37	2.3	1.58	2.9	1.39
7.0	2.90	6.8	2.53	6.6	2.06
12.2	3.13	11.5	2.85	10.3	2.43
21.1	3.21	16.7	2.97	17.2	2.75
29.8	3.26	23.2	3.06	25.8	2.92
40.6	3.31	31.3	3.14	34.7	3.02
49.7	3.35	41.3	3.21	46.0	3.12
59.5	3.39	50.0	3.25	58.3	3.21
64.0	3.40	61.0	3.30	68.5	3.24
69.8	3.41	69.8	3.34	79.1	3.28
34.0	3.27	78.8	3.36	88.8	3.30
25.8	3.24	85.0	3.38	99.0	3.32
8.5	3.00	55.0	3.28	104.5	3.32
		34.3	3.17	85.3	3.28
		7.8	2.60	40.2	3.07
				15.6	2.68
		tetrachloroethylene			
0.2	1.60	0.20	1.47	0.15	1.16
0.7	2.10	0.75	1.98	0.65	1.55
1.4	2.37	1.60	2.32	1.30	2.05
2.2	2.52	2.30	2.45	2.00	2.27
3.0	2.63	2.8	2.51	2.75	2.39
3.8	2.69	3.8	2.61	3.80	2.50
4.7	2.73	5.1	2.68	4.50	2.54
5.9	2.77	6.3	2.71	5.60	2.59
7.0	2.80	8.1	2.74	7.10	2.64
8.5	2.82	9.8	2.77	8.40	2.65
9.8	2.83	11.3	2.78	9.80	2.68
6.2	2.78	5.0	2.67	11.50	2.68
1.0	2.21	2.2	2.42	13.70	2.69
0.3	1.81	0.8	2.00	12.50	2.68
				5.80	2.60
				2.25	2.31
				0.85	1.80

Table II. Variation of Isosteric Heats of Adsorption with the Amount Adsorbed

adsorbate	amount adsorbed/ (mmol/g of solid)	q/ (kcal/mol)	q_c/ (kcal/mol)
$C_2H_3Cl_3$	1.2	31.8	7.14–7.34
	1.6	19.2	
	2.0	17.7	
	2.4	17.1	
C_2Cl_4	1.6	23.2	8.08–8.32
	1.8	18.4	
	2.0	14.7	
	2.4	11.3	

by the differences in the adsorptive strength of the sites. The heterogeneity of the adsorption system can be detected from the shape of the adsorption isotherms and is usually evaluated by comparing the isosteric heats of adsorption at different loadings. As can be seen from Table II, the isosteric heats of adsorption in the beginning of the adsorption process exhibit the commonly observed trend of a decreasing amount of heat being liberated as the loading on the surface increased. As the adsorption proceeds, most of the more active sites will be filled and the remaining less active sites will release less heat. However, the heats of adsorption remained nearly constant after a certain surface loading (near monolayer coverage) was reached. The decreasing heats of adsorption indicate that the surface of the adsorbent is nonhomogeneous for both adsorbates. Since the heats of adsorption shown in Table II are of the same order of magnitude as the heats of condensation, it may be concluded that the adsorption of 1,1,1-trichloroethane and tetrachloroethylene on silica gel is due primarily to physical forces.

Table III. Monolayer Coverages N_m and Area per Molecule A Calculated by Using the BET Model

adsorbate	T/K	$10^{19}A$/ (m^2/molecule)	surface coverage/ (m^2/g of solid)	N_m/ (mmol/g)
$C_2H_3Cl_3$	288	4.28	740	2.87
	293	4.32	739	2.85
	298	4.38	741	2.81
C_2Cl_4	288	5.52	741	2.23
	293	5.60	738	2.19
	298	5.68	742	2.17

The BET model fit the data very well in the low-pressure region ($P/P_S \leq 0.35$) and was used to obtain the monolayer coverage and the surface area occupied by the molecules. The results are shown in Table III.

The equilibrium data were correlated by three different types of isotherm models, the Langmuir equation, the Hines et al. equation (*9*), which accounts for surface heterogeneity, and the vacancy solution model (*10*) developed using the Flory–Huggins activity coefficient equation (VSM-FH). The analytical form of these models is provided in Appendix 1. The parameters of the models were obtained by nonlinear regression analyses. Although all three models correlated the data with an average absolute deviation of less than 5%, the Hines et al. model provided the best correlation. The model parameters and average absolute deviations are presented in Table IV. In Figures 1 and 2, the experimental data at 288 K for 1,1,1-trichloroethane and tetrachloroethylene, respectively, were compared with values predicted by the model of Hines et al. and the VSM-FH model. As can be seen from the table, the parameter of the Hines et al. model showed a consistent decreasing or increasing trend with temperature, depending on the parameter,

Table IV. Comparison of Model Correlations[a]

		params of Langmuir eq			params of Hines et al. eq					params of VSM-FH eq[b]			
adsorbate	T/ K	m/ (mmol/g)	a/ mmHg	av abs dev/%	q_m/ (mmol/g)	K_1/ mmHg	K_2	K_3/ mmHg	av abs dev/%	N_1^∞/ (mmol/g)	b_1/ (mmol/ (g mmHg))	α_{1v}	av abs dev/%
$C_2H_3Cl_3$	288	3.447	0.711	1.06	3.500	2.223	−0.0825	0.450	0.99	3.529	2732.1	8.482	2.05
	293	3.405	0.439	2.54	3.474	4.001	−0.0289	0.335	1.95	3.550	2072.8	8.809	3.13
	298	3.408	0.250	3.21	3.455	5.691	−0.0025	0.084	1.53	3.498	1.683	1.593	2.18
C_2Cl_4	288	2.814	5.381	3.25	2.960	0.017	−51.15	0.803	0.21	2.933	19.89	1.465	2.33
	293	2.771	4.076	3.44	2.908	0.012	−98.85	0.829	0.30	2.880	17.10	1.488	2.22
	298	2.778	2.633	3.87	2.858	0.010	−200.00	0.943	1.75	2.763	7.59	$6.997\ 10^{-5}$	4.47

[a] Average absolute deviation (av abs dev) = (experimental − predicted)/experimental × 100 (%). [b] Vacancy solution model based on the Flory–Huggins activity coefficient model.

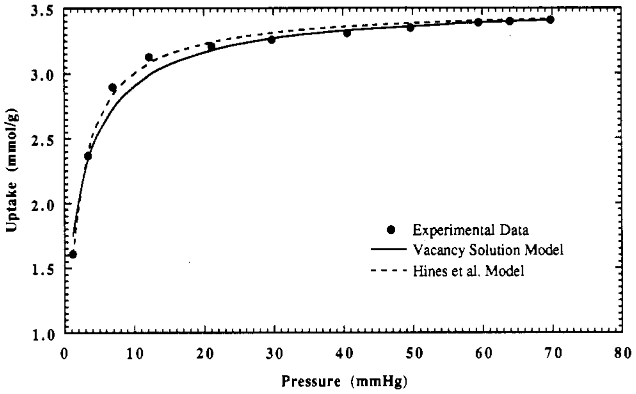

Figure 1. Comparison of 1,1,1-Trichloroethane data at 288 K with model predictions.

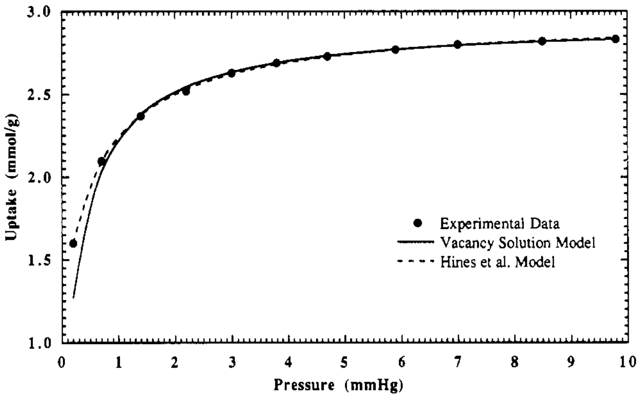

Figure 2. Comparison of tetrachloroethylene data at 288 K with model predictions.

whereas the parameters of the vacancy solution model did not exhibit consistent behavior.

Glossary

A	surface area of a molecule
a	Langmuir parameter
b_1	parameter in the VSM-FH equation
K_1	parameter in the Hines et al. equation
K_2	parameter in the Hines et al. equation
K_3	parameter in the Hines et al. equation
m	saturation adsorption capacity given by the Langmuir equation
N	equilibrium adsorption capacity
N_m	monolayer adsorption capacity
N_1^∞	saturation adsorption capacity given by the VSM-FH equation
P	system pressure
P_S	saturation pressure
q	isosteric heat of adsorption
q_c	heat of condensation
q_m	saturation adsorption capacity given by the Hines et al. equation
R	gas constant
T	system temperature
α_{1v}	parameter in the VSM-FH equation

Appendix 1

Langmuir equation:

$$N = \frac{maP}{1 + aP}$$

Hines et al. equation:

$$N = q_m\left[1 - \left(\frac{K_3}{K_3 - K_1K_2}\right)\left(\frac{K_1}{P + K_1} - \frac{K_1K_2}{P + K_3}\right)\right]$$

VSM-FH equation:

$$P = \left(\frac{N_1^\infty}{b_1}\frac{\theta}{1-\theta}\right)\exp\left(\frac{\alpha_{1v}{}^2\theta}{1 + \alpha_{1v}\theta}\right)$$

where $\theta = N/N_1^\infty$.

Registry No. $C_2H_3Cl_3$, 71-55-6; C_2Cl_4, 127-18-4.

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