solution temperature for the salt-saturated DEMA/water/sodium sulfate system is 20 °C.

Registry No. DEMA, 124-40-3; H_2O, 7732-18-5; sodium chloride, 7647-14-5; sodium sulfate, 7757-82-6.

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Effects of Regeneration Conditions on the Characteristics of Water Vapor Adsorption on Silica Gel

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Equilibrium adsorption and desorption isotherms of water vapor on a silica gel were measured at 288, 298, and 308 K. Isotherms were of type I according to Brunauer's classification and provided a single characteristic curve when correlated according to Polanyi's potential theory. Literature data on different samples of silica gel exhibited differences in uptake capacity from each other and from the present data. The uptake capacity at 298 K did not change significantly when regeneration temperatures were varied in the range of 373–442 K, nor when the regeneration time was increased from 4 to 16 h. The heats of adsorption suggest that silica gel has an energetically heterogeneous surface for water vapor adsorption.

Introduction

Silica gel has been employed widely as a dehumidifying material in the chemical and petroleum industries, food industries, and construction industries, as well as in solar desiccant cooling. Recently it has found a major application in desiccant-based air conditioning systems, in which silica gel is employed in a rotary dehumidification wheel to adsorb water vapor from moist air. After a predetermined period of time, silica gel is regenerated by an auxiliary heat source, such as by hot air or electrical heating. For applications in which silica gel undergoes repeated water adsorption/regeneration cycles, data on regeneration temperatures and times are needed to optimize the design of a desiccant system.

Although silica gel is one of the major solid desiccants employed in industry, limited equilibrium isotherm data for water vapor are reported in the open literature for commercially available silica gel. Pedram and Hines (*1*) obtained equilibrium adsorption data of water vapor on Mobil Sorbead R silica gel at three temperatures. Although Polanyi's potential theory (*2*) provided a good correlation of the data, the Brunauer–Emmett–Teller (BET) equation fitted the data only in the relative pressure range of 0.05–0.40. They also noted that adsorption capacities for water vapor obtained in their experiments were approximately 20% lower than Mobil's values. They attributed this discrepancy to differences in regeneration temperatures. Machin and Stuckless (*3*) used Davison Grade 03 silica gel in their study at 273.65 and 298.15 K, but work was mainly focused on understanding the pressure–volume behavior of condensed water in capillaries. Pesaran et al. (*4*) carried out a comprehensive literature survey on water vapor adsorption by silica gel, and also measured water adsorption capacities of three batches of silica gel (Davison Grade 40). They noted that adsorption capacities varied from batch to batch and found large differences between their observations and the manufacturer's data.

Table I. Physical Properties of Silica Gel

particle size[b]	6 × 12 mesh
surface area, $S/(m^2/g)$[a]	
micropores	663
meso- and macropores	9
total	672
pore volume, $V/(cm^3/g)$[a]	
micropores	0.38
meso- and macropores	0.02
total	0.40
average pore diameter, $4V/S$/Å[a]	23.6
bulk density/(g/cm^3)[b]	0.72

[a] Analysis made by Porous Materials, Inc., Ithaca, NY. [b] Analysis provided by the manufacturer.

In this study, adsorption isotherms for water vapor on silica gel were measured at three temperatures, and the effects of regeneration temperatures and times on adsorption capacities at 298 K were studied. The equilibrium data were used to calculate heats of adsorption and thereby to determine the role of surface heterogeneity on the adsorption process. The data were correlated according to Polanyi's potential theory.

Experimental Section

The silica gel used in this study was grade 40, 6 × 12 mesh (lot no. MIL-D-3716 type II) and was supplied by Davison Chemical Co. The properties of the silica gel are presented in Table I. The adsorbate was double-distilled water that was further purified by passing through an ion-exchange column. The experimental adsorption and desorption studies were carried out gravimetrically in an all-glass apparatus using a Cahn C-2000 electrobalance. The description of the apparatus is given elsewhere (*5*). A vacuum of 10^{-4} mmHg can be attained in the system prior to initiating an adsorption run, with a leak rate of the complete system of approximately 10^{-3} mmHg/h. Pressures below 10^{-4} mmHg were measured by ionization gauges and pressures from 10^{-3} by using convectron gauges. The adsorption pressures during an experimental run were

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Table II. Equilibrium Adsorption and Desorption Data for Water Vapor on Silica Gel[a]

288 K		298 K		308 K	
pressure/ mmHg	uptake/ (mg/g)	pressure/ mmHg	uptake/ (mg/g)	pressure/ mmHg	uptake/ (mg/g)
		Adsorption			
0.1	37	0.3	30	3.2	49
1.2	80	1.5	55	6.3	86
2.1	112	3.0	83	9.0	118
4.0	165	4.9	111	12.2	157
6.9	260	7.1	170	16.8	207
9.0	281	10.9	236	21.1	248
11.2	294	13.8	270	22.9	256
12.0	300	16.9	280	24.8	263
		19.1	287		
		22.4	303		
		Desorption			
7.0	288	12.1	287	19.0	248
4.8	264	8.9	265	14.0	206
3.5	231	7.0	199	9.9	139
2.1	162	3.9	136	5.1	89
0.9	107	1.1	85	2.1	56

[a] 101.325 kPa = 760 mmHg.

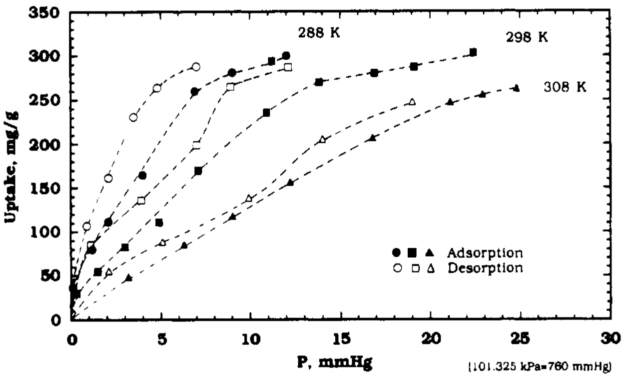

Figure 1. Adsorption/desorption curves for water vapor on silica gel.

measured using a Wallace and Tiernan absolute pressure gauge (model 61A-ID-0800). The calibration of the Wallace and Tiernan gauge is traceable to the National Institute of Standards and Technology. Approximately 60 mg of silica gel was used in an adsorption/desorption run. Silica gel was regenerated by heating the sample under vacuum at a specified temperature for a predetermined period of time. Following regeneration, the sample was cooled to the desired adsorption temperature and water vapor was introduced into the system in steps. After equilibrium was reached, as indicated by a constant sample weight, the pressure and weight gain were recorded. Equilibrium isotherm data were taken from approximately 0.1 mmHg up to 80–90% of the saturation pressure. Desorption measurements were carried out by reducing the system pressure in incremental steps. The same silica gel sample was used in all experimental runs, since it could be regenerated completely after each adsorption/desorption cycle.

Results and Discussion

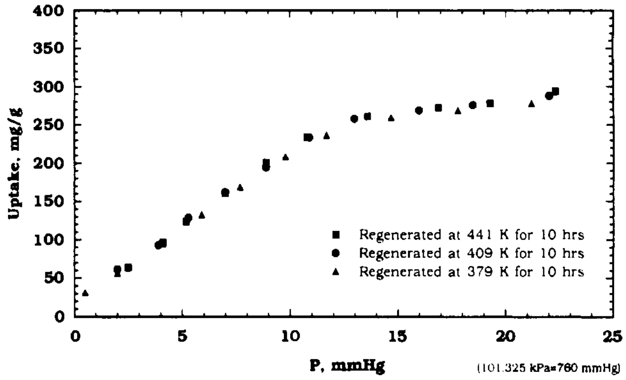

Figure 2. Effect of regeneration temperatures on adsorption capacities for water vapor at 298 K.

The equilibrium adsorption data for water vapor on silica gel were obtained at 288, 298, and 308 K after 10 h of regeneration under vacuum at 442 ± 1 K. The equilibrium adsorption and desorption data are presented in Table II and are plotted in Figure 1. The data were reproducible with an average deviation of ±0.68%. Generally, the isotherms appeared to be of type I and exhibited hysteresis upon desorption. The hysteresis loops were observed to decrease with an increase in temperatures. Pedram and Hines (*1*) and Machin and Stuckless (*3*) also observed hysteresis loops in their studies, which suggest the presence of "ink bottle" type pores (*6*, *7*). As a pore is emptied, the pressure is controlled by the smaller diameter at the neck of the pore, which retains a liquid meniscus and causes hysteresis. The uncertainty in the weight and pressure measurements was calculated by using the approach shown by Holman (*8*). The uncertainty, M_R, in a measured value R can be expressed as

$$M_R = \left[\left(\frac{\partial R}{\partial x_1} M_1\right)^2 + \left(\frac{\partial R}{\partial x_2} M_2\right)^2 + \ldots \left(\frac{\partial R}{\partial x_n} M_n\right)^2\right]^{1/2} \qquad (1)$$

where $x_1, x_2, \ldots, x_n$ are independent variables and $M_1, M_2, \ldots, M_n$ are uncertainties in the measurement of individual independent variables, respectively. In calculating the uncertainty in the weight measurement, it is assumed that an error is introduced during the measurement of the initial sample weight and in each weight increment during a run. The uncertainty was assumed to be ±0.01 mg in both cases. The uncertainty in the pressure reading from the pressure gauge was assumed to be ±0.01 mmHg up to a pressure of 2 mmHg and ±0.1 mmHg at higher pressures. The error in the temperature that was used to calculate the saturation pressure was ±0.1 K. The average errors introduced in the weight and pressure measurements calculated from eq 1 were ±0.21% and ±6.95%, respectively. The error introduced by the buoyancy effect was found to be negligible.

The adsorption capacity of water vapor on silica gel depends to a large extent on the concentration of hydroxyl groups on the silica gel surface. When the silica gel is heated during regeneration, it undergoes dehydration due to the removal of hydroxyl groups. The degree of removal of this functional group is expected to be a function of regeneration temperature. It can be seen from Figure 2 that uptake capacities increased marginally with the increase of regeneration temperatures over the range of 379–441 K. Pedram and Hines, however, reported a 16.7% decrease in the adsorption capacity at a relative pressure of 0.61 when the regeneration temperature was increased from 428 to 488 K. It should be noted that the highest regeneration temperature employed in the present study was 442 K. Naono et al. (*9*) observed a small increase in the adsorption capacity up to a regeneration temperature of 473 K, although a higher regeneration temperature had a detrimental effect on the adsorption capacity. The adsorption capacity decreased significantly as the regeneration temperature was further increased. During regeneration, the removal of hydroxyl groups from the surface prevents the formation of hydrogen bonds and reduces the adsorption capacity. The proportion of the isolated groups increases with increasing regeneration temperature, thereby reducing the uptake capacity. A detailed explanation of this subject is provided by Gregg and Sing (*10*). As shown in Figure 3, increasing the regeneration time from 4 to 16 h produced only a small effect on the uptake capacity at 298 K. Silica gel retains approximately 5 wt % water (*11*) after

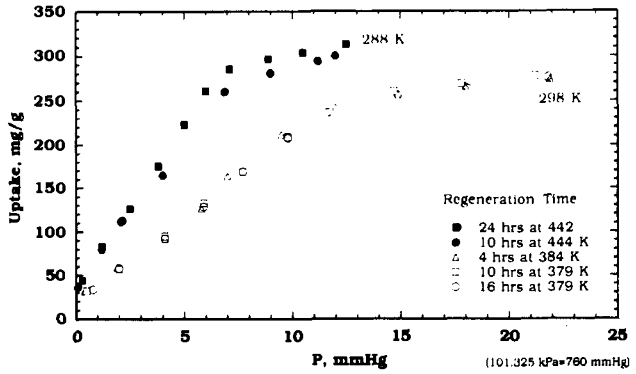

Figure 3. Effect of regeneration times on adsorption capacities for water vapor.

Table III. Heats of Adsorption at Different Loadings

loadings/ (g/g)	heats of adsorption/ (kJ mol^{-1})	loadings/ (g/g)	heats of adsorption/ (kJ mol^{-1})
0.10	53.6	0.20	46.0
0.15	48.5	0.25	45.2

activation, which is chemically bound to the surface and difficult to remove. However, a heating period up to 24 h resulted in greater dehydroxylation, as observed in the change of the uptake capacity at 288 K. Nevertheless, it appears that most of the physically bound water and other gases can be removed from silica gel surfaces by 4 h of heating at 440 K under vacuum.

The equilibrium data were used to calculate the heat of adsorption and provide a better understanding of the nature of the silica gel surface. The isosteric heat of adsorption at constant loading can be calculated from the following expression:

$$H_{st} = -R[\partial \ln P/\partial(1/T)]_q \qquad (2)$$

The heats of adsorption were determined graphically from plots of ln P versus $1/T$ at different loadings. The calculated values are presented in Table III. As can be seen from this table, the heats of adsorption decreased as the loading increased, which is typical of adsorption on heterogeneous surfaces. The heat of adsorption approached the heat of condensation of water at higher loadings. This phenomenon and the fact that the adsorbed water vapor could be removed completely from the silica gel surface during regeneration suggest that the adsorption is physical in nature.

Polanyi's potential theory was used to correlate the adsorption data and provided a consistency check of the data. According to this theory, a plot of the volume adsorbed versus the adsorption potential should provide a single characteristic curve that is independent of temperatures. As shown in Figure 4, the data for all three temperatures lie close to a single characteristic curve, as required by Polanyi's potential theory. Since the manufacturer's data and other published literature data (*1*, *3*, *4*) were reported at various temperatures, the potential theory was used to compare these data with those of the present study. Significant differences among these data were observed as can be seen from Figure 5. The difference may be due to several factors such as different regeneration temperatures, regeneration times, surface area of that particular batch of silica gel, and the concentration of hydroxyl groups on the surface. Therefore, each batch of silica gel should be carefully characterized prior to its use in a particular desiccant dehumidification system.

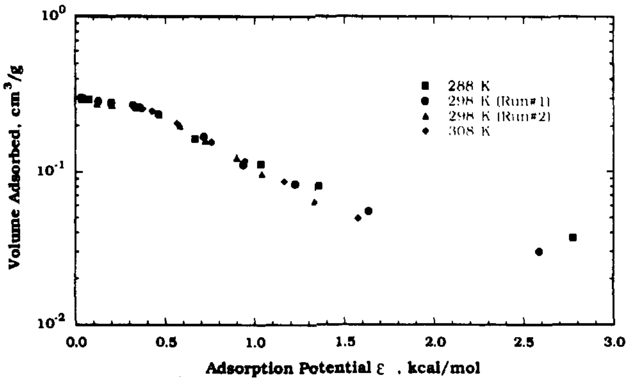

Figure 4. Characteristic curve of water vapor on silica gel.

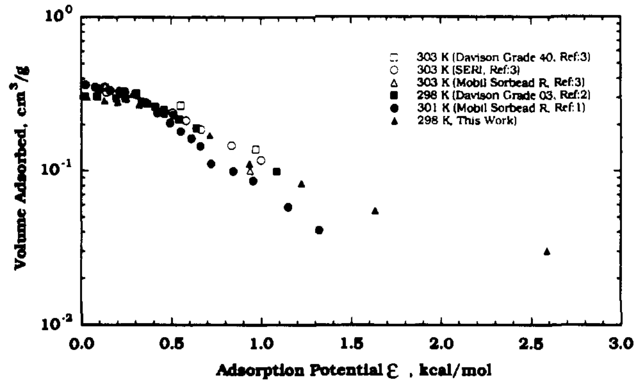

Figure 5. Comparison with the literature data.

Acknowledgment

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Glossary

H_{st}	isosteric heat of adsorption (kJ mol^{-1})
R	gas constant (cal/(mol K))
P	system pressure (mmHg)
T	absolute temperature (K)
q	amount adsorbed (g of adsorbate/g of adsorbent)

Registry No. H_2O, 7732-18-5.

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