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Analysis of Ammonia Adsorption on Silica Gel Using the Modified Potential Theory

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The adsorption of NH_3 on Davison silica gel was studied at 298, 313, and 333 K by using a packed bed method. Equilibrium isotherms were calculated from the adsorption data and were modeled by the Langmuir and modified Polanyi potential equations. Experimental breakthrough curves were obtained for six concentrations of NH_3 in dry helium gas at each temperature. The isosteric heats of adsorption were also calculated at three adsorbent loadings and were found to be nearly independent of loading. A calculated heat of adsorption of the same order of magnitude as the heat of condensation indicated that the adsorption was primarily due to physical forces.

Introduction

The adsorption of ammonia on silica gel has received considerable interest recently because of its potential use in solar energy cooling cycles. Relatively few studies, however, have been made in which silica gel was used as the adsorbent. Clark et al. (*1*) used the Freundlich equation to correlate the adsorption isotherm data for ammonia on 11 silica-alumina gels. Following this, Szczepanska and Malinowski (*2*) investigated the adsorption of ammonia on seven SiO_2 catalysts which contained up to 22.7×10^{-3} mg Na^+ ions/m^2 of catalyst surface. Their data covered the temperature range 20-300 °C and were correlated by using the Langmuir equation. More recently, Tishin and Rumyantsev (*3*) compared the adsorption capacity of ammonia on several adsorbents, including two types of silica gel, and found that the adsorption capacity of silica gel is greater than that of zeolites.

In this work, the adsorption of ammonia on Davison silica gel grade 59 was studied by using a packed bed method. The equilibrium adsorption data were correlated by the Langmuir (*4*, *5*) model, the Polanyi (*6*, *7*) adsorption potential theory, and the theory of pore filling proposed by Dubinin and co-workers (*8*-*11*).

Experimental Section

The Davison grade 59 silica gel adsorbent, which had particle sizes that ranged from 3 to 8 U.S. mesh, was used as the adsorbent for this study. It had a total surface area of 340 m^2/g (as found by a BET analysis), a bulk density of 0.4 g/cm^3, a pore volume of 1.15 mL/g, and a mean pore diameter of 1.4×10^{-8} m.

The adsorption studies were conducted in a packed bed that utilized an ultraviolet detector to measure gas concentrations and obtain experimental breakthrough curves. The adsorption column was a 1.3-cm-o.d. stainless steel tube, 19.0 cm in length. It had union reducers at both ends so that one end could be connected to a heating coil in which the gas was heated to the adsorption temperature. Thermocouples were attached to each end of the packed column to monitor any change in the gas stream temperature that might occur during the adsorption run. The gas flow rate was controlled with a mass flow meter that had been calibrated at the experimental conditions. The adsorption column and heating coils were immersed in a constant temperature bath in order to maintain isothermal conditions.

Table I. Equilibrium Adsorption Data

gas concn^a	T, K	NH_3 uptake^b
1.839	298	6.03
3.734		7.40
5.717		8.02
9.442		8.95
13.270		9.53
18.823		10.89
1.734	313	4.08
3.522		5.41
5.391		6.21
8.904		7.25
12.515		7.75
17.752		8.54
1.641	333	2.52
3.266		3.76
5.000		4.34
8.258		5.05
11.606		5.95
16.463		6.47

^{a} In (kg of NH_3/m^3 of gas) $\times 10^3$. ^{b} In (kg of NH_3/kg of solid) $\times 10^2$.

The adsorption process was started by flowing pure helium through the packed bed of silica gel to remove any impurities from the system. After the bed reached thermal equilibrium with the bath, a gas mixture of ammonia in helium was started. The effluent gas concentration was continuously monitored until it became equal to the inlet concentration. A gas flow rate of 1.64×10^{-2} m^3/h was used. The inlet gas pressure to the bed was 243 kPa, and the pressure drop across the bed was 1.0 kPa.

Results and Discussion

Experimental breakthrough curves were obtained at 298, 313, and 333 K for gas concentrations of 997, 1984, 3037, 5016, 7050, and 10 000 ppm NH_3 in dry helium gas; breakthrough curves for 313 K are shown in Figure 1. Replicate runs were made to ensure reproducibility of the adsorption data; the average of those runs were used to determine the uptake. Special care was taken when packing the column to ensure that the same amount of adsorbent was used per unit length of bed.

The equilibrium capacities for the various inlet gas concentrations were determined by finding the area behind the breakthrough curves, and are presented in Table I for the three adsorption temperatures. The equilibrium data were correlated with the Langmuir isotherm equation

$$q = a_1C/(1 + a_2C) \qquad (1)$$

where a_1 is the first Langmuir constant with units of m^3 of gas/kg of adsorbent and a_2 is the second Langmuir constant with the units used in this study of m^3 of gas/kg of adsorbate.

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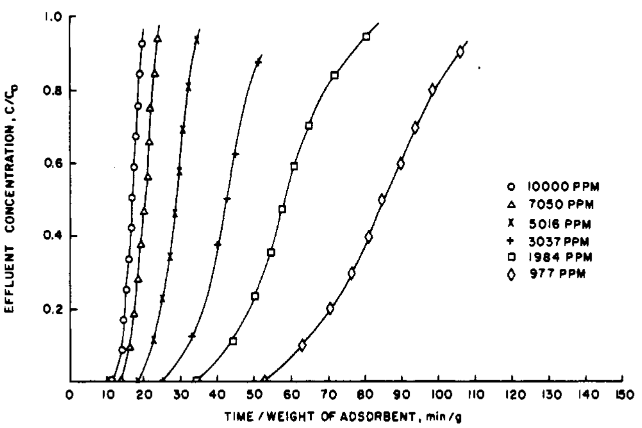

Figure 1. Experimental breakthrough curves for the adsorption of NH_3 on silica gel at 313 K.

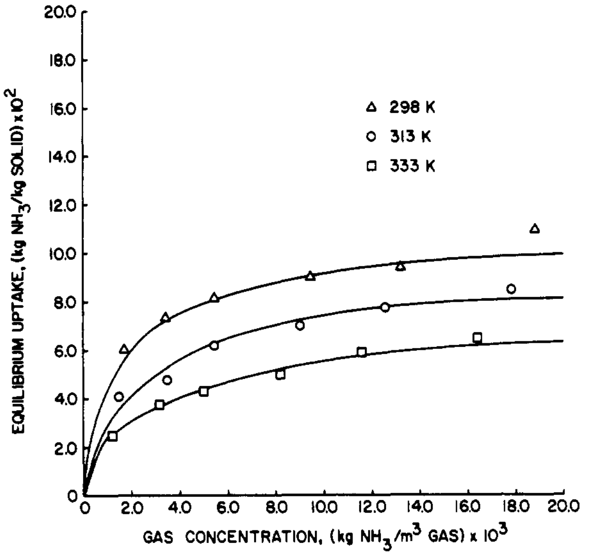

Figure 2. Comparison of the equilibrium data to the Langmuir equation.

Table II. Parameters of Eq 1

T, K	a_1[a]	a_2[b]	coeff of determination
298	72.36	685.96	0.950
313	41.70	461.90	0.988
333	23.22	316.76	0.994

[a] In m^3 of gas/kg of adsorbent. [b] In m^3 of gas/kg of adsorbate.

The constants for the Langmuir equation for each temperature are given in Table II. A comparison of the Langmuir equations and the experimental data is presented in Figure 2. The adequacy of the fit was checked by calculating the correlation coefficient; values of 0.950, 0.988, and 0.994 were found at 298, 313, and 333 K, respectively.

The equilibrium data also were used to calculate the heats of adsorption. Hersh (*12*) has shown that the isosteric heat of adsorption at constant loading is given by the equation

$$H_{\rm iso} = -R\left[\frac{\partial(\ln C)}{\partial(1/T)}\right]_q \qquad (2)$$

The isosteric heats of adsorption were determined graphically from plots of ln C vs. $1/T$. The calculated values for the heat of adsorption were 10.1, 10.1, and 9.8 kcal/(g mol) for loadings of 0.02, 0.03, and 0.04 kg of NH_3/kg of solid, respectively. Since these values are of the same order of magnitude as the heat of condensation, it may be concluded that the adsorption of ammonia on silica gel is primarily the result of physical forces. Complete removal of ammonia from the silica gel was possible by flowing pure helium through the bed.

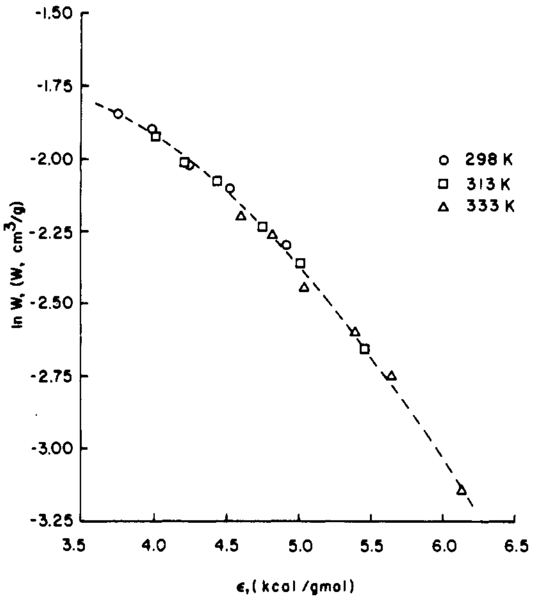

Figure 3. Characteristic curve of NH_3 on silica gel.

The potential theory proposed by Polanyi (*6*, *7*) has been applied successfully for both monolayer and multilayer adsorption of gases on both porous and nonporous adsorbents. This theory assumes that a potential field exists at the surface of the solid and it exerts a strong attractive force on the surronding gas, with the potential decreasing as the distance from the adsorbent surface increases. The adsorption potential can be expressed as

$$\epsilon = RT \ln (P^\circ/P) \qquad (3)$$

where P is the pressure of the adsorbate gas in the system and P° is the vapor pressure of the gas at the system temperature. Based on the potential theory, a graph of the amount adsorbed vs. the adsorption potential should yield a characteristic curve which is independent of temperature. The characteristic curve obtained from the adsorption data is given in Figure 3. As shown, the data for all temperatures lie close to a single characteristic curve as required by the Polanyi theory.

Bering et al. (*9*, *11*) showed that the volume adsorbed in the adsorbent pores can be described by the expression

$$W = W_0 \exp[-(\epsilon/\beta E)]^n \qquad (4)$$

where W is the volume of the adsorption space, E is a constant characteristic energy, β is the affinity factor, W_0 is the volume of the adsorption space at saturation, and n is a constant. According to eq 4, a plot of ln W vs. ϵ^n should give a straight line with a slope of $-(1/\beta E)^n$ and an intercept of ln W_0. This is shown in Figure 4. A value of n equal to 2.6 was found to give a straight line at all temperatures studied in this work. The adequacy of the fit was checked by calculating the coefficient of determination; a value of 0.996 was found for this study. Values for n have been shown by Huber et al. (*13*) to vary from 1.0 to 6.0, depending on the adsorbate–adsorbent system. They reported an n equal to 1.0 for one type of silica gel.

Although the experimental adsorption data could be fit relatively well with the Langmuir equation except for the higher concentrations, a better fit was obtained with the modified Polanyi potential equation. This is demonstrated in Figure 5 for the adsorption temperature of 298 K. The experimental data for all isotherms were reduced to a Dubinin–Polanyi type potential plot and were found to obey this type of relationship relatively well. The fact that the data could be reduced to a single curve demonstrates the consistency of the data for all

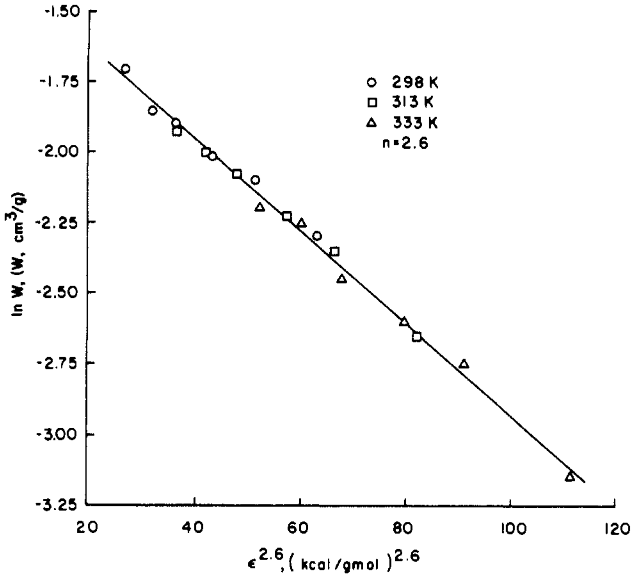

Figure 4. Plot of ln W vs. ϵ^n for the adsorption of NH_3 on silica gel.

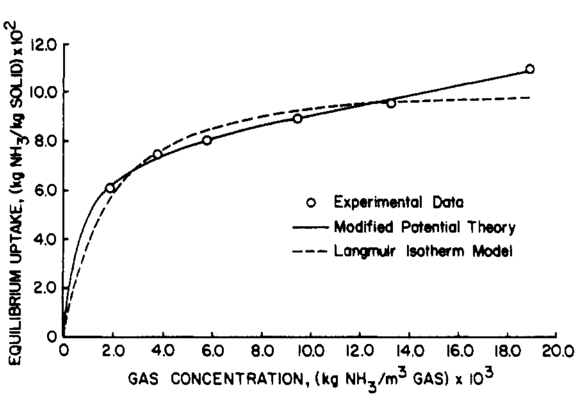

Figure 5. Comparison of experimental and predicted isotherms at 298 K using the Langmuir and potential models.

temperatures. Furthermore, the successful application of the modified potential theory to the experimental data makes it possible to predict equilibrium isotherm data at other temperatures.

Glossary

a_1	first Langmuir constant (m^3 of gas/kg of adsorbent)
a_2	second Langmuir constant (m^3 of gas/kg of adsorbate)
C	gas-phase concentration (kg of adsorbate/m^3 of gas)
C_0	inlet gas concentration (kg of adsorbate/m^3 of gas)
E	constant characteristic energy (kcal/(g mol))
H_{iso}	isosteric heat of adsorption (kcal/(g mol))
n	constant in the generalized isotherm equation
P	pressure of the adsorbate (kPa)
P^0	saturation pressure (kPa)
q	equilibrium concentration of adsorbed gas (kg of adsorbate/kg of adsorbent)
R	gas constant
T	absolute temperature (K)
W	volume of the adsorbed phase (cm^3/g of adsorbent)
W_0	volume adsorbed at saturation (cm^3/g of adsorbent)
β	affinity factor
ϵ	adsorption potential (kcal/(g mol))

Registry No. NH_3, 7664-41-7.

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Vapor-Liquid Equilibrium Data for the Binary System Water-Ammonia at 403.1, 453.1, and 503.1 K up to 7.0 MPa

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A static method described in a previous paper has been used to obtain vapor-liquid equilibrium data for the water-ammonia system at three temperatures, 403.1, 453.1, and 503.1 K, and pressures up to 7 MPa. Comparison with lower pressure literature data is presented.

Introduction

The thermodynamic properties of the water-ammonia system, especially vapor-liquid equilibria, are needed to design absorption heat pumps and refrigeration processes. Some data on this system are already available in the literature (*2-13*), but only for pressure and temperature ranges up to 3.5 MPa and 503.1 K, except in the work of Tsiklis et al. (*8*). Unfortunately, the data are often smoothed or scattered and therefore difficult to use. The present work extends the range of pressure up to 7 MPa, at three temperatures, two of them above the critical temperature of ammonia (405.6 K).

Experimental Section

Apparatus. The experimental setup described in a published paper (*1*) is based on a static method. The equilibrium cell is made of nonmagnetic stainless steel 316 LSS (AFNOR:

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