Short Articles

Adsorption Equilibrium of Water on Silica Gel

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A new test rig for measuring the adsorption equilibrium of water on silica gel has been developed. The adsorption equilibrium of water on silica gel was then measured using the weight method. The measured temperature ranged from (25 to 90) °C, and the absolute pressure was in the range of (300 to 20 000) Pa. The water uptake of silica gel varied from (0.03 to 0.30) $kg \cdot kg^{-1}$. Data obtained were fitted to three equations: the Dubinin−Astakhov (DA) equation, the Freundlich equation, and the modified Freundlich equation. The modified Freundlich equation showed the best agreement with the experimental data, while the DA equation and Freundlich equation had a large deviation with the experimental data for low water uptake.

Introduction

Due to the continuous increase in global primary energy consumption and the environmental effects caused by the use of traditional non-natural refrigerants, much research is now aimed at the development of refrigerating technologies which can reduce energy consumption and environmental pollution.[1] Adsorption refrigeration systems using natural substances (such as water and ammonia among others) as refrigerants can be driven by waste heat and solar energy. As a result, these systems are environmentally benign and energy saving compared with traditional vapor compression refrigeration systems. As one of the most prospective adsorption refrigeration systems, silica gel−water adsorption refrigeration systems have attracted great attention.[2−6]

The research group of SJTU developed a novel silica gel−water adsorption chiller, in which only one vacuum valve was adopted to fulfill the mass recovery process.[7−9] Performance of the chiller was numerically and experimentally studied. The adsorption equations employed for the simulation were the Freundlich equation and simplified DA equation, and the values of other parameters were obtained from refs 10 and 11. Because the silica gel in this chiller was different from the one studied in refs 10 and 11, the simulated result had a deviation with the experimental result.[8] To get an accurate adsorption equation, the adsorption equilibrium of water on silica gel should be tested.

There are various methods for determining the adsorption quantity of adsorption refrigeration working pairs. According to Aristov et al.,[5] the sorption equilibrium between a composite adsorbent of silica gel impregnated with hydrophilic salts and water was measured by a thermal balance method. Zhong et al.[12] tested silica gel, zeolite, and carbon−CO_2 adsorption working pairs. The adsorbents were placed in a small basket, which was suspended in a sealed CO_2 chamber. The mass adsorbed, temperature, and pressure were measured by a magnetic suspension balance, thermocouples, and a pressure sensor, respectively. However, the mass measured by the magnetic suspension balance must be corrected for gas buoyancy. Ng et al.[13] assembled a control−volume−variable-pressure apparatus with the moisture balance technique to investigate the adsorption isotherms of silica gel−water. This was done by using two tanks connected by a valve: a dosing tank and a charging tank. The silica gel was placed in the charging tank. The measuring procedure consisted of three steps. First, water vapor was introduced into the dosing tank, and the mass of the water vapor was calculated by the ideal gas law. Second, the valve was opened until the pressures of the two tanks approached equilibrium. Finally, the mass of water vapor which remained in the dosing tank was recalculated, and then the mass of water adsorbed was obtained from the mass difference of water vapor in the dosing tank. Wang et al.[14] studied the composite adsorbent of $CaCl_2$ and expanded graphite−ammonia working pair. The mass of ammonia adsorbed was calculated from the level change of ammonia liquid in the evaporator by using a magnetostrictive displacement sensor. A laboratory-scale experimental rig was set up to study a composite adsorbent of silica gel and calcium chloride−water working pairs.[15] The amount of water uptake was indicated by water level change in a graduated hard plastic tube. Freni et al.[16] used a laboratory-scale chiller to test an advanced adsorbent bed. The bed consisted of a fin tube heat exchanger with the external surface coated by composite adsorbent and bentonite clay. The composite adsorbent was made by impregnating calcium chloride into mesoporous silica gel. The cooling power was calculated from the difference in the chilled water inlet and outlet temperatures.

The above-mentioned systems are however not suitable for testing the adsorption equilibrium of water on silica gel. This is because there are two main problems for testing silica gel (including silica gel-based composite adsorbent) and water working pairs. The first problem is that cyclic water uptake by silica gel is really small. If water uptake is calculated by the water liquid level change or the difference of chilled water inlet and outlet temperatures, the test rig should be large enough to have a high testing precision.[14,15] Additionally, heat and mass transfer should also be considered in a large system. This would take a long time to prepare experiments and be very costly.

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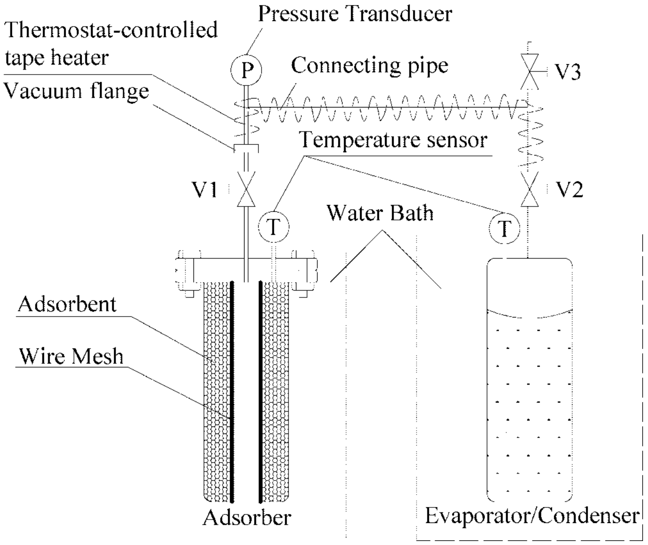

Figure 1. Schematic diagram of the test rig.

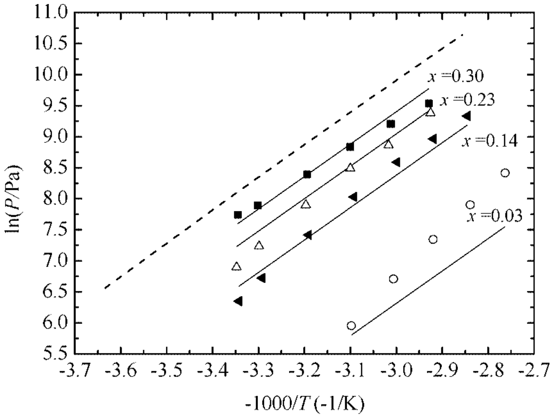

Figure 2. Equilibrium pressure (P) of water on silica gel as a function of temperature (T) and water uptake (x). Dashed line indicates the saturation line of water vapor. The solid lines denote the fittings with the Freundlich equation. The filled and empty symbols show experimental points.

The second problem is that water vapor condenses easily in the gas flowing pipes during the desorption process. As a result, a test rig, similar to that of Zhong,[11] is not suitable for the silica gel—water working pair. Also if a control-volume apparatus is adopted, a low testing precision can be expected. To solve the problems mentioned, the water uptake of silica gel was obtained by the weight method. A test rig was built, and the adsorption equilibrium performance of the silica gel—water working pair was investigated systemically.

Experimental Procedure

The test rig (shown in Figure 1) was designed and used to measure the adsorption capacity of silica gel. It consisted of one adsorber, one evaporator/condenser, three vacuum valves, and measuring cells. The measuring cells were: one four-wire PT1000 to measure the temperatures of the silica gel, one pressure transducer which measures pressure in the range from 0 Pa to 50 kPa with a precision of 100 Pa, one four-wire PT100 to measure the evaporating/condensing temperature, and one Sartorius electronic balance BS2202S with a precision of 0.01 g to measure the equilibrium water uptake of silica gel. Two constant-temperature water baths were used to control the temperature of adsorbent and the evaporating/condensing temperature. The temperature variation was within ± 0.1 °C. A thermostat-controlled tape heater was used to heat the connecting pipe to avoid condensation of water vapor inside the pipe. A wire mesh was placed in the middle of the adsorber and acted as a mass transfer channel. The gap between the inner wall of the adsorber and the wire mesh was filled with silica gel adsorbent.

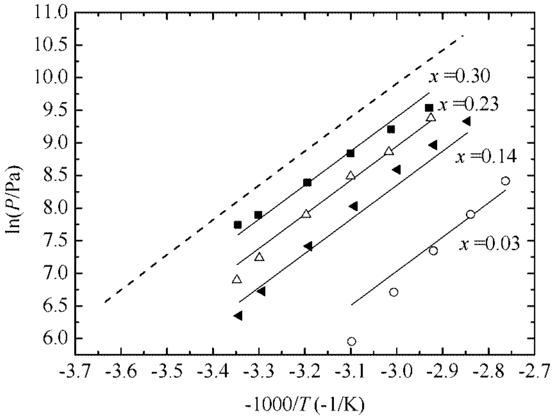

Figure 3. Equilibrium pressure (P) of water on silica gel as a function of temperature (T) and water uptake (x). Dashed line indicates the saturation line of water vapor. The solid lines denote the fittings with the DA equation. The filled and empty symbols show experimental points.

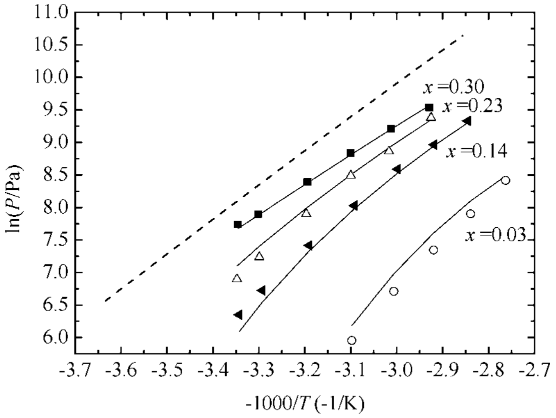

Figure 4. Equilibrium pressure (P) of water on silica gel as a function of temperature (T) and water uptake (x). Dashed line indicates the saturation line of water vapor. The solid lines denote the fittings with the modified Freundlich equation. The filled and empty symbols show experimental points.

Table 1. Equilibrium Pressures (P) of Water on Silica Gel versus Water Uptake (x) under Different Temperatures (T)

T (°C)	x	P (Pa)
25.8	0.30	2297
29.7	0.30	2679
39.9	0.30	4411
49.4	0.30	6875
58.8	0.30	9963
68.3	0.30	13833
25.6	0.23	990
30.0	0.23	1389
39.6	0.23	2694
49.4	0.23	4860
58.3	0.23	7074
68.7	0.23	11869
26.0	0.14	572
30.6	0.14	831
40.3	0.14	1663
50.2	0.14	3067
60.4	0.14	5370
69.4	0.14	7823
78.3	0.14	11293
49.7	0.03	385
59.5	0.03	819
69.3	0.03	1548
79.1	0.03	2703
88.8	0.03	4518

Table 2. Comparisons of the Water Uptake Calculated by the Freundlich, DA, and Modified Freundlich Equations ($x_{\mathrm{Freundlich}}$, x_{DA}, and $x_{\mathrm{Modified,Freundlich}}$) with the Experimental Water Uptake (x) under the Equilibrium Temperatures (T) and the Equilibrium Pressures (P)

T (°C)	P (Pa)	$(x_{\mathrm{Freundlich}} - x)/x$	$(x_{\mathrm{DA}} - x)/x$	$(x_{\mathrm{Modified,Freundlich}} - x)/x$
25.8	2297	13.9%	6.7%	2.9%
29.7	2679	7.7%	3.5%	0.7%
39.9	4411	2.7%	0.6%	1.0%
49.4	6875	−0.9%	−1.7%	2.5%
58.8	9963	−7.4%	−6.3%	0.3%
68.3	13833	−14.5%	−11.8%	−3.6%
25.6	990	−20.0%	−16.0%	−9.1%
30.0	1389	−14.9%	−10.4%	−8.8%
39.6	2694	−6.2%	−1.3%	−6.2%
49.4	4860	−0.3%	4.5%	−1.3%
58.3	7074	−4.6%	0.3%	−5.3%
68.7	11869	−1.9%	3.0%	3.7%
26.0	572	−14.3%	−18.3%	13.2%
30.6	831	−7.0%	−8.8%	10.3%
40.3	1663	5.0%	6.4%	6.3%
50.2	3067	12.9%	16.2%	4.5%
60.4	5370	18.7%	23.3%	6.5%
69.4	7823	15.3%	19.2%	2.0%
78.3	11293	13.8%	17.3%	3.6%
49.7	385	14.5%	−56.1%	−18.2%
59.5	819	40.6%	−33.6%	−24.1%
69.3	1548	61.3%	−13.6%	−25.9%
79.1	2703	78.5%	4.2%	−21.7%
88.8	4518	94.4%	21.7%	−8.3%

Table 3. Fitted Parameters of the Freundlich and DA Equations and Standard Error of the Estimate

equation	x_0	n	k	standard error σ
Freundlich	0.444	1.342	–	0.023
DA	0.348	1.609	0.449	0.019

The experimental procedure used is described as follows:

1) The adsorber was evacuated by a vacuum pump connected to valve V3, then disconnected from the system, and its mass including that of valve V1 was measured using an electronic balance.

2) The adsorber was connected back to the system, and the connecting pipe was vacuumed. The valves V1 and V2 were then kept open for 3 h, so that the water vapor in the evaporator can be adsorbed by the silica gel in the adsorber.

3) The adsorber was removed from the system again, and the outside surface of the adsorber was dried using an electric dryer. The mass of the adsorber was measured, and the mass of water vapor adsorbed by silica gel was obtained from the mass variation of the adsorber.

4) The adsorber was connected to the system, and the connecting pipe was vacuumed again. Then valves V2 and V3 were closed, while valve V1 was opened. The temperature of the adsorber was set at 25 °C by the water bath, and an equilibrium pressure was measured. Then, the temperature of the adsorber was changed from (25 to 90) °C, and the corresponding equilibrium pressures were obtained.

5) Valve V2 was open for 5 min. So, some water vapor flowed out of the adsorber and condensed in the condenser. Another different water uptake was obtained. The third step was then repeated.

Theory. Three equations adopted widely for the simulation of silica gel−water adsorption chillers were fitted to the experimental data. These equations are

1) The Freundlich equation (eq 1)

$$x = x_0 \cdot \left(\frac{P(T_{\mathrm{w}})}{P(T_{\mathrm{s}})}\right)^{1/n} \tag{1}$$

where x is water uptake of the silica gel and is defined as the mass of the water adsorbed to the mass of silica gel; x_0 and n are constants and determined by a fitting process; and T_{w} and T_{s} are the temperatures of water vapor and silica gel, respectively. $P(T_{\mathrm{w}})$ and $P(T_{\mathrm{s}})$ are the corresponding saturation vapor pressure of the refrigerant at T_{w} and T_{s}.

2) The DA equation (eq 2)

$$x = x_0 \cdot \exp\left(-k \cdot \left(\ln \frac{P(T_{\mathrm{s}})}{P(T_{\mathrm{w}})}\right)^{n}\right) \tag{2}$$

where x_0, k, and n are constants and determined by a fitting process.

3) The modified Freundlich equation (eq 3):[17]

$$x = A(T_{\mathrm{s}}) \cdot \left[\frac{P(T_{\mathrm{w}})}{P(T_{\mathrm{s}})}\right]^{B(T_{\mathrm{s}})}$$

$$A(T_{\mathrm{s}}) = A_0 + A_1 T_{\mathrm{s}} + A_2 T_{\mathrm{s}}^2 + A_3 T_{\mathrm{s}}^3$$

$$B(T_{\mathrm{s}}) = B_0 + B_1 T_{\mathrm{s}} + B_2 T_{\mathrm{s}}^2 + B_3 T_{\mathrm{s}}^3 \tag{3}$$

where A_0 to A_3 and B_0 to B_3 are constants and determined by a fitting process.

The least-squares method was used to fit the three equations to the experimental data. To measure the accuracy of prediction, the standard error of the estimate was adopted and defined as follows

$$\sigma = \sqrt{\frac{\sum (y - y')^2}{N}} \tag{4}$$

where σ is the standard error of the estimate; y is the measured value; y' is the predicted value; and N is the number of pairs of the values. The numerator is the sum of the squared difference between the measured value and the predicted one.

Results and Discussion

Figures 2 to 4 show the measured adsorption equilibrium data fitted with the Freundlich equation, DA equation, and modified Freundlich equation, respectively, whereas the measured adsorption data under different water uptake are shown in Table 1. Comparisons of the water uptake calculated by the Freundlich, DA, and modified Freundlich equations with the experimental water uptake under the equilibrium temperatures and the equilibrium pressures are shown in Table 2.

As is shown in Figures 2 and 3, the Freundlich equation and DA equation have a large deviation from the experimental data under low water uptake. This was because the pressures obtained under low water uptake were somewhat influenced by the precision of the pressure transducer. Table 3 shows the fitted parameters of the Freundlich equation and DA equation and also the standard error of the estimate.

As shown in Figure 4, the modified Freundlich equation agrees well with the experimental points. The standard error of the estimate was about 0.010, which was 50 % less than that of the DA equation or Freundlich equation. The modified Freundlich equation was therefore adopted for the simulation of the silica gel−water adsorption chiller developed by the research group of SJTU. The fitted parameters were

$$A_0 = -14.2904 \quad A_1 = 0.1546\ \mathrm{K}^{-1}$$

$$A_2 = -5.5498 \cdot 10^{-4}\ \mathrm{K}^{-2} \quad A_3 = 6.7512 \cdot 10^{-7}\ \mathrm{K}^{-3}$$

$$B_0 = 36.1487 \quad B_1 = -0.3820\ \mathrm{K}^{-1}$$

$$B_2 = 1.3016 \cdot 10^{-3}\ \mathrm{K}^{-2} \quad B_3 = -1.4150 \cdot 10^{-6}\ \mathrm{K}^{-3}$$

Conclusion

The adsorption equilibrium of water on silica gel was tested by a new test rig, and the results were presented. The adsorption isotherms of the silica gel–water adsorption refrigerating system were also obtained. The Freundlich equation and DA equation were fitted to the experimental data, and a large deviation was observed between the two fitted equations and the data for low water uptake. To minimize the standard error of the estimate, the experimental data were fitted with the modified Freundlich equation. The standard error of estimate reduced to 50% of that of the DA equation or Freundlich equation.

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