J. Chem. Eng. Data **1983**, *28*, 11–14

Pure Vapor Adsorption of Water on Mobil Sorbead R Silica Gel

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Adsorption isotherms of water vapor on Mobil Sorbead R silica gel were obtained gravimetrically at 301, 310, and 326 K up to the saturation pressure. The equilibrium data were used to calculate the heat of adsorption at constant adsorbent loading. The magnitude of the heats of adsorption is indicative of physical adsorption. The BET method was also used to calculate the monolayer capacity and the surface area. Straight lines were obtained when applying the BET model over the relative pressure range 0.05–0.40. The equilibrium adsorption data were also correlated by the modified Polanyi potential theory.

Introduction

Silica gel is an excellent adsorbent of water from air, particularly at high relative humidities. In addition to its high adsorptive capacity (silica gel has the ability to adsorb over 40% of its own weight of water), it exhibits long life and resistance to fouling, and it can be reactivated economically. Silica gel has found wide use as a dehumidifier in the chemical and petroleum industry and also in the construction industry.

The adsorption isotherms for water on Mobil Sorbead R silica gel were measured gravimetrically at three different temperatures in this study. The equilibrium data were used to calculate the heats of adsorption and the surface area of the silica gel. The Polanyi potential theory (*1*, *2*) and the theory of Dubinin (*3*, *4*) were used to correlate the adsorption data.

Experimental Section

Mobil Sorbead R silica gel was selected as the adsorbent for this study. It has a surface area of over 650 m^2/g as found by a BET analysis using nitrogen, an average particle diameter of 0.368 cm, a pore volume of 0.39 mL/g, an average pore diameter of 2.1 nm, and a bulk density of 0.817 g/cm^3. Mobil Sorbead R is in the form of hard, spheroidal beads. The adsorbate used was double-distilled water that had been purified by flowing through an ion-exchange column.

Table I. Adsorption and Desorption Data for Water Vapor on Mobil Sorbead R Silica Gel at 301 K

P, kPa	mg of water/ (g of silica gel)	P, kPa	mg of water/ (g of silica gel)
	Adsorption		
0.45	41	2.03	237
0.60	58	2.24	279
0.83	86	2.47	316
1.00	99	2.73	329
1.23	111	2.87	331
1.36	144	3.13	336
1.48	162	3.47	343
1.63	180	3.60	352
1.80	204	3.93	365
	Desorption		
3.88	361	1.83	323
3.47	359	1.63	317
3.24	351	1.48	234
3.09	346	1.33	164
2.83	336	1.07	131
2.64	335	0.60	100
2.23	329	0.39	81
2.00	326		

The experimental adsorption studies were carried out gravimetrically with a Cahn R-100 electrobalance which has a sensitivity of 0.5 μg. The sample weight was monitored with a strip chart recorder, connected to the electrobalance control unit. A refrigerated–heated bath and a copper circulation coil wrapped around the sample hangdown tube were used to control the adsorption temperature. A vacuum system which consisted of two vacuum pumps, a sorption trap, and a diffusion pump were used to obtain a vacuum of 0.1333 Pa for the system prior to initiating an adsorption run. The leak rate of the complete system was approximately 1.333 Pa/h. Two thermister gauges were used to monitor the pressure when the system was evacuated and during the adsorption runs. Pressures between 0.2 and 106 kPa were measured with a Wallace and Tiernan absolute pressure gauge to ±0.067 kPa. For pressures greater than 106 kPa, a pressure transducer and digital pressure readout were used. The accuracy of the transducer is ±0.689 kPa. The maximum error in pressure measurements for pressures greater than 106 kPa is 0.65%. The calibration of the Wallace and Tiernan pressure gauge and the pressure transducer are traceable to the National Bureau of Standards. Temperatures were measured with Tagliabue thermometers which are also traceable to the National Bureau of Standards. The equilibrium temperature was controlled to within ±0.1 °C of the desired value.

Before adsorption data were obtained, the electrobalance was calibrated to agree with the output signal of the recorder. The weight changes of the silica gel sample due to the adsorption of the water vapor were detected by the electrobalance; equilibrium isotherms were measured from very low pressure up to saturation. The adsorbent was regenerated by evacuating the system and applying heat at 450 K to the silica gel contained in the sample hangdown tube until a constant sample weight was attained. Following regeneration, the silica gel was cooled to the desired adsorption temperature and the water vapor was introduced into the system at a given pressure. After equilibrium was reached, as indicated by a constant sample weight, the pressure and weight were recorded. This process was continued up to the saturation pressure of water. Desorption measurements were made by applying a vacuum and reducing the system pressure.

Results and Discussion

Water vapor adsorption isotherms on Mobil Sorbead R silica gel were measured gravimetrically at 301, 310, and 326 K after overnight regeneration of the adsorbent at 450 K in vacuo. The experimental equilibrium values are presented in Tables I–III. As shown in Figures 1–3, hysteresis was observed to occur when desorbing. It has been noted by Iler (*5*, *6*) that the "hysteresis loop" occurs because in most gel structures the pore cavities are larger in diameter than the openings leading into them. As a pore is emptied, the pressure is controlled by the smaller diameter of the opening which retains a liquid meniscus as the larger inner cavity is emptied. The effect of the adsorption temperature on the equilibrium uptake is shown in Figure 4. The equilibrium uptake of water vapor by Mobil Sorbead R silica gel decreased at higher adsorption tempera-

0021-9568/83/1728-0011$01.50/0

Table II. Adsorption and Desorption Data for Water Vapor on Mobil Sorbead R Silica Gel at 310 K

P, kPa	mg of water/ (g of silica gel)	P, kPa	mg of water/ (g of silica gel)
	Adsorption		
0.45	25	3.08	167
0.73	37	3.23	178
0.95	44	3.40	188
1.19	53	3.49	195
1.44	66	3.69	245
1.63	75	3.81	254
1.89	84	3.99	261
2.03	89	4.16	280
2.16	94	4.33	289
2.37	103	4.53	296
2.57	111	4.93	302
2.79	113	5.47	318
2.91	114	5.89	329
	Desorption		
5.80	326	2.47	254
5.23	317	2.37	203
4.67	308	2.13	178
4.27	304	1.91	162
3.87	297	1.63	149
3.37	295	1.20	123
3.13	293	0.76	98
2.84	290	0.45	53
2.64	284		

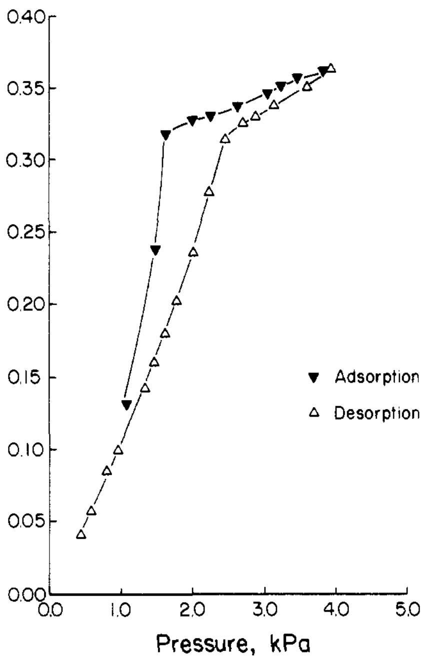

Figure 1. Water vapor adsorption on Mobil Sorbead R silica gel at 301 K.

tures as expected. The maximum error introduced by the buoyancy effect on the sample weight was evaluated and found to be less than 0.5%. Since this error was small, the buoyancy effect on the adsorption measurements was neglected.

The adsorptive and other surface properties of various silicas are known to depend on the presence of silanol hydroxyl groups on the surface (*7–10*). When the silica gel is heated during reactivation, it undergoes dehydration due to the removal of the hydroxyl groups. The degree of dehydroxylation of the surface is a function of the regeneration temperature. Table IV presents the variation of adsorption capacities with regeneration temperature. The adsorption data at 301 K indicate that at relative pressures of 1.0, 0.68, and 0.61 the amount of water uptake decreased by 6.4%, 12.0%, and 16.7%, respectively, when the regeneration temperature increased from 428 to 488 K. A regeneration temperature of 450 K was used in this study.

Table III. Adsorption and Desorption Data for Water Vapor on Mobil Sorbead R Silica Gel at 326 K

P, kPa	mg of water/ (g of silica gel)	P, kPa	mg of water/ (g of silica gel)
	Adsorption		
0.71	18	8.04	190
2.60	50	8.49	206
3.50	70	8.93	241
4.40	90	9.41	253
5.23	118	9.80	260
5.60	124	10.09	275
6.11	133	10.60	299
6.47	136	10.89	312
6.69	146	11.33	323
7.16	168	11.60	333
7.47	172	11.96	338
7.73	186	12.13	340
	Desorption		
11.89	339	5.77	162
11.04	333	5.13	151
10.84	332	4.04	130
10.40	331	3.24	123
9.24	321	2.44	112
8.20	306	1.96	89
7.67	283	1.36	84
7.20	218	0.64	44
6.83	193		

Table IV. Variation of Adsorption Capacities with Regeneration Temperature for Adsorption at 301 K

P/P^{o} [a]	regen temp, K	mg of water/ (g of silica gel)
1	428	360
	488	337
0.68	428	332
	488	292
0.61	428	312
	488	260

[a] Relative pressure.

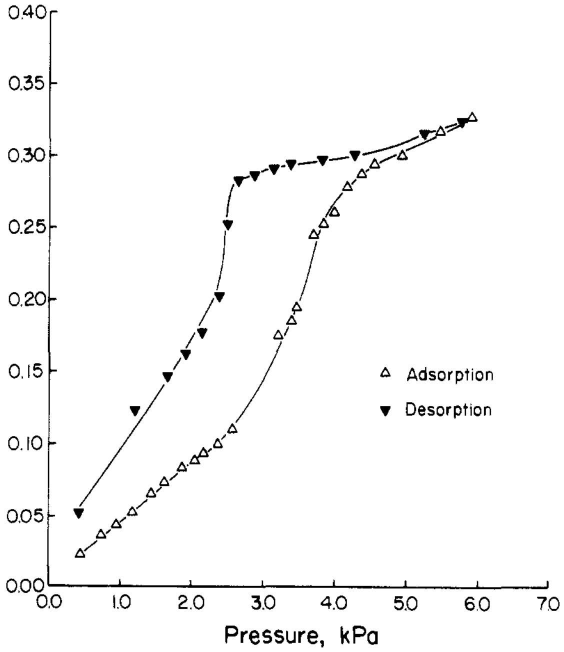

Figure 2. Water vapor adsorption on Mobil Sorbead R silica gel at 310 K.

The BET method (*11–13*) was used to calculate values of the monolayer capacity and the surface area from the adsorption and desorption isotherms. On the basis of eq 1, the

$$\frac{P}{V(P^{0}-P)}=\frac{1}{V_{m}C}+\frac{(C-1)P}{V_{m}CP^{0}} \qquad (1)$$

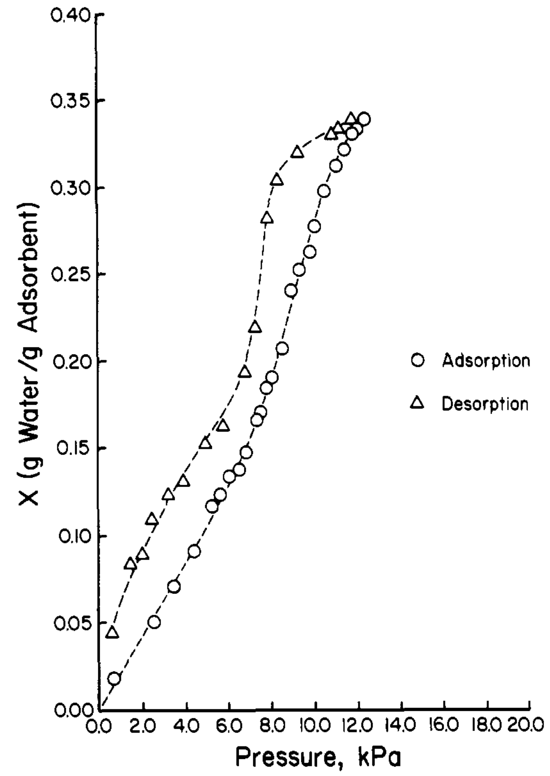

Figure 3. Water vapor adsorption on Mobil Sorbead R silica gel at 326 K.

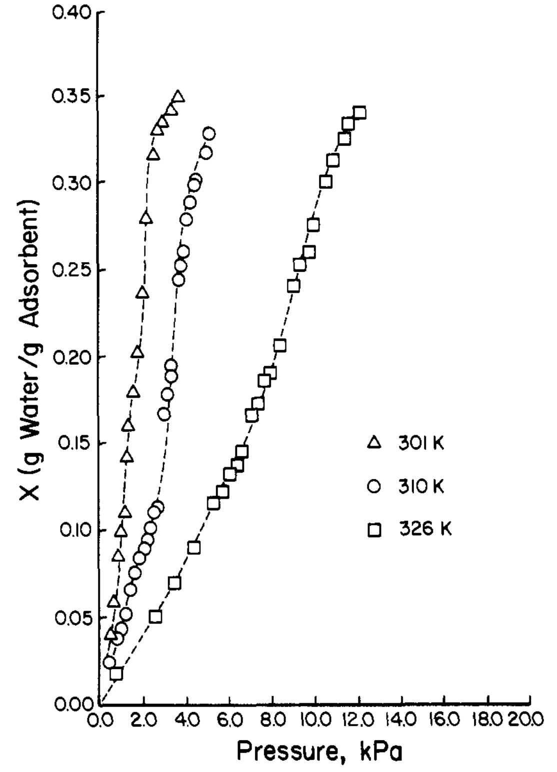

Figure 4. Water vapor adsorption on Mobil Sorbead R silica gel at 301, 310, and 326 K.

Table V. Isosteric Heat of Adsorption of Water Vapor on Mobil Sorbead R Silica Gel

amount adsorbed, g of water/(g of adsorbent)	isosteric heat of adsorpn, kcal/g-mol	amount adsorbed, g of water/(g of adsorbent)	isosteric heat of adsorpn, kcal/g-mol
0.15	−11.9	0.25	−11.4
0.20	−11.6	0.30	−11.5

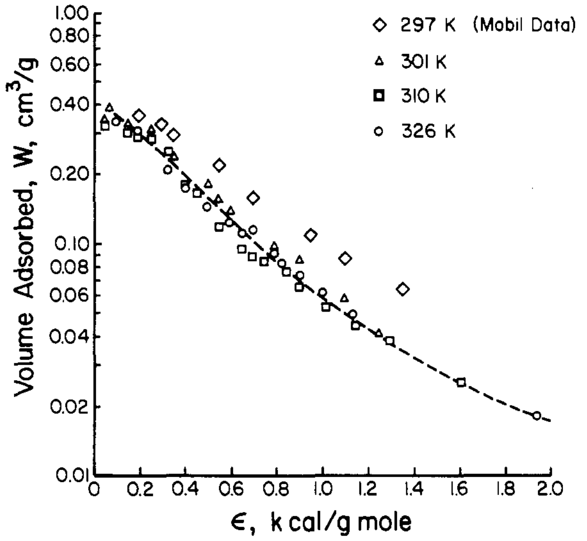

Figure 5. Characteristic curve of water vapor on Mobil Sorbead R silica gel.

surface area can be found plotting $P/[V(P^0 - P)]$ vs. P/P^0 and determining the slope and the intercept of the straight-line portion. When the BET equation was applied, relatively straight lines were obtained over the relative pressure range 0.05–0.40. The monolayer capacity was found to be 0.178 g of water/(g of adsorbent) by using both adsorption and desorption data. Surface area calculations were made by using both the adsorption and desorption curves and a value of 10.6×10^{-16} cm^2 for the cross-sectional area of the water molecule. This value corresponds to a closed-packed arrangement of the molecule on the surface. The values of the surface area based on this adsorption and desorption study were 690 and 687 m^2/g, respectively. These are very close to the value of 650 m^2/g obtained by BET analysis from nitrogen adsorption.

The equilibrium data also were used to calculate the heat of adsorption. Hersh (*14*) has shown that the isosteric heat of adsorption at constant loading is given by the equation

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

The isosteric heats of adsorption were determined graphically from plots of ln P vs. $1/T$. The calculated values for the heat of adsorption were found to decrease as loading increased. The heats of adsorption shown in Table V are of the same order of magnitude as the heat of condensation.

The adsorption potential theory proposed by Polanyi (*1*, *2*) has been widely used to correlate gas-phase adsorption data. The Polanyi theory assumes that the adsorbent exerts long-range attractive forces on the gas or vapor surrounding it. These forces give rise to a potential field with the potential decreasing as the distance from the adsorbent surface increases. For an equilibrium pressure P, the adsorption potential is given by

$$\epsilon = RT \ln P^0/P \qquad (3)$$

where P^0 is the vapor pressure of the adsorbate at the system temperature. Thus, a plot of the volume adsorbed vs. the adsorption potential should yield a characteristic curve that is independent of temperature. The characteristic curve calculated from the equilibrium isotherms is shown in Figure 5. The data for all temperatures lie close to a single characteristic line

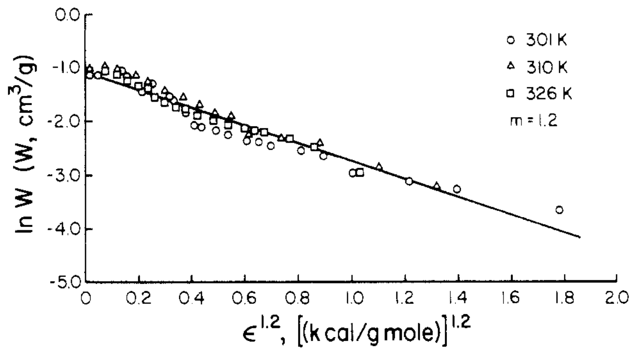

Figure 6. Plot of ln W vs. ϵ^m for the adsorption of water vapor at all temperatures on Mobil Sorbead R silica gel.

as required by the Dubinin–Polanyi theory (*3*).

The equilibrium data obtained in this study are compared in Figure 5 with the data presented by Mobil (*15*). As shown, the adsorption capacities presented herein are approximately 20% lower then Mobil's values. Although the regeneration temperature was not specified in that study, it may be concluded that the reactivation temperature must have been less than the value used in this work.

Bering et al. (*16*) showed that the volume of the adsorption space can be expressed by the relation

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

where W_0 is the volume of the adsorption space at saturation, E is a constant characteristic energy, β is the affinity factor, and m is a constant. Based on eq 4, a plot of ln W vs. $(\epsilon)^m$ should give a straight line with a slope of $[-(1/\beta E)]^m$ and an intercept of ln W_0. A value of m equal to 1.2 was found to give a straight line at all temperatures studied in this work (see Figure 6). The adequacy of the fit was checked by calculating the coefficient of determination; a value of 0.94 was found for this study. Huber et al. (*17*) reported that the values of m can be varied from 1.0 to 6.0 depending on the adsorbate–adsorbent system.

Glossary

C	BET constant
E	constant characteristic energy (kcal/g-mol)
m	constant in the generalized isotherm equation
q_{st}	isosteric heat of adsorption (kcal/g-mol)
P	equilibrium vapor pressure (kPa)
P^0	saturation pressure (kPa)
R	gas constant (cal/(g-mol K))
T	absolute temperature (K)
W	volume of the adsorbed phase given in eq 4 (cm³/(g of solid))
W_0	volume adsorbed at saturation (cm³/(g of solid))
X	amount adsorbed (g of adsorbate/(g of adsorbent))
V	amount adsorbed (cm³ of adsorbate/(g of adsorbent))
V_m	amount adsorbed in the monolayer (cm³ of adsorbate/(g of adsorbent))
β	affinity factor
ϵ	adsorption potential (kcal/g-mol)

Registry No. H_2O, 7732-18-5.

Literature Cited

(1) Polanyi, M. *Verh. Dtsch. Phys. Ges.* **1916**, *18*, 55.
(2) Polanyi, M. *Z. Phys.* **1920**, *2*, 111.
(3) Dubinin, M. M. *Chem. Rev.* **1960**, *60*, 235.
(4) Dubinin, M. M. *J. Colloid Interface Sci.* **1967**, *23*, 487.
(5) Iler, R. K. "The Colloid Chemistry of Silica and Silicates"; Cornell University Press: Ithaca, NY, 1955.
(6) Iler, R. K. "The Chemistry of Silica"; Wiley: New York, 1979.
(7) Sing, K. S. W.; Madeley, J. D. *J. Appl. Chem.* **1953**, *3*, 549.
(8) Sing, K. S. W.; Madeley, J. D. *J. Appl. Chem.* **1954**, *4*, 365.
(9) Sing, K. S. W.; Bhambhani, M. R.; Cutting, P. A.; Turk, D. H. *J. Colloid Interface Sci.* **1976**, *55*, 605.
(10) Bartell, F. E.; Bower, J. E. *J. Colloid Sci.* **1952**, *7*, 80.
(11) Brunauer, S.; Emmet, P. H.; Teller, E. *J. Am. Chem. Soc.* **1936**, *60*, 309.
(12) Brunauer, S.; Deming, L. S.; Deming, W. E.; Teller, E. *J. Am. Chem. Soc.* **1940**, *62*, 1723.
(13) Brunauer, S. "The Adsorption of Gases and Vapors"; Princeton University Press: Princeton, NJ, 1945; Vol. I.
(14) Hersh, C. K. "Molecular Sieves"; Reinhold: New York, 1961.
(15) "Dehydration with Sorbead Desiccant: Design and Operational Guide for Users and Designers of Dehydration Equipment"; Mobil Oil Co, Commercial Marketing Department: New York.
(16) Bering, B. P.; Dubinin, M. M.; Serpinskii, V. V. *J. Colloid Interface Sci.* **1966**, *21*, 378.
(17) Huber, U.; Stoeckli, F.; Houriet, J. P. *J. Colloid Interface Sci.* **1978**, *67*, 195.

Received for review January 28, 1982. Revised manuscript received August 6, 1982. Accepted September 3, 1982.

Adsorption of Synthesis Gas-Mixture Components on Activated Carbon

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Pure-gas isotherms have been determined for CH_4, CO, CO_2, and H_2 on type BPL activated carbon at 298.2 K by using a volumetric-type apparatus. Data for binary, ternary, and quaternary mixtures of these gases were obtained at the same temperature and a total pressure of 344.7 kPa. Two thermodynamic models which can predict gas-mixture equilibria from the pure-gas isotherms—the ideal adsorbed solution model (IASM) and the vacancy solution model (VSM)—have been evaluated with these data.

Introduction

There are several reasons for the success of activated carbon as an adsorbent. First, it can be prepared in a wide variety of structures having different pore sizes and pore volumes. Second, it exhibits high adsorption selectivity. For low boiling point compounds, the selectivity associated with activated carbon makes it an attractive alternative to other separational processes, such as fractional distillation which requires low temperatures and high pressures. Thus, activated carbon is used for such applications as the deodorization of air, the

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