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Adsorption of Acetaldehyde, Propionaldehyde, and Butyraldehyde on Molecular Sieve 13X

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Abstract

Adsorption isotherms for acetaldehyde, propionaldehyde, and butyraldehyde on Davison molecular sieve 13X were determined gravimetrically at three temperatures. The isoteric heat of adsorption of acetaldehyde and propionaldehyde decreased initially with the increase in loading, then increased up to a certain point after which it decreased again. For butyraldehyde the heat of adsorption initially increased and then decreased with increased loading. The equilibrium adsorption data reduce to a single characteristic curve when correlated according to Polanyi's potential theory. Recently proposed isotherm equations for heterogeneous surfaces by Sircar and Hines et al. were used to correlate the isotherm data. The BET equation gave a good correlation of the data for a relative pressure range of $0.05 \le P/P_s \le 0.25$. The monolayer surface coverage and surface area were calculated by the Langmuir and the BET equations. The Langmuir equation consistently provided a larger estimate of the surface area than did the BET equation.

INTRODUCTION

One method of removing air pollutants from both indoor and outdoor air is to adsorb them in porous materials, such as silica gel, molecular sieve, and activated carbon. Although molecular sieve and silica gel are hydrophilic, they can coadsorb various gases, including hydrocarbons, in the presence of water vapor (*1–3*). Besides having offensive odors, pollutants such as the aldehydes may cause a number of health problems. The most common effects are headaches, narcotic action on the nervous system, and a rise in blood pressure (*4, 5*).

The design of an adsorption process to remove these compounds from air requires pure component equilibrium data as a function of temperature

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and pressure. Very little experimental work on the adsorption of aldehydes on porous materials has been reported in the literature. Nayar and Rao (*6*) studied the adsorption of propionaldehyde and butyraldehyde on silica gel and silica aerogel at one temperature only (303 K). Tanada (7) examined the adsorption of acetaldehyde by 20 different adsorbents. Most of the adsorbents studied by Tanada were varieties of activated carbons, although that study did include silica gel and molecular sieve. His experiments were designed to determine the maximum adsorption capacities of the adsorbent at various concentrations of acetaldehyde, rather than determining the complete adsorption isotherm. None of the data in the previous studies were correlated with theoretical adsorption models.

In the present work, adsorption isotherms of acetaldehyde, propionaldehyde, and butyraldehyde on molecular sieve 13X were obtained at three temperatures. The equilibrium adsorption data were correlated according to Polanyi's potential theory to check the consistency of the experimental data. Data were also correlated with different theoretical models. The isoteric heat of adsorption was calculated as a function of loading to determine the heterogeneity of the molecular sieve 13X surface.

EXPERIMENTAL SECTION

Materials and Apparatus

Grade 542, 8 mesh bead molecular sieve 13X was supplied by the Davison Chemical Co., Baltimore,. Maryland. Acetaldehyde and butyraldehyde were obtained from Fluka AG and had stated purities of 99.5 and 99+%, respectively. Propionaldehyde, which was obtained from Aldrich Chemical Co., Milwaukee, Wisconsin, had a minimum purity of 99%.

A Cahn C-2000 electrobalance with a sensitivity of 0.1 μg was used for the adsorption study. The electrobalance and the flow diagram of the experimental apparatus were described in a paper by Kuo and Hines (*8*). A vacuum of 1×10^{-4} mmHg was obtained in the system prior to the adsorption run. The leak rate of the complete experimental set-up was approximately 0.0054 mmHg/h. The system pressure was measured with 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 each adsorption run, the molecular sieve was heated at a temperature of 423 ± 2 K under vacuum to remove moisture and other gases that might had been adsorbed on the surface; heating under vacuum was continued until a constant sample weight was obtained. Although approximately 8 h were required to attain constant weight, a heating period of 12 h was used for all the runs. During regeneration, the temperature was controlled within ±2 K. The amount that could be adsorbed on the molecular sieve was found to be a function of regeneration temperature up to 423 K. After regeneration of the sample, the adsorption chamber and the molecular sieve were cooled to a predetermined temperature. The adsorbate vapor was introduced into the system in steps, and the system was allowed to attain equilibrium as indicated by the constant weight of the sample. The system pressure and sample weight were recorded after each equilibrium step. Following adsorption, desorption was carried out by reducing the system pressure in small pressure increments. A fresh sample of molecular sieve was used in each run because of the inability to remove the adsorbate completely from the molecular sieve, in spite of several hours of heating under vacuum. The error introduced in the weight measurement due to the buoyancy effect was negligible.

RESULTS AND DISCUSSION

Equilibrium Data

The adsorption isotherms for acetaldehyde, propionaldehyde, and butyraldehyde at the higher temperatures appeared to be of Type I, but were of Type II at the lower temperatures. The adsorption and desorption curves for the aldehydes are shown in Figs. 1 through 3. Adsorption curves begin

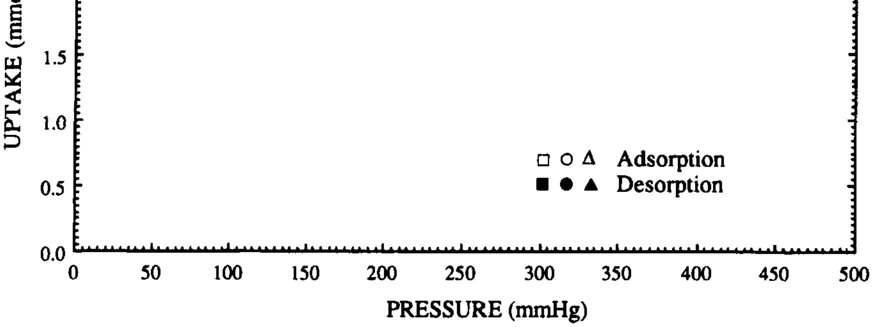

FIG. 1. Adsorption and desorption curves for acetaldehyde on molecular sieve 13X.

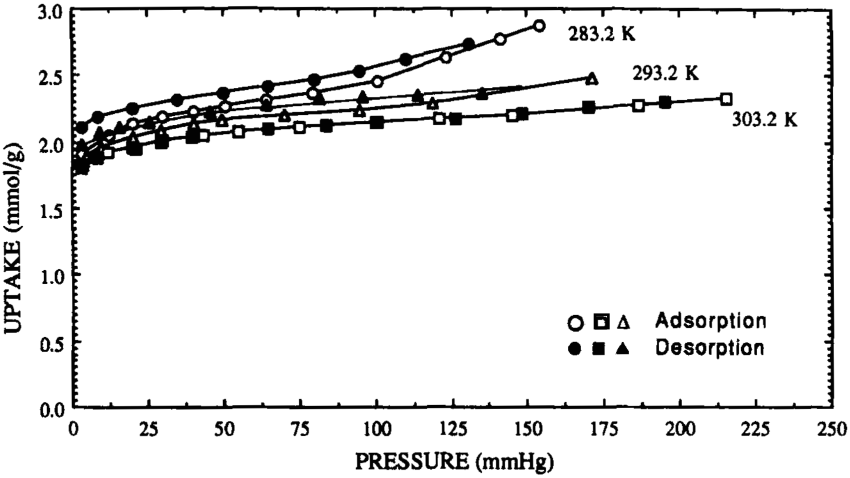

FIG. 2. Adsorption and desorption curves for propionaldehyde on molecular sieve 13X.

to increase more rapidly at adsorption pressures greater than half of the saturation pressure. From Figs. 2 and 3 it can be seen that multilayer adsorption and pore filling become more pronounced at low temperatures as the adsorption pressure approaches the saturation pressure. During the desorption runs, hysteresis was observed to decrease for all of the aldehydes

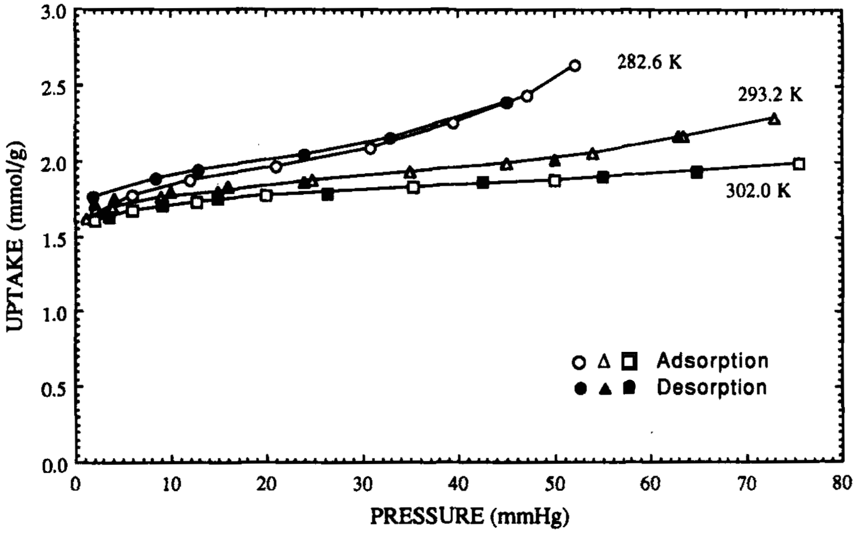

FIG. 3. Adsorption and desorption curves for butyraldehyde on molecular sieve 13X.

as the temperature increased. Above 300 K, hysteresis was not present for either propionaldehyde or butyraldehyde. The presence of hysteresis loops at low temperatures is probably due to the combination of several factors: 1) the sieving action of the adsorbent on the expanded adsorbate, 2) the chemisorption of aldehydes, 3) a different mechanism during desorption than during adsorption, and 4) the polar nature of the aldehyde molecules. Ponec et al. (*9*) noted that at a certain pressure, capillary condensation can occur following multilayer adsorption in the same pore. Cohan (*10*) pointed out that condensation and evaporation from pores occur at different relative pressures, and this results in hysteresis.

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

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

Plots of the heats of adsorption at different loadings are presented in Fig. 4. Both acetaldehyde and propionaldehyde showed a minimum and maximum point in the curve, while butyraldehyde showed a maximum only. The heat of adsorption at lower loading could not be calculated due to the lack of adsorption data in the low pressure region. However, the lack of low pressure data does not change the shape of the curve at higher loading. Beebe and Young (*11*) observed behavior similar to that shown in Fig. 4

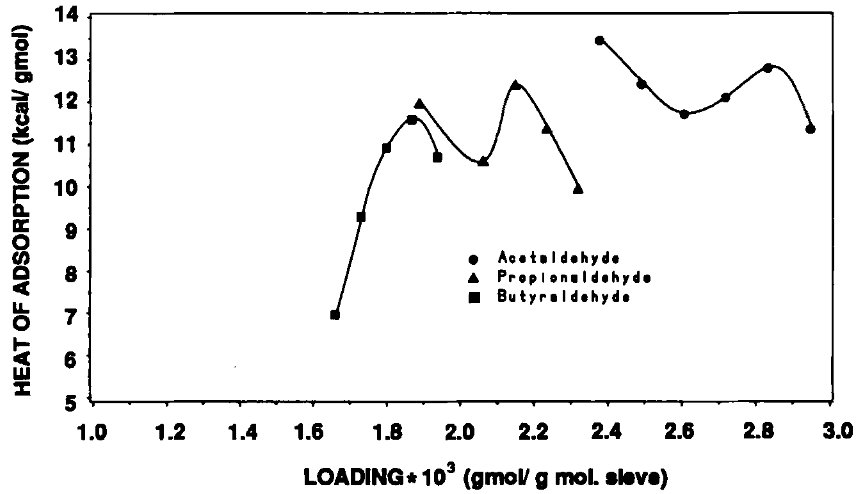

FIG. 4. Heat of adsorption at different loadings for aldehydes on molecular sieve 13X.

for argon on nonporous spheron carbon blacks. The isotherms for the argon–spheron system are also of Type II. Typically, the heat of adsorption should be expected to increase on a molar basis, approximately as the molecular weight of the aldehydes increase. Due to the sieving of the adsorbate, however, this is not true here and should not be expected. The decrease in the heat of adsorption in the initial period with increasing coverage is typical behavior for adsorption on a heterogeneous surface. As the higher energy sites are gradually filled, the heat of adsorption starts to decrease. But with the increase of coverage, the lateral interaction between the molecules also increases, which causes the heat of adsorption to increase. When multilayer adsorption starts, the energy released by the second layer and subsequent layers is much lower than the first layer. Therefore, the overall heat of adsorption starts to decrease, as observed in the present work. This is described by Adamson (*12*) and Joyner and Emmett (*13*) for the adsorption of nitrogen on carbon black.

Data Correlation

The consistency of the adsorption data was checked by correlating the data according to the potential theory of Polanyi. This theory was initially developed for multilayer gas adsorption and assumes that a potential field which exists at the solid surface exerts long range attractive forces on the surrounding gas or vapor phase. The potential field decreases as the distance between the gas phase and the solid surface increases. The potential theory of Polanyi can be expressed as

$$\varepsilon = RT \ln (P_s/P) \tag{2}$$

where ε is the adsorption potential and P_s is the saturation pressure of the adsorbate at the system temperature, T. Polanyi further assumed that the adsorption potential given by Eq. (2) is independent of temperature. Therefore, a plot of adsorption potential (ε) versus the volume adsorbed on the solid surface should yield a single characteristic curve. Such plots for acetaldehyde, propionaldehyde, and butyraldehyde are presented in Figs. 5, 6, and 7, respectively. The shape of the characteristic curve is typical of that found for multilayer gas adsorption.

The equilibrium adsorption data were also correlated by applying the BET model and the heterogeneous surface models developed by Sircar (*14*) and Hines et al. (*15*). The BET equation was derived for nonporous surfaces, but it has been used extensively to determine the surface area of porous material (*16*). Although multilayer adsorption was considered in developing the BET equation, the heterogeneity of the solid surface and

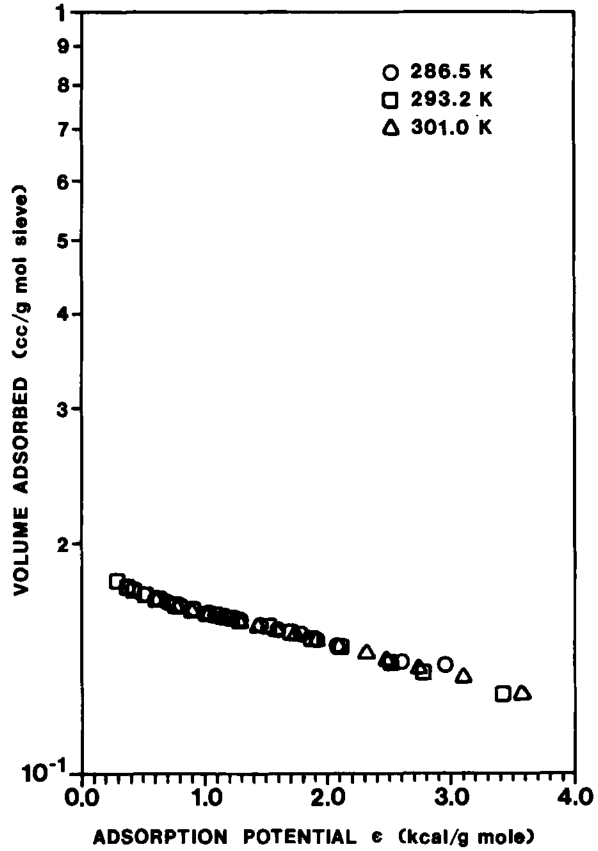

FIG. 5. Characteristic curve for acetaldehyde on molecular sieve 13X.

the lateral interaction of the molecules were not included. A good correlation of the data was obtained for the pressure range of $0.05 \leq P/P_s \leq 0.25$ by using the BET equation. This is the pressure range over which the BET equation typically gives the best correlation of experimental data as observed by other researchers (*17*, *18*). Larger deviations from the calculated data were observed both at low pressures ($P/P_s < 0.05$) and higher pressures ($P/P_s > 0.25$). Although the BET equation is best suited for Type II isotherms, the failure of the equation to predict the aldehydes–molecular sieve data may be due in part to the heterogeneity of the solid surface and the lateral interaction between the aldehyde molecules.

Both the Langmuir and the BET equations were used to calculate the surface area and the monolayer coverage of the molecular sieve. The area occupied by an aldehyde molecule on the solid surface was calculated by

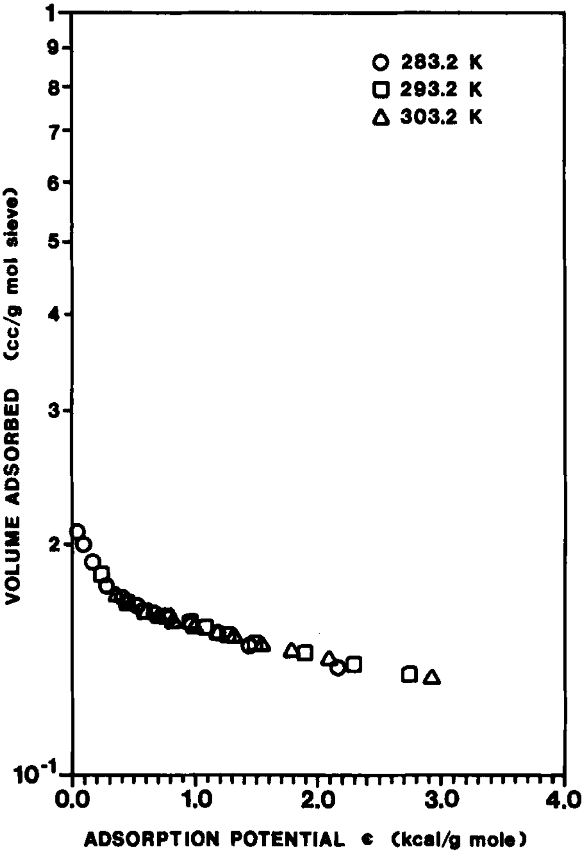

FIG. 6. Characteristic curve for propionaldehyde on molecular sieve 13X.

assuming hexagonal close packing of the aldehyde molecules on the solid surface. Estimated surface areas and the monolayer coverages at different temperatures are presented in Table 1. Surface areas predicted by the Langmuir equation are found to be consistently higher than those estimated from the BET equation. The aldehyde molecules covered less than the available surface area of the molecular sieve, which is 456 m^2/g (measured by an Orr Surface Area-Pore Volume Analyzer, Model 2100D Micromeritics Instrument Corporation, using N_2 as the adsorbate at 77.3 K). Such a low coverage of the surface can be attributed to the inability of the aldehyde molecules to penetrate the pores of the molecular sieve.

Sircar (*14*, *19*) and Hines et al. (*15*) proposed isotherms which took into consideration the heterogeneity of the solid surface. They assumed that the solid surface consisted of energetically different heterogeneous sites which could be described by a probability density function. Sircar used a

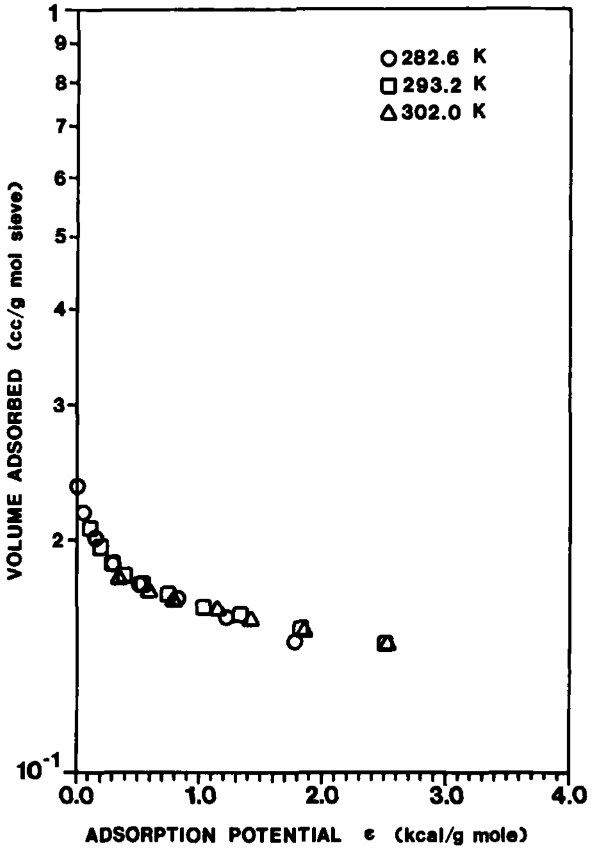

FIG. 7. Characteristic curve for butyraldehyde on molecular sieve 13X.

gamma probability density function while Hines et al. used a probability density function obtained by modifying the Morse potential. Sircar described the local adsorption with the Langmuir and the Jovanovic isotherms, whereas Hines et al. employed the Jovanovic (*20*) isotherm for monolayer coverage to model the adsorption on a specific site. In the present study, the Sircar model using the Jovanovic equation was compared with the Hines et al. model. The isotherm equation developed by Sircar and based on the Jovanovic equation is given by

$$q = m\left[1 - \left(\frac{\alpha}{\alpha + P}\right)^n\right] \tag{3}$$

where m, α, and n are the unknown constants, but are related to the Henry's law constant.

TABLE 1
Monolayer Coverages and Calculated Surface Areas of Molecular Sieve 13X

System	Temperature (K)	Molecular cross section (Å^2)	Monolayer coverage (cm^3/g)		Surface area (m^2/g)	
			Langmuir	BET	Langmuir	BET
Acetaldehyde–molecular sieve	286.5	22.38	65.13	54.67	392	329
	293.2	22.55	64.40	52.34	390	317
	301.2	22.75	62.79	51.14	384	312
Propionaldehyde–molecular sieve	283.2	26.44	52.48	40.91	373	291
	293.2	26.69	49.72	39.46	357	283
	303.2	26.96	47.71	38.44	346	279
Butyraldehyde–molecular sieve	282.6	30.43	45.08	31.83	369	260
	293.2	30.70	42.31	30.26	349	251
	302.0	30.95	41.50	30.16	345	250

The Hines et al. equation can be written as

$$q = m\left[1 - \frac{K_3}{K_3 - K_1K_2}\left(\frac{K_1}{P + K_1} - \frac{K_1K_2}{P + K_3}\right)\right] \tag{4}$$

where m, K_1, K_2, and K_3 are functions of temperature only and are also related to the Henry's law constant.

The parameters of Eqs. (3) and (4) are obtained by using a nonlinear regression analysis (Marquardt-S method) for all experimental data. The best fit values of the parameters are given in Table 2. The best fit curves provided by the Sircar and the Hines et al. equations are shown along with the experimental data in Figs. 8 through 10. As can be seen from the figures, the Hines et al. model provided a better fit of the experimental data than did Sircar's model. When multilayer adsorption became more prominent, a large deviation between the calculated and the experimental values was observed. Although Sircar and Hines et al. considered the surface heterogeneity in the model, multilayer adsorption was not considered. The Jovanovic isotherm used to describe the local adsorption is for monolayer adsorption only. Therefore, the poor correlation by these models when multilayer adsorption occurs is not surprising. A comparison of the experimental data with the calculated values was made 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 Table 3. In general, the Hines et al. equation provided a better fit to the data than did the Sircar model.

TABLE 2
Best Fit Parameters for the Hines et al. and Sincar Models

		Hines et al.				Sircar		
System	Temperature (K)	m (mmol/g)	K_1 (mmHg)	K_2 (—)	K_3 (mmHg)	m (mmol/g)	n (—)	α (mmHg)
Acetaldehyde–molecular sieve	286.5	3.246	88.563	-7.951×10^{-3}	0.2007	3.270	0.314	0.0816
	293.2	3.219	88.150	-6.797×10^{-3}	0.1958	3.328	0.278	0.0745
	301.0	3.014	67.676	-1.028×10^{-2}	0.1934	3.049	0.327	0.0818
Propionaldehyde–molecular sieve	283.2	8.013	968.147	-3.219×10^{-5}	0.0956	7.055	0.0516	0.0177
	293.2	3.144	236.996	-7.246×10^{-4}	0.1075	2.580	0.268	0.0384
	303.2	2.645	179.505	-1.824×10^{-3}	0.1305	2.458	0.280	0.0475
Butyraldehyde–molecular sieve	282.6	8.231	341.793	-4.941×10^{-5}	0.0680	7.016	0.0498	0.0145
	293.2	4.512	312.944	-1.428×10^{-4}	0.0753	2.536	0.218	0.0247
	302.0	3.063	258.762	-4.290×10^{-4}	0.0928	2.043	0.354	0.0402

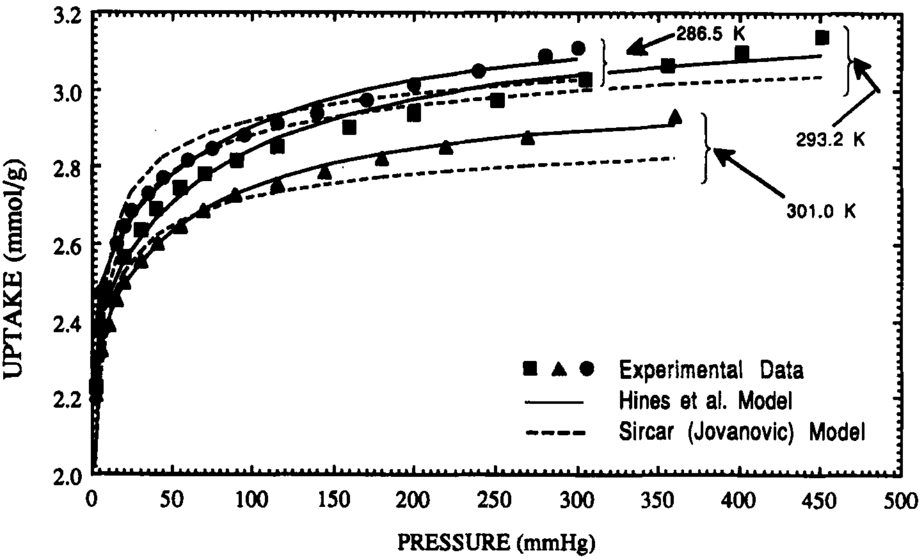

FIG. 8. Comparison of experimental data for acetaldehyde–molecular sieve systems with predictions by the Hines et al. and Sircar models.

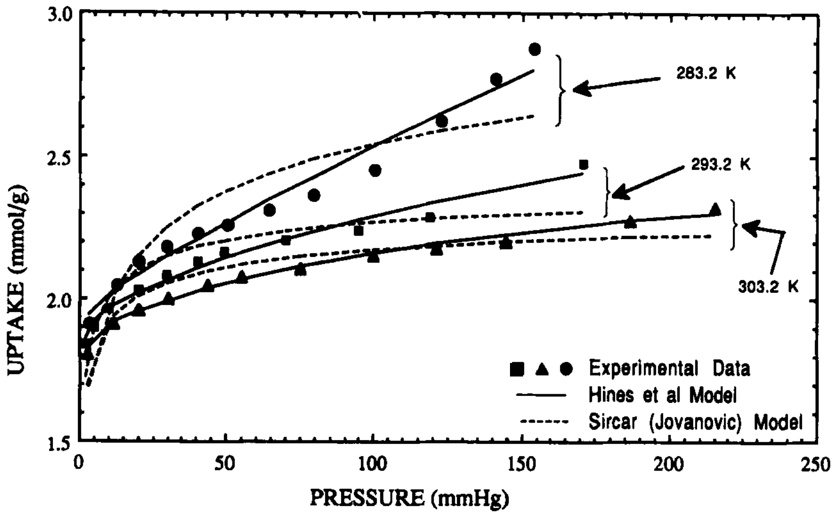

FIG. 9. Comparison of experimental data for propionaldehyde–molecular sieve systems with predictions by the Hines et al. and Sircar models.

TABLE 3
Comparison of Model Correlations

System	Temperature (K)	Absolute average error[a] (%)		Maximum positive error[a] (%)		Maximum negative error[a] (%)	
		Hines et al.	Sircar	Hines et al.	Sircar	Hines et al.	Sircar
Acetaldehyde–molecular sieve	286.5	0.51	1.69	0.96	5.83	0.87	1.81
	293.2	0.77	2.08	1.71	8.97	1.25	2.54
	301.0	0.28	1.70	0.82	6.62	0.51	2.07
Propionaldehyde–molecular sieve	283.2	1.65	4.61	2.68	11.72	3.53	5.50
	293.2	1.06	2.66	1.60	6.89	2.03	3.23
	303.2	0.60	2.22	1.02	6.34	1.16	2.59
Butyraldehyde–molecular sieve	282.6	2.52	5.79	4.88	10.88	4.41	8.76
	293.2	1.27	4.55	3.24	10.03	2.17	5.96
	302.0	0.36	2.47	0.87	4.40	0.66	3.03

[a] Error $= \frac{\text{experimental} - \text{calculated}}{\text{experimental}}$.

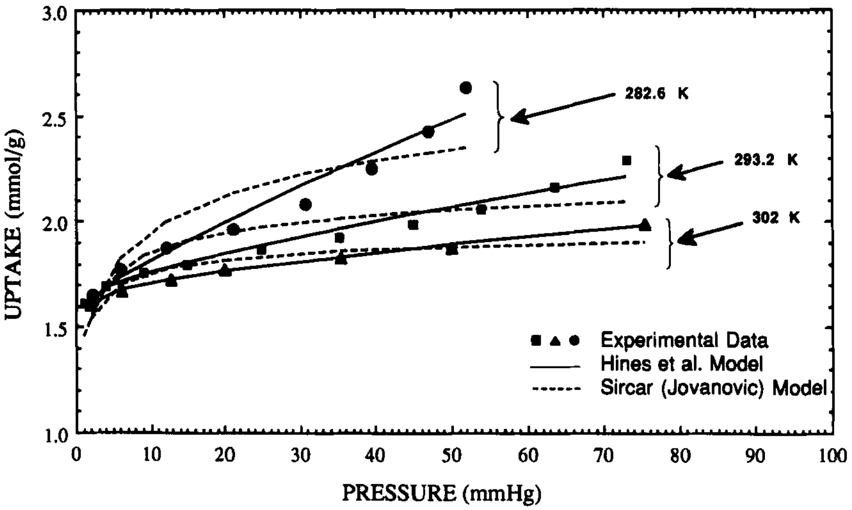

FIG. 10. Comparison of experimental data for butyraldehyde–molecular sieve systems with predictions by the Hines et al. and Sircar models.

NOMENCLATURE

ε	adsorption potential
ΔH_{iso}	isoteric heat of adsorption
K_1, K_2, K_3	constants in the Hines et al. equation
m	constant in the Sircar and the Hines et al. equations
n, α	constants in the Sircar equation
P	system pressure
P_s	saturation pressure of the adsorbate at the system temperature
q	uptake of the adsorbate
R	gas constant
T	system temperature

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