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Correlation of Methyl Chloride, Methylene Chloride, Chloroform, and Carbon Tetrachloride Adsorption Data on Silica Gel

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Abstract

Adsorption data of the homologous series methyl chloride, methylene chloride, chloroform, and carbon tetrachloride on silica gel were measured gravimetrically at 288, 293, and 298 K. For all the chlorinated hydrocarbons examined, the isotherms were Type I, showing no apparent hysteresis between the adsorption and desorption cycles. Experimental data were compared with the calculated equilibrium uptake as predicted by a synthetic heterogeneous isotherm model in which the local isotherm on a site is given by the Jovanovic equation and the distribution of energetically different sites is represented by a Morse-type energy distribution function. The absolute errors between the values calculated by the heterogeneous isotherm model and the experimental data ranged from 1.17 to 2.67%. Energy distribution functions showed that silica gel exhibits the same degree of heterogeneity for all of the adsorbates in the homologous series.

INTRODUCTION

Air pollution generally has been considered as the pollution of outdoor air, mainly caused by smoke from factories and the exhaust from motor vehicles. However, recent studies have shown that indoor air is often dirtier than outdoor air, and indoor air pollutants are the primary sources of many family diseases (*1*). Among several indoor air pollutants, the chlorinated hydrocarbons have drawn the most attention due to their presence in large amounts in several widely used consumer products. Of all the indoor air pollutants, methylene chloride and chloroform are considered to be two of the most dangerous. Methylene chloride is brought into homes in the

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form of paint strippers and is considered to pose the highest cancer risk of any household chemical. Chloroform is introduced into the home with chlorine-treated water in hot showers and also is considered to be one of the leading causes of cancer. Methyl chloride and carbon tetrachloride are also thought to be responsible for many respiratory diseases even though they are not present in large amounts as compared to the other household chemicals (*2*).

The majority of the studies on indoor air pollution so far have focused on determining the types and levels of the indoor air pollutants and their influence on human health. Studies on the removal of indoor air pollutants, however, are very limited and the results are not definitive. Recently, a survey of indoor air pollutants was conducted by Kuo and Hines (*3*), who studied the removal of six chlorinated hydrocarbons at 298 K using adsorption techniques. In the present work, their study is extended to include the adsorption of methyl chloride, methylene chloride, chloroform, and carbon tetrachloride on silica gel at three temperatures, 288, 293, and 298 K, from low pressure up to saturation. The adsorption isotherm data were correlated by using the heterogeneous adsorption isotherm model developed by Hines et al. (*4*).

EXPERIMENTAL SECTION

Materials

The silica gel used in this study was type PA 40, 80–100 mesh supplied by Davison Chemical Co. The chlorinated hydrocarbons consisted of the homologous series methyl chloride, methylene chloride, chloroform, and carbon tetrachloride. The methyl chloride was obtained from Union Carbide and had a minimum purity of 99.5%. The methylene chloride, chloroform, and carbon tetrachloride were obtained from Fisher Scientific Co. with purities of 99.9, 99.9, and 99.5%, respectively.

Apparatus

The experimental adsorption studies were carried out gravimetrically by using a Cahn R-2000 electrobalance which has a sensitivity of 0.1 μg. The adsorption apparatus was housed in a vacuum bottle assembly and was designed such that either gases or vapors could be studied. The assembly was equipped with two sample hangdown tubes surrounded by a cylindirical shell through which water could flow to keep the balance temperature relatively constant during sample regeneration. The system was designed such that a sample weight of 3.5 g could be tested. The sample weight was monitored with a strip chart recorder connected to the electrobalance control unit. A refrigerated-heated bath and circulator with a temperature control of ±0.1 K was used to control the adsorption temperature. A special vapor supply flask was used to introduce the liquid adsorbates into the system. A vacuum system which consisted 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 0.05 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 measurement was estimated to be ±10 μg.

Procedure

The electrobalance was calibrated to agree with the output signal of the chart recorder. The weight changes of the silica gel due to adsorption were detected by the electrobalance. The adsorbent was regenerated by evacuating the system and applying heat at 423 K to the sample hangdown tube. Heating was continued until a constant sample weight was obtained. Such operation typically required from 4 to 10 h. After regeneration, the adsorbent was cooled to the adsorption temperature and the adsorbate was introduced into the system. After 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 methyl chloride, methylene chloride, chloroform, and carbon tetrachloride 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 1. The weight of the sample was measured to within 10 μg. Since the regenerated sample

TABLE 1
Adsorption Isotherm Data for Chlorinated Hydrocarbons on Silica Gel

	288 K		293 K		298 K	
Adsorbate	*P* (mmHg)	*N* (mmol/g)	*P* (mmHg)	*N* (mmol/g)	*P* (mmHg)	*N* (mmol/g)
Chloromethane	31.1	1.155	4.1	0.407	3.2	0.356
	105.8	2.504	40.0	1.142	45.8	1.109
	189.4	3.433	96.3	2.083	93.8	1.826
	259.2	3.954	161.1	2.886	139.6	2.366
	350.0	4.406	234.5	3.480	190.7	2.865
	445.1	4.755	310.0	3.941	249.6	2.332
	531.8	5.004	375.8	4.255	304.1	3.601
	615.2	5.174	457.9	4.526	354.5	3.839
	700.0	5.329	512.7	4.725	409.6	4.056
	559.4	5.066	603.0	4.906	464.4	4.253
	382.5	4.535	674.0	5.049	516.0	4.401
	220.0	3.676	572.7	4.836	562.0	4.526
	62.4	1.803	401.6	4.333	609.8	4.632
	6.4	0.534	285.7	3.811	670.0	4.736
			130.8	2.549	720.0	4.826
			12.2	1.023	547.8	4.483
					428.0	4.126
					227.5	3.151
					122.2	2.182
					22.4	0.656
Dichloromethane	3.0	0.961	2.8	0.785	2.5	0.671
	6.4	1.374	8.9	1.384	8.4	1.219
	14.9	2.045	17.7	1.890	19.3	1.746
	23.7	2.489	29.2	2.438	32.0	2.210
	36.8	3.057	42.2	2.892	50.3	2.727
	49.8	3.491	55.0	3.274	70.5	3.202
	63.9	3.873	68.9	3.594	94.2	3.666
	78.2	4.143	83.7	3.904	110.2	3.914
	95.4	4.400	98.7	4.173	128.0	4.183
	108.8	4.513	114.0	4.389	148.4	4.359
	122.3	4.606	128.8	4.482	169.0	4.462
	140.4	4.709	146.7	4.565	189.7	4.513
	158.6	4.751	163.2	4.617	240.2	4.565
	208.7	4.854	193.3	4.668	315.6	4.637
			233.3	4.709		
Trichloromethane	1.4	0.976	1.6	0.899	1.5	0.779
	6.3	1.764	3.1	1.205	6.1	1.367
	12.2	2.271	8.7	1.793	13.7	1.955
	19.8	2.704	16.7	2.373	23.0	2.410
	29.1	2.998	25.6	2.734	32.2	2.719
	39.3	3.248	37.8	3.101	51.4	3.138
	50.0	3.380	49.9	3.270	64.4	3.255

(*continued*)

TABLE 1 (*continued*)

	288 K		293 K		298 K	
Adsorbate	*P* (mmHg)	*N* (mmol/g)	*P* (mmHg)	*N* (mmol/g)	*P* (mmHg)	*N* (mmol/g)
Trichloromethane	60.2	3.439	63.8	3.365	82.1	3.329
	71.4	3.468	74.2	3.395	107.2	3.351
	87.3	3.498	89.7	3.410	150.3	3.373
	105.9	3.519	114.1	3.432		
Tetrachloromethane	0.8	0.656	0.5	0.399	0.6	0.405
	2.0	0.947	1.1	0.604	1.2	0.559
	4.7	1.483	3.2	0.987	4.1	1.038
	9.2	1.982	7.2	1.653	7.8	1.552
	14.7	2.282	11.6	2.013	12.0	1.825
	20.2	2.435	18.2	2.252	15.8	2.025
	25.4	2.566	25.7	2.446	20.8	2.188
	31.0	2.651	33.5	2.578	27.4	2.336
	40.2	2.754	43.5	2.664	35.0	2.455
	49.3	2.809	53.5	2.706	43.5	2.526
	56.9	2.811	71.3	2.743	55.1	2.593
					69.2	2.666
					82.7	2.680

weight was 0.2137 g, the error in the weight measurement was 0.005%. Pressure was measured with an accuracy of ±0.15 mmHg. Except for the lowest pressures, the maximum error in pressure measurements was less than 0.3%. The average error over the entire adsorption range was estimated to be less than 1%. Several of the data points were reproduced with an error less than 1%.

The adsorption data for all four chemicals on silica gel were Type I according to the Brunauer (5) classification and showed no apparent hysteresis when desorbing. The absence of capillary condensation, as shown by the equilibrium data, indicates that the silica gel contains mostly micropores. For the homologous series, the amount of adsorbate removed by the silica gel increased as the molecular weight of the adsorbate increased as shown in Table 1. The fact that the maximum uptake of each adsorbate by the silica gel was in the range of 0.395–0.435 g adsorbate/g silica gel suggests that silica gel is an effective adsorbent for removing any of the chlorinated hydrocarbons found in the homologous series. The maximum uptake of each adsorbate was also plotted with respect to the molar volume of each adsorbate as shown in Fig. 1. It can be seen from the figure that the maximum adsorption capacities for the homologous series fall on a

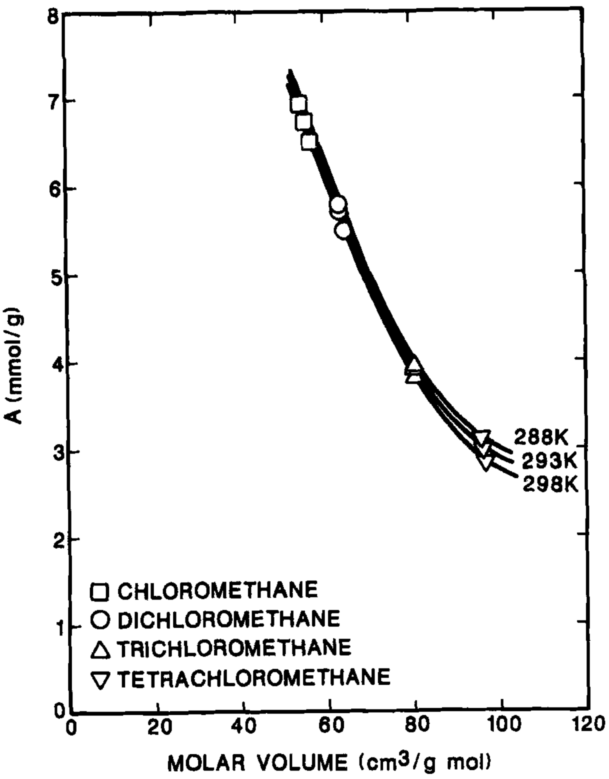

FIG. 1. Plots of maximum adsorption capacities as a function of molar volume.

single curve for each temperature. This suggests that the maximum capacity curve may be used to predict the maximum uptake of other compounds in the series.

Data Correlation

An attempt was made to correlate the equilibrium data by using the Langmuir and BET models. The average absolute percent deviation ranged from 2.2 to 6.8% for the Langmuir model and from 3.6 to 16.1% for the BET model. Because of the magnitude of the errors and the apparent heterogeneity of the systems studied, more sophisticated models were considered.

The generally accepted approach used to describe adsorbent heterogeneity is to postulate that the heterogeneous surface exhibits a distribution of energetically distinct sites and the overall adsorption isotherm can be obtained by integrating the contribution of each site over the total energy range (*6*). This can be expressed as

$$Q(P,T) = \int_0^\infty Q_1(P,T,g)E(g)dg \tag{1}$$

where $Q(P,T)$ is the overall adsorption isotherm on the heterogeneous adsorbent, $Q_1(P,T,g)$ is a local adsorption isotherm for homotattic sites of adsorptive energy g, and $E(g)$ is the energy distribution function. Both Q and Q_1 are amounts adsorbed per unit mass of adsorbent.

Several combinations of local isotherm equations and energy distribution functions have been used to derive analytical expressions for $Q(P,T)$ (*4*, *7–12*). Because the model developed by Hines et al. (*4*) is the newest and possibly the most versatile of the heterogeneous models, it was used to correlate the experimental data obtained in this study. In their model is was assumed that the local isotherm for homogeneous sites can be described by the Jovanovic model (*13*) as

$$Q_1(P,T,g) = A[1 - \exp(-bP)] \tag{2}$$

with the energy distribution function being represented by a modified Morse-type probability density function of g (*14*) given by

$$E(g) = \frac{K_1K_3}{K_3 - K_1K_2}[e^{-K_1g} - K_2e^{-K_3g}], \qquad 0 \le g \le \infty \tag{3}$$

In Eqs. (2) and (3), A is the saturation adsorption capacity, K_1, K_2, and K_3 are the energy distribution parameters, and b is the Jovanovic parameter which can be related to the heat of adsorption by

$$b = b_0 \exp(\Delta H_S/RT) \tag{4}$$

The resulting overall adsorption isotherm for adsorption on a heterogeneous adsorbent is

$$Q(P,T) = A\left[1 - \frac{K_1K_3}{K_3 - K_1K_2}\left(\frac{1}{P + K_1} - \frac{K_2}{P + K_3}\right)\right] \tag{5}$$

where A, K_1, K_2, and K_3 are related to the Henry's law constant, K_L, by

$$A\left[\frac{K_3^2 - K_1^2K_2}{K_1K_3(K_3 - K_1K_2)}\right] = K_L(T) \qquad \text{as } P \to 0 \tag{6}$$

In deriving Eqs. (5) and (6), the contribution of b_0 to the overall isotherm equation was neglected since, as demonstrated by Sircar (*12*), b_0 is usually a very small quantity (less than 10^{-4} for most practical systems).

The adsorption data of methyl chloride, methylene chloride, chloroform, and carbon tetrachloride on silica gel were correlated using Eq. (5). Figures 2 through 5 show the experimental data and the isotherms obtained from Eq. (5). The four adjustable model parameters for each adsorbate were determined by using a nonlinear regression analysis. The best fit parameters for the systems studied are presented in Table 2. As one can see, the heterogeneous isotherm model developed by Hines et al. (*4*) describes the experimental isotherm data extremely well over the entire range of pressure and temperature. The average absolute percent deviation over the entire pressure range for most of the systems studied was less than 2%. The maximum average percent deviation calculated was 2.67%.

All model parameters were found to be temperature dependent. Among them, K_1 exhibited the strongest temperature dependence, increasing with increasing temperature. K_3 showed an inverse dependence on temperature, although its dependence was observed to be relatively weak. The dimensionless parameter K_2 was the least dependent on temperature; it decreased very slightly or remained nearly constant as the temperature increased.

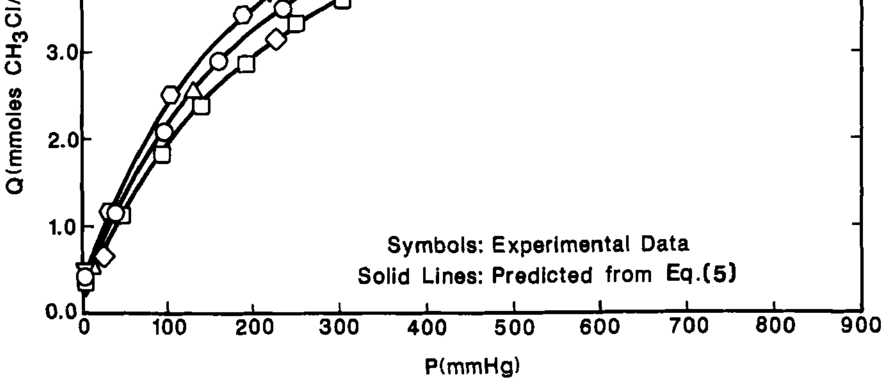

FIG. 2. Adsorption of methyl chloride on silica gel.

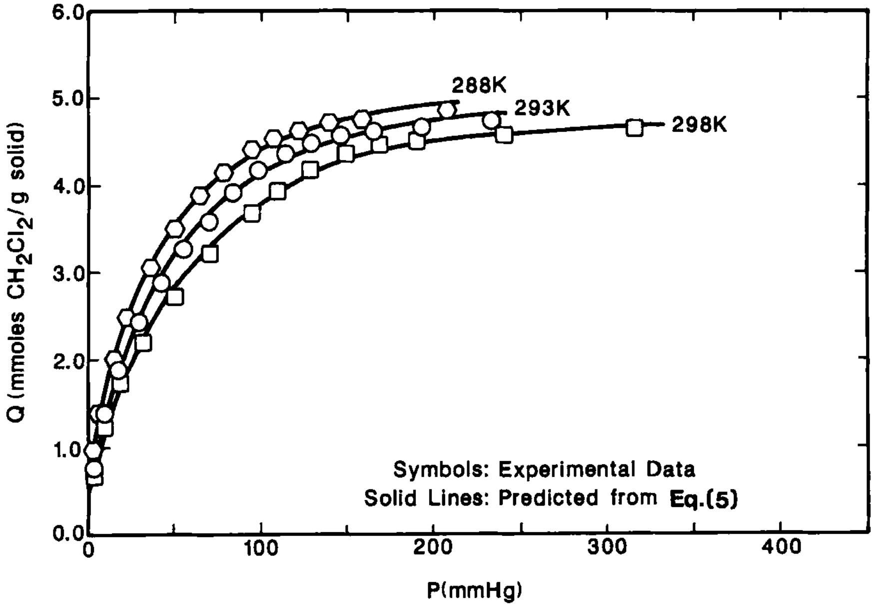

FIG. 3. Adsorption of methylene chloride on silica gel.

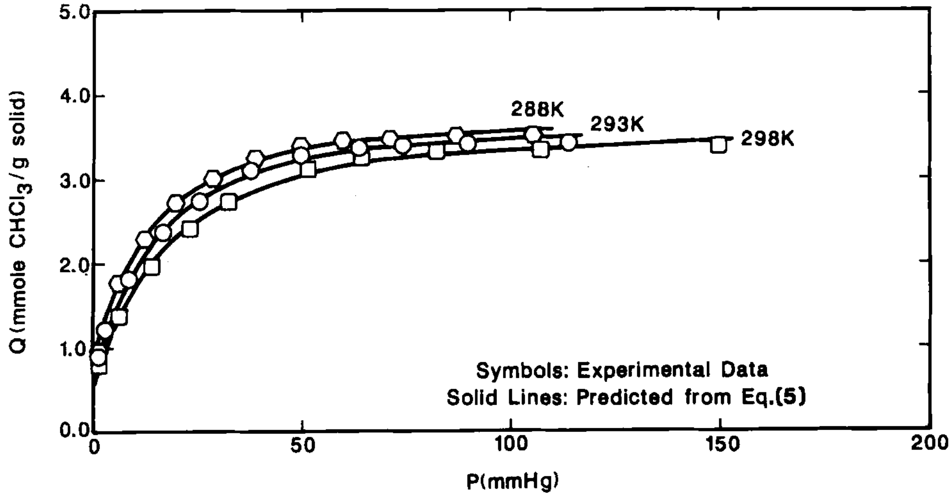

FIG. 4. Adsorption of chloroform on silica gel.

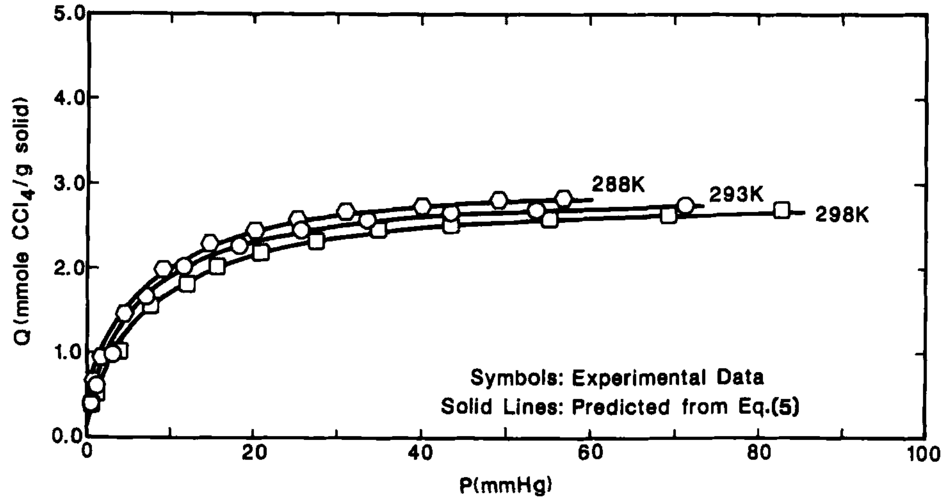

FIG. 5. Adsorption of carbon tetrachloride on silica gel.

The saturation capacity A was also weakly influenced by the temperature, its value decreasing slightly with increasing temperature. As one can observe from Table 2, the trends of the model parameters are very consistent with respect to temperature, and, in almost every case, exhibit a linear variation. This suggests that the model parameters may be correlated with respect to temperature and can be used to interpolate between isotherms.

TABLE 2
Best Fit Model Parameters

Adsorbate	Temperature (K)	A (mmol/g)	K_1 (mmHg)	K_2 (—)	K_3 (mmHg)	Absolute average % deviation
CH_3Cl	298	6.61	273.64	−0.00014	1.040	2.45
	293	6.81	260.11	−0.00052	1.781	1.73
	288	6.93	255.56	−0.00057	1.790	1.98
CH_2Cl_2	298	5.98	74.81	−0.00165	0.925	2.67
	293	6.08	59.78	−0.00227	0.982	1.82
	288	6.10	50.54	−0.00453	1.248	1.36
$CHCl_3$	298	3.80	14.59	−0.00005	0.007	2.03
	293	3.84	12.43	−0.00009	0.008	2.34
	288	3.92	11.28	−0.00014	0.009	1.37
CCl_4	298	2.97	8.43	−0.00003	0.003	1.51
	293	3.05	7.04	−0.00004	0.004	2.37
	288	3.14	6.59	−0.00008	0.005	1.17

Figure 6 illustrates the variation of best fit model parameters for methyl chloride on silica gel with temperature.

The heterogeneity of an adsorbent surface is generally due to the differences in the adsorptive strength of the energetic sites, which leads to a variation in the isosteric heat of adsorption at different loadings. The isosteric heats of adsorption for the chlorinated hydrocarbons on silica gel at different loadings were calculated in the usual manner from the Clasius–Clapeyron equation:

$$\Delta H_S = -R\left[\frac{\partial\,(\ln P)}{\partial\,(1/T)}\right]_Q \tag{7}$$

The results are presented in Table 3. In all cases except one, the isosteric heats of adsorption in the beginning of the adsorption process exhibit the commonly observed trend of a decreasing amount of heat being given off as the loading on the solid surface is increased. Adsorption initially occurs on the most active sites, giving rise to the greatest interaction energy. As these sites are filled, adsorption proceeds on the less active sites, giving off a smaller amount of heat. However, the heat of adsorption remains practically constant after monolayer coverage is reached. Since the heats of adsorption given in Table 3 are observed to be of the same order of magnitude as the heat of condensation, it may be concluded that the adsorption of all four chlorinated hydrocarbons is primarily the result of physical forces.

The energy probability density function $E(\Delta H_S/RT)$ can be obtained by defining the energy parameter $g = b_0[\exp(\Delta H_S/RT) - 1]$ and com-

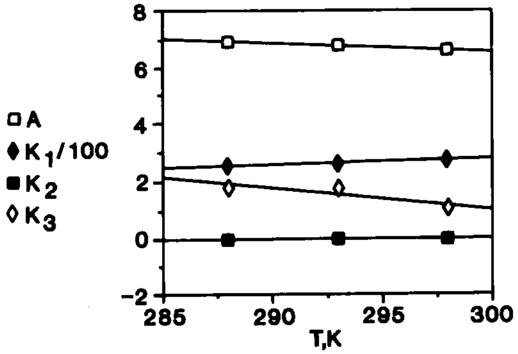

FIG. 6. Variation of best fit model parameters for methyl chloride on silica gel with temperature.

bining it with Eqs. (3) and (4) to give the following expression (*4*):

$$E\left(\frac{\Delta H_S}{RT}\right) = \frac{K_1K_3}{K_3 - K_1K_2}[e^{-K_1g} - K_2e^{-K_3g}][g + b_0] \qquad (8)$$

Figure 7 presents the distribution of $E(\Delta H_S/RT)$ for all of the systems at 288 K, and Fig. 8 shows the influence of temperature on the energy probability density function. As observed in the figures, Eq. (8) yields a skewed Gaussian-like energy distribution function which is characteristic of the Morse-type probability density function. Since the distributed E functions for all the systems are very similar as shown in Fig. 7, it may be concluded that silica gel exhibits the same degree of heterogeneity for all of the chlorinated hydrocarbons in the homologous series.

TABLE 3
Variation of Isosteric Heats of Adsorption with the Amount Adsorbed

Adsorbate	Amount adsorbed (mmol/g solid)	$-\Delta H_S$ (kcal/g·mol)	ΔH_C (kcal/g·mol)
CH_3Cl	2.0	6.36	4.85–5.05
	2.5	6.38	
	3.0	6.43	
	3.5	6.41	
	4.0	6.46	
	4.5	6.48	
CH_2Cl_2	2.0	10.31	6.89–7.05
	2.5	9.48	
	3.0	9.44	
	3.5	9.14	
	4.0	8.70	
	4.5	9.26	
$CHCl_3$	1.4	11.20	7.53–7.77
	1.8	9.40	
	2.2	8.75	
	2.6	8.15	
	3.0	8.05	
	3.3	8.27	
CCl_4	0.9	10.34	7.39–7.70
	1.2	8.79	
	1.5	7.83	
	1.8	7.98	
	2.1	8.08	
	2.4	8.43	

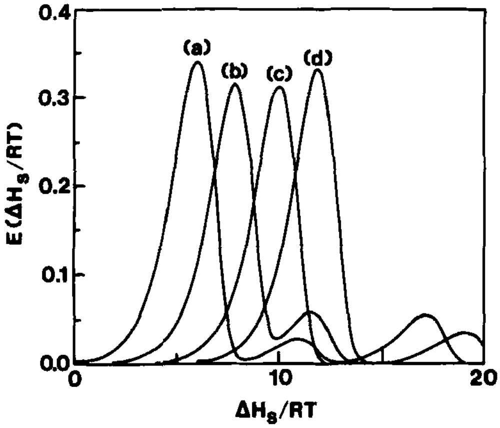

FIG. 7. Energy probability density functions for chlorinated hydrocarbons on silica gel at 288 K. (a) Methyl chloride; (b) methylene chloride; (c) chloroform; (d) carbon tetrachloride.

CONCLUSIONS

The adsorption of the homologous series methyl chloride, methylene chloride, chloroform, and carbon tetrachloride was investigated using silica gel as the adsorbent. The adsorption isotherms of the four chlorinated hydrocarbons on silica gel were determined gravimetrically at 298, 293, and 288 K and pressures up to saturation. The maximum adsorption capacities for the homologous series fell on a single curve for each temper-

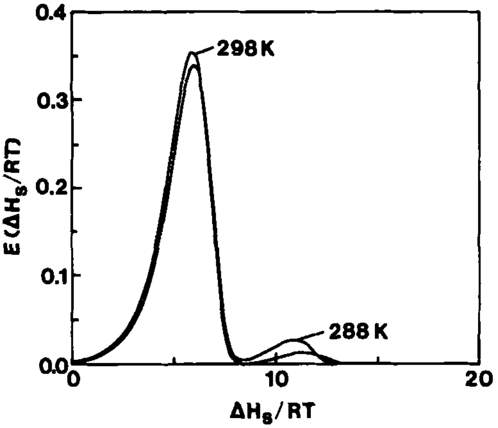

FIG. 8. Influence of temperature on the energy probability density function for methyl chloride on silica gel.

ature, which suggests that the maximum capacity curve may be used to predict the maximum uptake of other compounds in the homologous series. On the basis of this study, it was concluded that silica gel can be effectively used to adsorb many chlorinated hydrocarbons.

The heterogeneous isotherm model developed by Hines et al. successfully describes the experimental isotherms for the chlorinated hydrocarbons investigated in the present work. The relative shapes of the energy distribution functions suggest that silica gel exhibits the same degree of heterogeneity for each member of the homologous series.

NOTATION

A	saturation adsorption capacity
b	Jovanovic parameter as defined in Eq. (4)
b_0	limiting value of b at infinite temperature
e	energy of a particular site
E	energy distribution function
g	energy parameter defined by Eq. (6)
ΔH_C	heat of condensation
ΔH_S	isosteric heat of adsorption
K_0	parameter in the energy distribution function
K_1	parameter in the energy distribution function
K_2	parameter in the energy distribution function
K_3	parameter in the energy distribution function
K_L	local Henry's law constant
N	equilibrium uptake
P	system pressure
Q	overall adsorption isotherm
Q_1	local adsorption isotherm
R	universal gas constant
T	system temperature

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