Adsorption of Acetaldehyde, Propionaldehyde, and Butyraldehyde on Silica Gel

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Abstract

Adsorption isotherms of acetaldehyde, propionaldehyde, and butyraldehyde on Davison silica gel were determined gravimetrically at three temperatures. The isoteric heat of adsorption initially increased at low loading and then decreased monotonically with an increase in loading. The equilibrium adsorption data were successfully correlated by Polanyi's potential theory. The equilibrium data were also correlated with the Langmuir, BET, Freundlich, and the Hines et al. models. The Freundlich and the Hines et al. models provided the best fit to the data, while the BET equation was found to be applicable only for a relative pressure range of 0.05 to 0.2. The monolayer surface coverages of silica gel by all of the aldehydes estimated by the Langmuir equation were found to be consistently higher than those calculated from the BET equation, except for acetaldehyde at 306.5 K.

INTRODUCTION

The aldehydes have been recognized as outdoor air pollutants for some time. Although formaldehyde is usually the most prevalent, in some areas the combined concentrations of the higher molecular weight aldehydes, i.e., acetaldehyde, propionaldehyde, and butyraldehyde, may be higher than formaldehyde alone (*1*). Aldehydes are introduced into the atmosphere from a variety of sources including gasoline-powered, propane-powered, or diesel-powered engines, incinerator smoke, and stack gases from the combustion of various organic substances (*2*).

It has been long believed that indoor air, i.e., air inside homes, offices etc., is cleaner than outside air. Recently, researchers have found that indoor air may be more polluted than outdoor air (*3*), and the aldehydes

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are major pollutants. Primary sources of aldehydes in indoor air include the products of combustion of natural gas (used for cooling and heating), tobacco smoke, and urine. The most common effect of aldehydes on humans is the irritation of eyes and mucous membranes. Other possible health problems are headaches, narcotic action on the nervous system, and a rise in blood pressure (4).

Growing public concern about the health hazards that might be caused by these chemicals is creating a challenge for the researcher to remove them effectively and economically from indoor and outdoor air. One way to remove the aldehydes from air is to adsorb them on porous materials, such as silica gel, activated carbon, and Molecular Sieve. However, the design of any adsorption system requires pure component adsorption data.

In the present work, the adsorption behavior of acetaldehyde, propionaldehyde, and butyraldehyde on silica gel was studied at three temperatures. Experimental data were correlated by applying the potential theory proposed by Polanyi to check the consistency of the data. Different adsorption models were employed to fit the equilibrium adsorption data, including the Langmuir, the BET, the Freundlich, and the model by Hines et al. The isoteric heats of adsorption were calculated at different loadings to evaluate the surface characteristics of the silica gel for these aldehydes.

EXPERIMENTAL SECTION

Materials and Apparatus

The silica gel used in the present work was Grade 40, 6–12 mesh, and was supplied by Davison Chemical, Baltimore, Maryland. Acetaldehyde and butyraldehyde were obtained from Fluka AG and had purities of 99.9 and 99% +, respectively. Propionaldehyde was obtained from Aldrich Chemical Company, Milwaukee, Wisconsin, and had a stated purity greater than 99%.

The adsorption study was carried out gravimetrically using a Cahn C-2000 electrobalance. The electrobalance was capable of measuring weights up to 3.5 g with a sensitivity of 0.1 μg. The description of the electrobalance and the flow diagram are given in detail in a paper by Kuo and Hines (3). A vacuum of 1×10^{-4} mmHg could be obtained in the system prior to an adsorption run. The leak rate of the complete assembly was approximately 0.0054 mmHg/h. The pressure was measured by a Wallace and Tiernan absolute pressure gauge to an accuracy of ±0.1 mmHg. The temperature during the adsorption and desorption run was controlled within ±0.1 K.

Procedure

Prior to an adsorption run, the silica gel was heated to a temperature of 373.15 ± 2 K under vacuum to remove the moisture and other gases

that might be adsorbed on the surface. Heating was continued until a constant sample weight was obtained, which typically required about 4–10 h. To maintain consistency, a heating period of 10 h was used for all runs. After regeneration of the silica gel, it was cooled to the adsorption temperature and the adsorbate was introduced into the system in steps. After each step the system was allowed to reach equilibrium as indicated by the constant weight of the sample. The pressure and weight changes were recorded after each equilibrium step. Following adsorption, desorption of the adsorbate was carried out by reducing the system pressure in steps. Fresh samples of silica gel were used for each run as a result of not being able to remove the adsorbate completely from the silica gel, in spite of several hours of heating under vacuum. Because the amount adsorbed on the silica gel was found to be dependent on the regeneration temperature, the temperature used during regeneration of the silica gel sample was controlled within ±2 K. The error introduced in the weight measurement due to the buoyancy effect was found to be negligible.

RESULTS AND DISCUSSION

Equilibrium Data

Adsorption isotherms were obtained at 287, 298.2, and 306.5 K for acetaldehyde, at 282, 297, and 304.3 K for propionaldehyde, and at 288.2, 299.3, and 308.2 K for butyraldehyde. All three aldehydes exhibited Type I adsorption isotherms and gave reproducible hysteresis loops upon de-
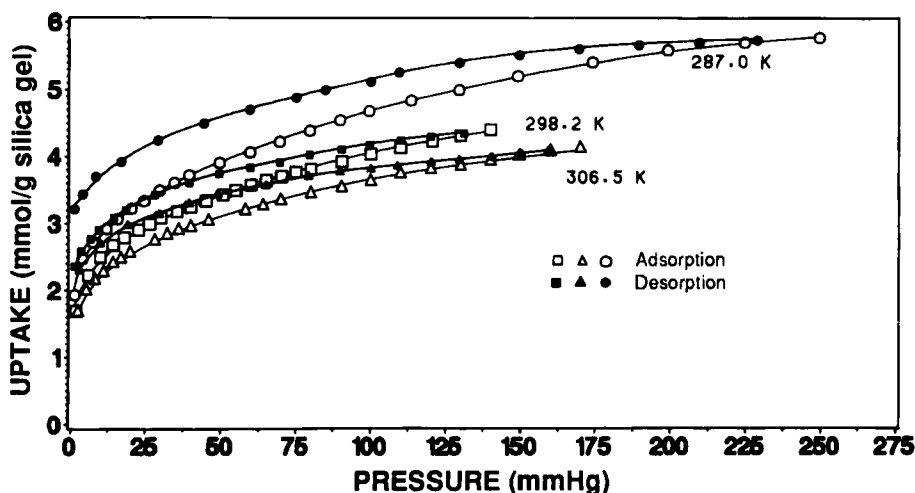
FIG. 1. Adsorption and desorption curves for acetaldehyde on silica gel (6–12 mesh).
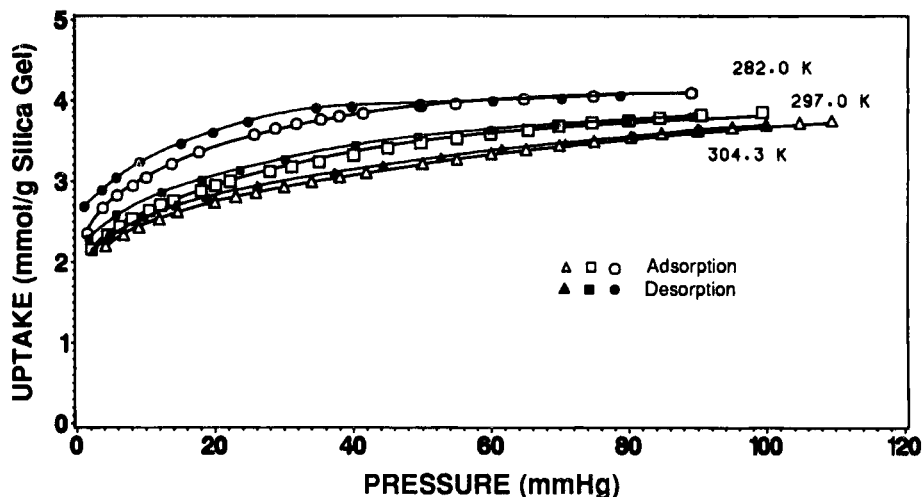
FIG. 2. Adsorption and desorption curves for propionaldehyde on silica gel (6–12 mesh).

sorption. The adsorption and desorption data for all the aldehydes are shown in Figs. 1–3. Nayar and Rao (5) also found that propionaldehyde and butyraldehyde gave Type I isotherms and hysteresis loops from their studies on silica gel at 303 K. In addition, they reported that the adsorbate was strongly attached to the silica gel and suggested that the aldehyde molecules were chemisorbed on the surface. Adsorption studies of aliphatic

FIG. 3. Adsorption and desorption curves for butyraldehyde on silica gel (6–12 mesh).

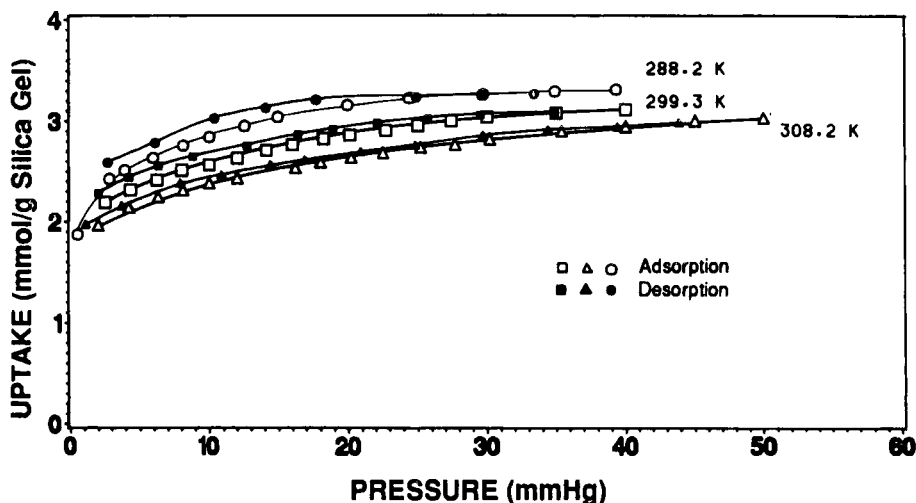hydrocarbons (6) and chlorinated hydrocarbons (7) on 80–100 mesh silica gels showed no apparent hysteresis during desorption.

The isoteric heat of adsorption was calculated at constant loading of the adsorbate from the following relationship:

$$\Delta H_{iso} = -R \left(\frac{\partial \ln P}{\partial (1/T)} \right)_q \qquad (1)$$

The heats of adsorption at different loadings are plotted in Fig. 4 for all three aldehydes. The heats of adsorption of acetaldehyde and butyralde-hyde increased with an increase in loading up to a certain point, then started to decrease. Due to the lack of adsorption data at lower loadings, the heat of adsorption of propionaldehyde could not be calculated in that region. However, the curve for propionaldehyde showed a trend similar to that of acetaldehyde. The initial increase in the heat of adsorption curves can be attributed to lateral interactions between the adsorbed aldehydes, which are known to form associated molecules on a solid surface. The subsequent decrease in the curves can be attributed to heterogeniety of the surface and multilayer coverage. Brunauer (8) reported a similar type of observation for both water and methanol, which are highly polar and exhibit a strong tendency toward association.
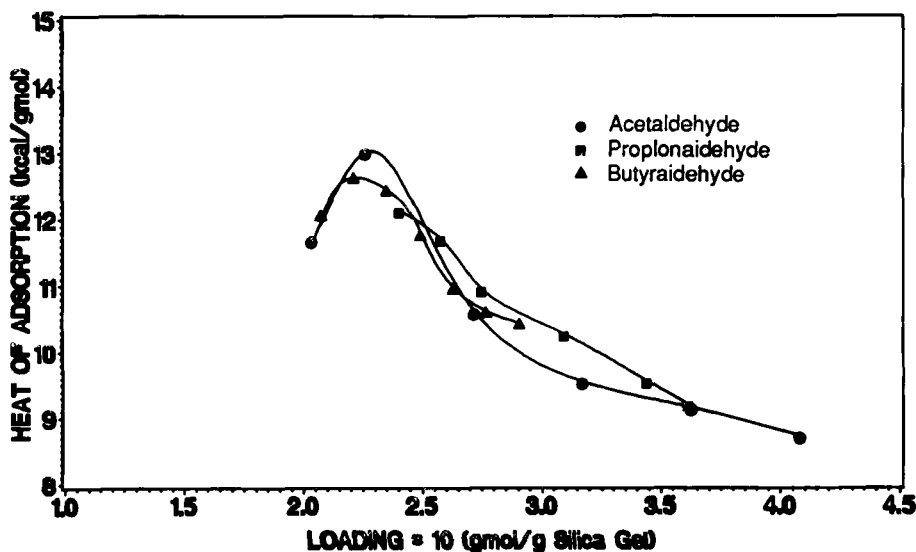

FIG. 4. Heat of adsorption at different loadings for aldehydes on silica gel (6–12 mesh).

Although silica gel generally provides a homogeneous surface for adsorption, some sites might become more energetic than others following regeneration. The heat of adsorption for adsorbates on silica gel surfaces has been frequently found to decrease as the loading increases and then remains practically constant. For all of the aldehydes, the hysteresis loop decreased with increasing temperature. This may be attributed to a sieving effect on the expanded adsorbate at the higher temperature. The surface areas predicted from the adsorption data also decreased with increasing temperature. This suggests that some of the micropores were inaccessible at the higher temperatures because the adsorbate had expanded.

Data Correlation

The potential theory of Polanyi was applied to the systems studied in this work to check the consistency of the data. The Polanyi theory assumes that the adsorbent exerts long-range attractive forces on the gas or vapor surrounding it. These attractive forces generate a potential field which decreases as the distance between the gas and adsorbent surface increases. The adsorption potential (ε) in its original form is given by

$$\varepsilon = RT \ln (P_s/P) \qquad (2)$$

where P_s is the saturation pressure of the adsorbate at the adsorption temperature. Thus a plot of the volume adsorbed versus the adsorption potential should produce a single characteristic curve independent of temperature as shown in Figs. 5–7.

The equilibrium data were next correlated by the Langmuir, the BET, and the Freundlich equations, in addition to a new isotherm proposed by Hines et al. (9) for heterogeneous surfaces.

The Langmuir equation was developed by using the assumption that the adsorbent surface is homogeneous and the surface is covered by a single layer of molecules. The Langmuir equation is given by

$$q = \frac{q_m KP}{1 + KP} \qquad (3)$$

where q_m is a constant and is defined as the amount of adsorbate that will be adsorbed on the surface in a monolayer. As shown in Table 3, the Langmuir equation did not provide a good fit to the data. This may be due to the combined effects of surface heterogeneity, multilayer adsorption, and the formation of associated molecules on the silica gel surface.

Although the BET equation was developed based on the assumption of

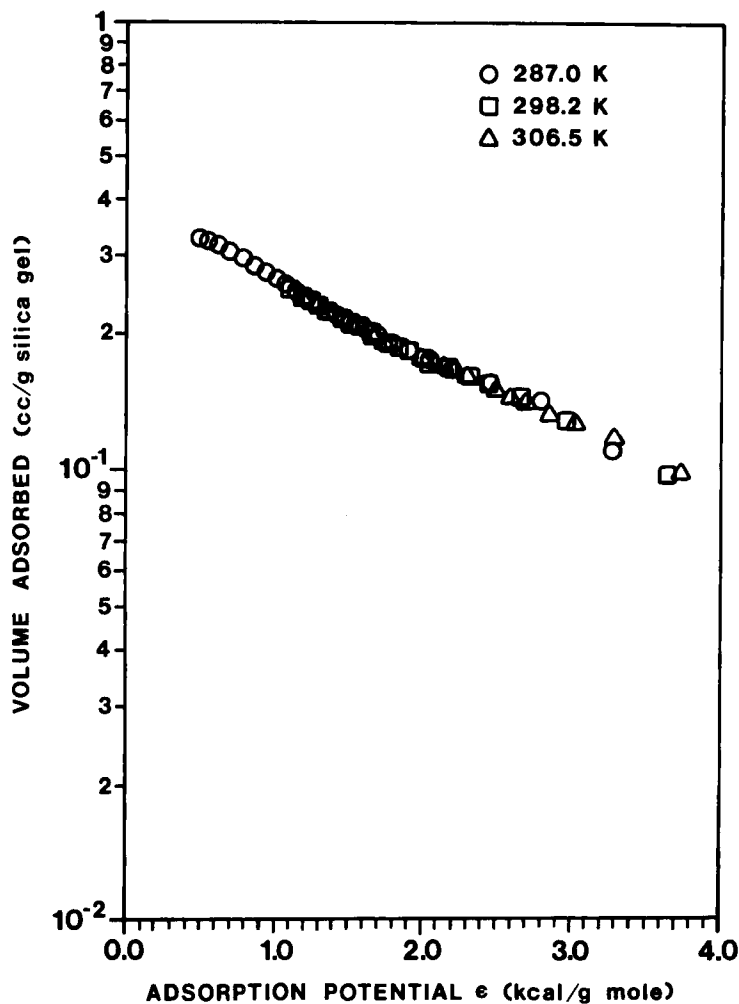FIG. 5. Characteristic curve for acetaldehyde on silica gel (6–12 mesh).

multilayer adsorption, the heterogeneity of the adsorbent surface was not considered. The BET equation can be written as

$$\frac{P}{q(P_s - P)} = \frac{1}{q_m C} + \frac{(C - 1)P}{C q_m P_s}$$ (4)

The BET equation provided a good correlation of the data for the range $0.05 \leq P/P_s \leq 0.2$. A large deviation between the calculated values and
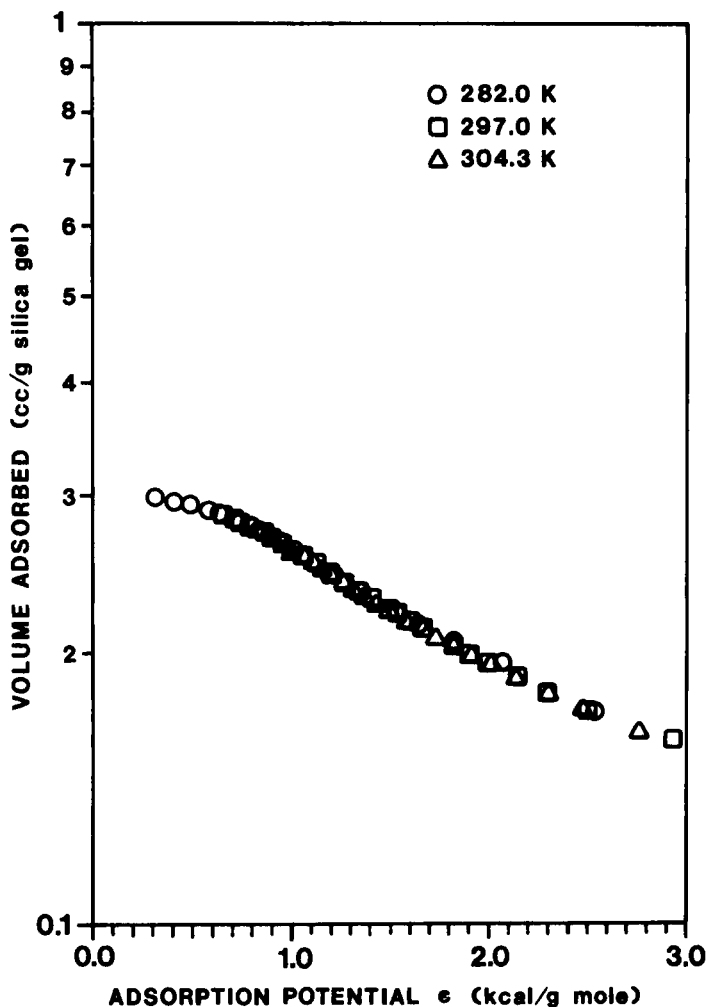
FIG. 6. Characteristic curve for propionaldehyde on silica gel (6–12 mesh).

the experimental data was observed at pressures higher than $P/P_s > 0.2$. This type of behavior has also been observed by other researchers (10). Because the BET model is more suitable for Types II and III isotherms, the failure of the BET model to predict the Type I behavior observed in the present study is not surprising.

Low pressure data (where the Langmuir and the BET equations provided a straight line) were used to calculate the monolayer coverage and the
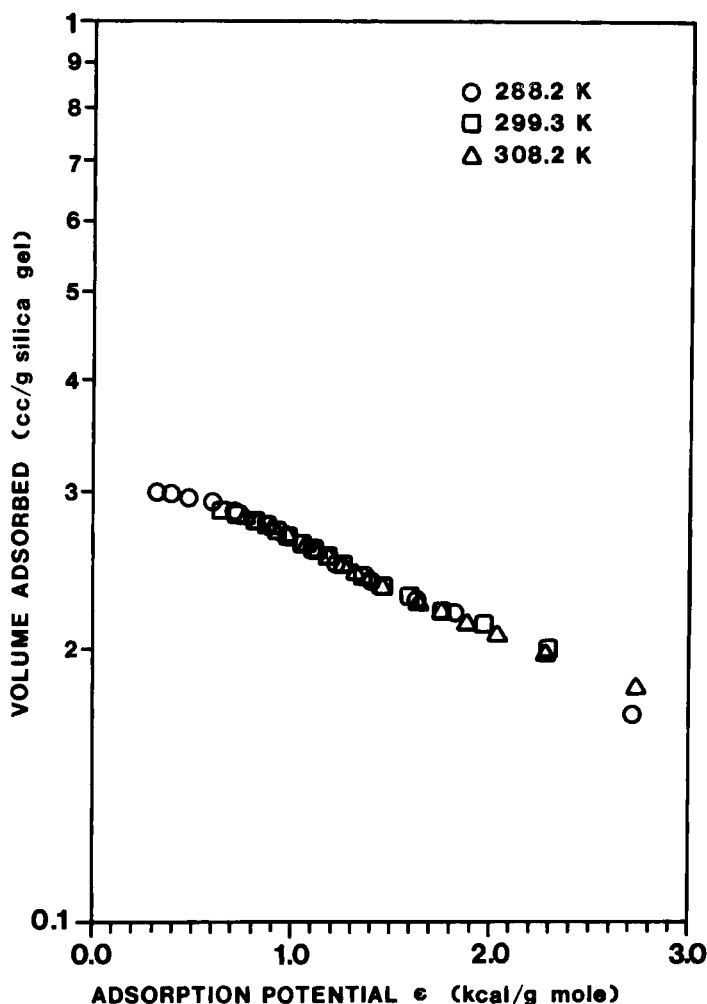
FIG. 7. Characteristic curve for butyraldehyde on silica gel (6–12 mesh).

surface area of silica gel; the results are presented in Table 1. The area occupied by a molecule was estimated by assuming hexagonal close packing of the aldehydes on the surface. The surface area predicted by the Langmuir equation was consistently higher than that predicted by the BET equation, except for acetaldehyde at 306.5 K. The surface areas obtained by using propionaldehyde and butyraldehyde are in close agreement with the values reported by Nayar and Rao (5) at 303 K. However, aldehydes occupy less

TABLE 1

Monolayer Coverages and the Calculated Surface Areas of Silica Gel

System	Temperature (K)	Molecular cross section (Å²)	Monolayer coverage (cm³/g)		Surface area (m²/g)	
			Langmuir	BET	Langmuir	BET
Acetaldehyde– silica gel	287.0	22.38	95.2	90.7	573	546
	298.2	22.67	88.7	87.8	541	535
	306.5	22.89	71.5	84.3	440	519
Propionaldehyde– silica gel	282.0	26.41	76.1	65.5	541	466
	297.0	26.79	70.8	64.3	510	463
	304.3	26.98	67.3	63.6	489	461
Butyraldehyde– silica gel	288.2	30.57	62.0	54.5	510	448
	299.3	30.88	61.2	53.3	508	442
	308.2	31.11	57.5	52.4	481	438

than the total surface area, which is 760 m²/g as measured by an Orr Surface Area-Pore Volume Analyzer (Model 2100D, Micromeritics Instrument Corporation) using N_2 as the adsorbent at 77.3 K. The low coverge by the aldehydes may be due in part to their inability to enter the pores of the silica gel and their orientation on the surface. Tanada (12) found that the amount of acetaldehyde that was adsorbed on several adsorbents depended on the pore radius rather than on the total pore volume.

The Freundlich equation provided a better fit to the experimental data than either the Langmuir or the BET equation. The Freundlich equation can be written as

$$q = a(P)^b \qquad (5)$$

where a and b are constants. The results are compared in Table 3. Hines et al. (9) developed an isotherm considering the heterogeneity of the surface. In developing the isotherm, Hines et al. assumed that the surface consisted of energetically heterogeneous sites and that the distribution of such sites could be described by a probability density function. The adsorption of the adsorbate on a particular site was described by the Jovanovic (11) equation for monolayer coverage. The resulting overall adsorption

TABLE 2

Henry's Law Constant and Best Fit Parameters for Hines et al. Model

System	Temperature (K)	Henry's law constant (mmol/g-mmHg)	m (mmol/g)	K_1	K_2
Acetaldehyde–	287.0	2.873	7.983	174.9	-3.164×10^{-3}
silica gel[a]	298.2	2.510	6.512	154.1	-4.002×10^{-3}
	306.5	2.277	5.736	141.2	-4.579×10^{-3}
Propionalde-	282.0	11.450	5.192	4.626×10^{-3}	-195.4
hyde–silica gel[b]	297.0	10.281	4.729	4.286×10^{-3}	-253.2
	304.3	9.933	4.477	4.113×10^{-3}	-274.7
Butyraldehyde–	288.2	12.346	4.602	4.804×10^{-3}	-166.2
silica gel[b]	299.3	11.333	4.328	4.796×10^{-3}	-182.2
	308.2	11.127	4.065	4.455×10^{-3}	-207.3

[a]K_1 in mmHg and $K_3 = 1$ mmHg.
[b]K_1 in psia and $K_3 = 1$ psia.
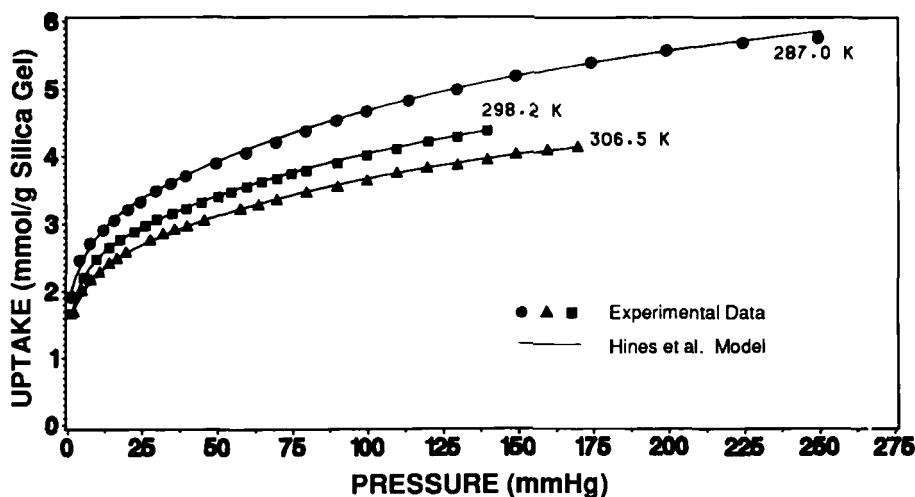

FIG. 8. Comparison of the experimental data with prediction by the Hines et al. model for acetaldehyde–silica gel system.
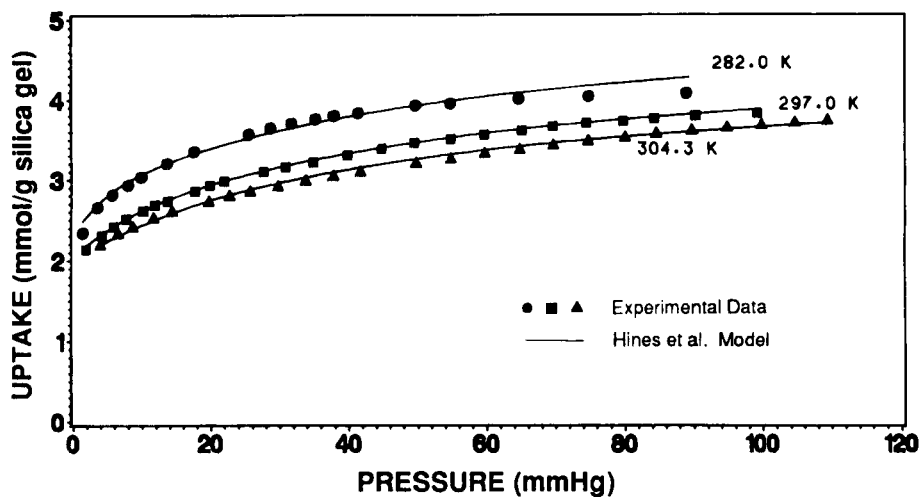
FIG. 9. Comparison of the experimental data with predictions by the Hines et al. model for propionaldehyde–silica gel system.
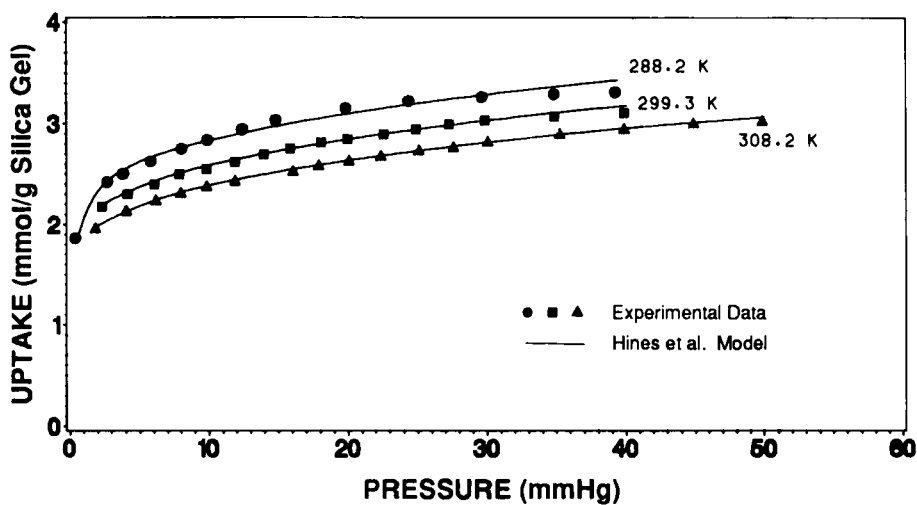

FIG. 10. Comparison of the experimental data with predictions by the Hines et al. model for butyraldehyde–silica gel system.

TABLE 3

Comparison of Model Correlations

System	Temperature (K)	Absolute average error (%)				Maximum positive error^a (%)				Maximum negative error^a (%)			
		Hines et al.	Langmuir	BET	Freundlich	Hines et al.	Langmuir	BET	Freundlich	Hines et al.	Langmuir	BET	Freundlich
Acetaldehyde–silica gel	287.0	0.58	12.49	15.40	1.71	2.06	72.69	8.78	7.98	1.17	9.25	105.95	2.37
	298.2	0.40	8.51	5.62	0.93	0.87	65.04	54.62	2.58	2.49	6.23	4.07	1.53
	306.5	0.46	9.82	6.50	0.89	1.01	59.69	50.67	3.23	1.20	9.00	5.44	1.34
Propionaldehyde–silic gel	282.0	1.73	5.15	142.36	1.27	2.10	42.92	1753.71	1.72	4.30	3.08	190.95	3.37
	297.0	0.26	6.61	8.23	0.88	0.62	52.01	3.83	5.66	0.82	5.64	54.33	1.54
	304.3	0.87	6.54	1.96	1.00	1.15	39.88	1.71	4.42	1.46	7.01	5.73	1.53
Butyraldehyde–silica gel	288.2	1.55	6.07	94.38	1.19	2.81	49.02	743.21	1.69	2.77	4.63	222.09	3.74
	299.3	0.66	3.44	10.01	0.61	0.88	23.68	5.64	1.99	1.78	2.57	70.58	1.28
	308.2	0.27	5.12	5.57	0.82	0.48	36.92	4.31	3.05	0.85	3.37	33.69	1.52

^{a}Error = $\dfrac{\text{experimental} - \text{calculated}}{\text{experimental}}$ × 100.

isotherm has the form

$$q = m\left[1 - \left(\frac{K_3}{K_3 - K_1K_2}\right)\left(\frac{K_1}{P + K_1} - \frac{K_1K_2}{P + K_3}\right)\right] \tag{6}$$

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

$$m\left[\frac{K_3^2 - K_1^2 K_2}{K_1K_3(K_3 - K_1K_2)}\right] = K_L \text{ as } P \to 0 \tag{7}$$

According to Hines et al., the parameter K_3 is a variable and a function of temperature. However, in the present study K_3 was set to unit pressure while other parameters m, K_1, and K_2 were determined by a trial-and-error procedure. It was observed that this approach can correlate the experimental data for the aldehyde–silica gel system adequately (within $\pm2\%$). Only marginal improvement can be achieved with K_3 as a varible parameter. The Henry's law constant, K_L, was obtained from the initial slope of the isotherm. A value of m was chosen and K_2 was calculated from Eq. (7) for different values of K_1. The entire isotherm was then generated by Eq. (6). This trial-and-error procedure was continued until a satisfactory fit of the experimental data was obtained. In the present study, the trial-and-error procedure continued until the calculated data were within $\pm2\%$ of the experimental data. The Henry's law constant and the best fit values for the constants K_1 and K_2 are shown in Table 2.

The best fit curves generated by the Hines et al. model and the experimental data are plotted in Figs. 8–10. The Hines et al. model provided an excellent fit for most of the aldehyde–silica gel data. However, a larger deviation was observed for propionaldehyde and butyraldehyde at low temperatures (282 K for propionaldehyde and 288.2 K for butyraldehyde) and high pressures.

A comparison of the Langmuir, BET, Freundlich, and Hines et al. (9) models is given in Table 3 for all the experimental runs. The average absolute percent error, maximum positive error, and maximum negative error over the complete pressure range are given in the table. The Hines et al. and the Freundlich models provided a better correlation of the data than did the Langmuir and the BET models when the entire pressure range was considered.

NOMENCLATURE

a	constant in the Freundlich equation
b	constant in the Freundlich equation

C	constant in the BET equation
ε	adsorption potential
ΔH_{iso}	isoteric heat of adsorption
K	constant in the Langmuir equation
K_L	Henry's law constant
K_1	constant in the Hines et al. equation
K_2	constant in the Hines et al. equation
K_3	constant in the Hines et al. equation
m	constant in the Hines et al. equation
P	system pressure
P_s	saturation pressure at system temperature
q	uptake of the adsorbate
q_m	equilibrium uptake of the adsorbate as defined by the Langmuir and the BET equations
R	gas constant
T	system temperature

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