

Adsorption Characteristics of Silica Gel + Water Systems

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The adsorption characteristics of pure water vapor onto two different types of silica gel at temperatures from (298 to 338) K and at different equilibrium pressures between (500 and 7000) Pa were experimentally studied by a volumetric technique. The thermophysical properties such as the skeletal density, Brunauer–Emmett–Teller surface area, pore size, pore volume, and total porosity of silica gel were determined. The Tóth isotherm model is found to fit all of the experimental data within the experimental errors. The experimental isotherms and the computed enthalpies of adsorption are compared with those of various researchers and found to be consistent with a chiller manufacturer's data.

Introduction

The adsorption characteristics of water vapor on silica gel are essential data in determining the energetic performance of adsorption chillers. From the viewpoint of the fundamental design of adsorption chillers, the investigation of the adsorption isotherm is pertinent for the purpose of system modeling.

This study investigated experimentally the isothermal adsorption of water vapor onto Fuji Davison type A and RD silica gel. The characterization of the thermophysical properties of these silica gels was also determined. We had followed the guidelines for reporting physisorption data for gas/solid systems by IUPAC.¹ The type RD silica gel had been commonly employed for the adsorption chiller as the adsorbent by the chiller manufacturers.

In terms of the adsorption chiller performance, the adsorbent must have good thermal conductivity as well as a large specific surface area. The above-mentioned adsorbents fulfill these requirements. The present data will be compared with the equilibrium data of the Fuji Davison type RD silica gel reported by the chiller manufacturer.² The comparison may provide more information to the manufacturers for cost-effective design. This study will further compare the present experimental results with the more recent literature results.^{3–5} Additionally, a comparison of the isotherms will be made among these grades of silica gel.

Experimental Section

The adsorption performance of adsorbents is influenced by the operation parameters as well as the thermophysical properties such as the surface area, pore size, and pore volume and their distributions, porosities, and skeletal densities. Yeh et al.⁶ carried out a comprehensive literature survey on physical properties of silica gel. Our experimentally determined thermophysical properties are summarized in Table 1. The standard nitrogen gas adsorption/desorption measurements on the silica gels at liquid nitrogen temperature (77 K) were performed on the

Table 1. Thermophysical Properties of Silica Gels^a

property	value	
	type A	type RD
BET/N ₂ surface area ^b (m ² ·g ⁻¹)	(716 ± 3.3)	(838 ± 3.8)
BET constant ^b	293.8	258.6
BET volume STP ^b (cm ³ ·g ⁻¹)	164.5	192.5
range of P_r ^b	0.05–0.19	0.05–0.23
pore size ^b (nm)	(0.8–5)	(0.8–7.5)
porous volume ^b (cm ³ ·g ⁻¹)	0.28	0.37
micropore volume ^b (%)	57	49
mesopore volume ^b (%)	43	51
skeletal density ^c (kg·m ⁻³)	2060	2027
particle bulk density ^d (kg·m ⁻³)	1306	1158
surface area ^e (m ² ·g ⁻¹)	650	720
average pore diameter ^e (nm)	2.2	2.2
porous volume ^c (cm ³ ·g ⁻¹)	0.36	0.4
apparent density ^{e,f} (kg·m ⁻³)	730	700
mesh size ^e	10–40	10–20
pH ^e	5.0	4.0
water content ^e (mass %)	<2.0	
specific heat capacity ^e (kJ·kg ⁻¹ ·K ⁻¹)	0.921	0.921
thermal conductivity ^e (W·m ⁻¹ ·K ⁻¹)	0.174	0.198

^a Manufacturer's representative chemical composition (dry mass basis): SiO₂ (99.7%), Fe₂O₃ (0.008%), Al₂O₃ (0.025%), CaO (0.01%), Na₂O (0.05%). ^b Values obtained using ASAP 2010. ^c Values obtained using AccuPyc 1330. ^d Computed values. ^e Values supplied by the manufacturer. ^f This value is inclusive of the bed porosity.

Micromeritics gas adsorption analyzer ASAP 2010 machine, which was equipped with ASAP analysis software (Micromeritics Version 4). Prior to the experiment, samples were degassed at 413 K for 48 h, to achieve the residual vacuum level in the sample tube to be not more than 10 mPa. In the Brunauer–Emmett–Teller (BET) plots of nitrogen adsorption data, required to compute surface areas, analysis points were selected over the range $P_r = 0.03–0.3$ ¹ to get the best linear fit, where P_r denotes the relative pressure or the ratio of the prevailing vapor pressure to the corresponding saturated pressure. The experimental adsorption data were analyzed using the density functional theory (DFT) plus software (Micromeritics Version 2.0) to determine pore volumes and size distributions. Figure 1 shows the pore size distributions for the two types of silica gel investigated. The Barrett–Joyner–Halenda (BJH) method using the Kelvin equation was also employed to calculate pore size distributions of

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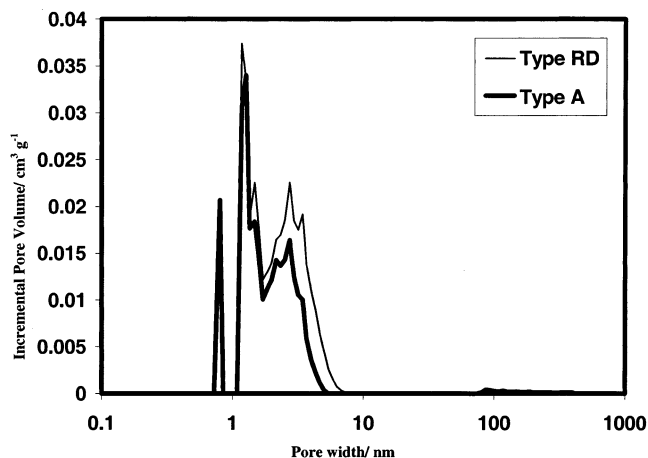


Figure 1. Pore size distribution (DFT slit model) for two types of silica gels.

the silica gels, but the results were not satisfactory because this method was usually used to calculate the mesopore structures.¹

The skeletal densities of dry silica gels were determined by the automated Micromeritics AccuPyc 1330 pycnometer at room temperature. In our experiments, each silica gel sample was regenerated at 413 K for 24 h and a dry mass sample was then introduced to the pycnometer. The particle bulk densities of silica gels were then calculated from values of skeletal densities and pore volumes by the DFT analysis.

In this study, the constant-volume variable-pressure (cvvp) apparatus had been employed for the experiments, so that, as far as possible, the silica gel could be assumed to be in contact only with pure water vapor, which closely resembled the actual condition in an adsorption chiller. The schematic diagram of the cvvp setup is shown in Figure 2.

The cvvp setup was mainly comprised of a charging tank, volume $(572.64 \pm 27) \text{ cm}^3$, stainless steel (SS) 304, whose volume was inclusive of related piping and valves, a dosing tank, volume $(698.47 \pm 32) \text{ cm}^3$, SS 304, whose volume was again inclusive of related piping and valves, and an

evaporator flask with a volume of 2000 cm^3 . The charging tank had been designed to have a high aspect ratio, so that the adsorbent could be spread on the large flat base. Its external wall was also coiled with copper pipes to enable in situ regeneration of the silica gel using a silicone oil bath.

The volumes of the charging and dosing tanks had been calibrated by charging helium with a purity of 99.9995% from a calibrated standard volume of $(210.9 \pm 0.2) \text{ cm}^3$. The standard volume had been calibrated by a liquid filling method using distilled water. The pressures in the two tanks were measured with two calibrated capacitance manometers (Edwards barocel type 622; 10 kPa span; total error in Pa: if $90 < P/\text{Pa} < 900$, the total error in Pa = $100[0.0025 + \{2.25 \times 10^{-6} + 1.764 \times 10^{-3}\}P^2]^{1/2}$, if $900 < P/\text{Pa} < 9000$, the total error in Pa = $100[0.0025 + \{2.25 \times 10^{-6} + 7.84 \times 10^{-4}\}P^2]^{1/2}$; maximum operating temperature $T = 338 \text{ K}$). The temperatures in the two tanks were measured with three Pt 100 Ω class A resistance temperature detectors (rtd's). The rtd for the charging tank, T1 in Figure 2, had been designed to be in direct contact with the silica gel so that a more representative adsorbent temperature could be obtained. Except for the 3.175 mm vacuum adaptors used to seal the rtd probes, all other interconnecting piping (SS 316), SS vacuum fittings, and vacuum-rated SS diaphragm valves (Nupro Swagelok) were chosen to be 12.7 mm to ensure good conductance during evacuation. To maintain the system as isothermal, the two tanks were immersed in a temperature-controlled bath (precision of control $\pm 0.01 \text{ K}$). To further reduce the measurement error caused by a temperature gradient along the piping, fittings, and valves, they were thermally jacketed using a SS 321 flexible hose, whose temperature was also maintained by the same bath. The exposed piping and fittings were then well insulated.

The cvvp setup was equipped with a two-stage rotary vane vacuum pump (Edwards bubbler pump) with a water vapor pumping rate of $315 \times 10^{-6} \text{ m}^3 \text{ s}^{-1}$. To prevent backmigration of oil mist into the setup, an alumina-packed foreline trap was installed immediately upstream of the vacuum pump. Argon, with a purity of 99.9995%, was sent through a column of packed calcium sulfate before being

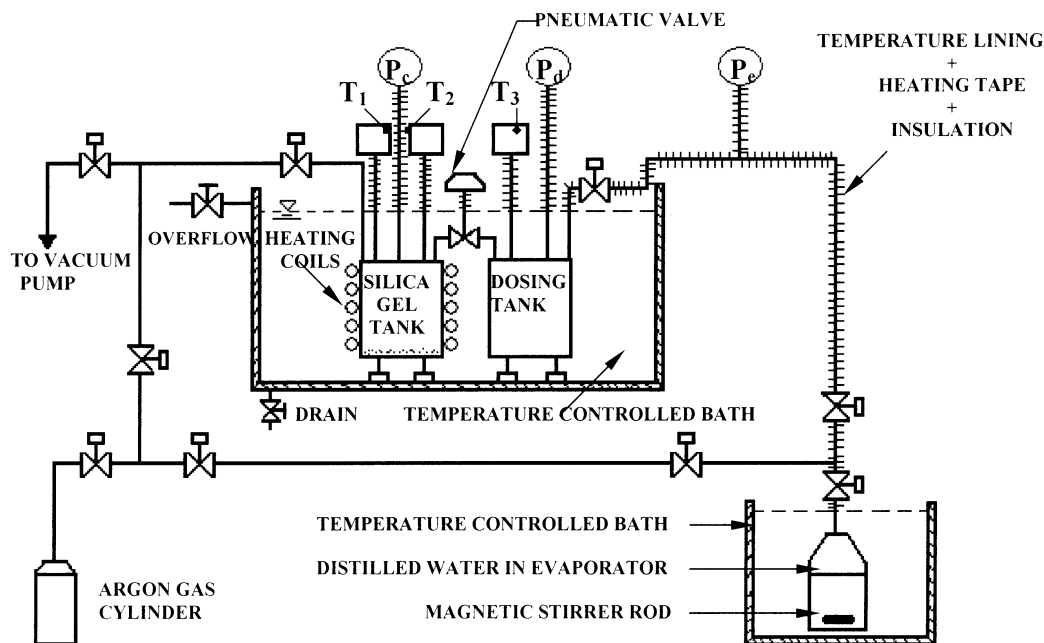


Figure 2. Schematic diagram of the constant-volume variable-pressure test facility. T1, T2, T3 = rtd's. Ps, Pd, Pe = capacitance manometers.

used to purge the vacuum system. Upon evacuation, a residual argon pressure of 100 Pa can be achieved in the setup.

The evaporator flask was immersed in a different temperature-controlled bath (precision of control ± 0.01 K). It was first purged with argon with a purity of 99.9995% and evacuated by the vacuum pump. Distilled water was then charged into the evaporator. Its temperature could be regulated to supply water vapor at the desired pressure. An immersion magnetic stirrer was used to ensure uniformity of temperature inside the evaporator flask.

All pressure and temperature readings were continuously monitored by a calibrated 18-bit ADDA data logger (Fluka Netdaq 2640A). The calibration of pressure transmitters, temperature sensors, and the data logger were traceable to national standards. In the present test facility, the major measurement bottleneck lied in the measurement of the vapor pressure.

The dry mass of silica gel was determined by the calibrated moisture balance (Satorious MA40 moisture analyzer; uncertainty 0.05% traceable to a DKD standard) at $T = 413$ K. The mass of silica gel was continuously monitored and only recorded when no change in mass was detected. For Fuji Davison type A and RD silica gels, a mass about 0.1–1.25 g was introduced into the charging tank.

The dosing and charging tanks plus all related piping systems, hereinafter called the test system, were purged by purified and dried argon, evacuated, and subsequently isolated. The silica gel was again regenerated in situ at $T = 413$ K for 24 h. At the end of the regeneration process, the test system was purged by argon and evacuated. The silica gel was further regenerated at $T = 413$ K for another 8 h, and the test system was evacuated again. On the basis of measurements involving only argon and silica gel, it was concluded that there was no measurable interaction between the inert gas and the adsorbent. The effect of the partial pressure of argon in the tanks was found to be small. Nevertheless, the partial pressure of water vapor had been adjusted for the presence of argon to avoid additional systematic error.

Water vapor was first charged into the dosing tank. Prior to charging, the tank temperature was initially maintained at about $T = 5$ K higher than the evaporator temperature to eliminate the possibility of condensation. The effect of condensation would cause significant error in the pressure reading. This would lead to significant error in calculating the actual mass of water vapor charged to the dosing tank. The evaporator was isolated from the dosing tank soon after the equilibrium pressure was achieved inside the dosing tank. The mass of water vapor was determined via pressure and temperature measurements, taking the effect of residual argon into account. Because the pressure transmitter was originally calibrated at room temperature, measuring the water vapor mass at this condition would ensure maximum accuracy.

The temperatures of the charging and dosing tank were subsequently raised to the typical adsorber and desorber temperature ranges as in a silica gel water adsorption chiller. Once the test system reaches thermodynamic equilibrium at the desired temperature, the pressurized pneumatic interconnecting valve between the dosing and charging tank was opened, and both tanks were allowed to approach equilibrium. The temperatures of both tanks are adjusted to the desired temperature via the oil bath before pressure and temperature measurements were taken for both tanks.

Table 2. Measured Isotherm Data for Type A Silica Gels

T (K)	P_1 (kPa)	q^* (kg·kg ⁻¹)	P_1 (kPa)	q^* (kg·kg ⁻¹)
298.15	5.1054	0.4014		
304.15	0.6675	0.0753	3.3496	0.3535
	0.9523	0.1084	4.1878	0.3651
	1.3888	0.1593	5.2226	0.3948
	2.3351	0.2682		
310.15	0.9473	0.0717	3.9451	0.3159
	1.3302	0.1019	4.7446	0.3465
	1.9090	0.1469	5.6442	0.3860
	3.0696	0.2376		
316.15	1.2730	0.0673	3.7915	0.2087
	1.7980	0.0946	4.7202	0.2705
	2.5116	0.1334	5.3888	0.2986
323.15	1.7948	0.0624	4.7487	0.1725
	2.4281	0.0855	5.7795	0.2121
	3.1658	0.1192		
338.15	3.2807	0.0489	5.4151	0.0814
	4.0972	0.0637		

With the initial mass of water vapor known, the temperature of the test system was varied to enable measurements at a different temperature and pressure. The test system was subsequently evacuated, silica gel was regenerated, and the system was purged with purified and dried argon before water vapor at different initial pressures was charged into the dosing tank to enable measurement along the isotherms. A number of test conditions were repeated at least twice with a fresh batch of silica gel to ensure that repeatability was achieved to within the reported experimental uncertainty.

Results and Analysis for Adsorption Isotherms

From Table 1, one could observe that the thermophysical properties of these two types of silica gel are similar. Although the type RD silica gel has a slightly higher thermal conductivity than the type A silica gel, the most significant difference between these two types of silica gel lies in their water vapor uptake characteristics. In the present study, the temperatures and pressures investigated range from (303 to 338) K and from (500 to 7000) Pa, respectively. The uncertainty of pressure ranges from (± 10 to 200) Pa. Emphasis is placed on the conditions experienced in the adsorber because this is the range of conditions that directly determines the cooling capacity.

Adsorption equilibrium data of water vapor on these two different types of silica gel were obtained. The measured isotherm data for type A and RD silica gels are furnished in Tables 2 and 3, respectively. Figures 3 and 4 depict the experimental equilibrium data for the type RD and A silica gels with water vapor, respectively.

The performance of the type RD silica gel water system employed by the adsorption chiller manufacturer² available in the form of Henry's isotherm^{7,8} is also superimposed for comparison. The data of the manufacturer have been obtained for temperatures from (328 to 358) K and for pressures from (1000 to 5000) Pa. However, the uncertainties of measurements are not available from the manufacturer. Apparently, the manufacturer is focusing more on the desorber conditions. When the manufacturer's data of the type RD silica gel are compared with our data for the same type of silica gel, the performance of the type RD silica gel–water system is found to be consistent in trend with that of the manufacturer's data, as shown in Figure 3.

From Figures 3 and 4, the isotherms of $T = 304$ K and 310 K for both type RD and A silica gel–water systems exhibit signs of onset of monolayer saturation at higher

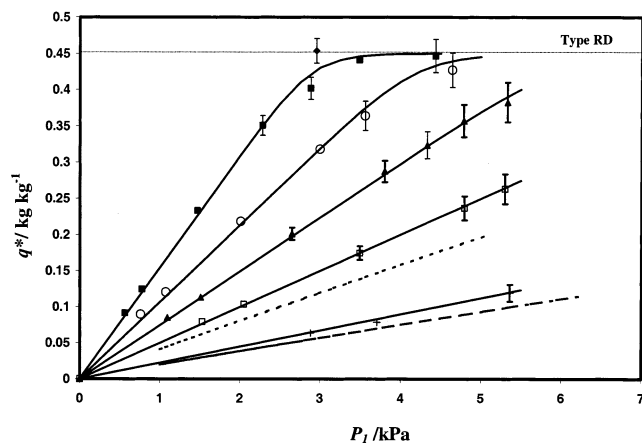


Figure 3. Isotherm data for water vapor onto the type RD silica gel: for experimental data points with (■) $T = 303$ K, (○) $T = 308$ K, (▲) $T = 313$ K, (□) $T = 323$ K, and (+) $T = 338$ K; for computed data points with solid lines for Tóth's equation; for manufacturer's data points with (---) $T = 323$ K of NACC² and (---) $T = 338$ K of NACC²; for one experimental data point with (◆) $T = 298$ K for the estimation of monolayer saturation uptake.

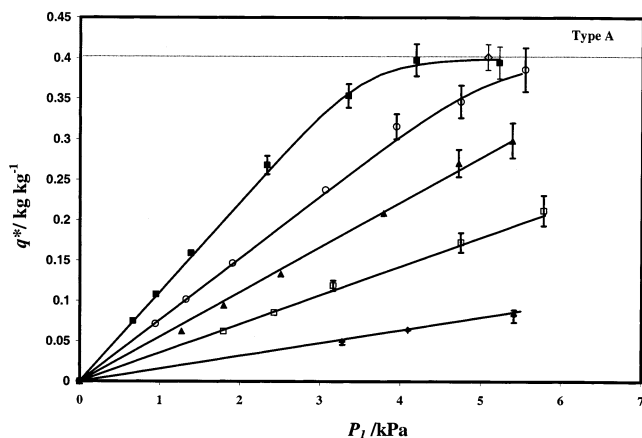


Figure 4. Isotherm data for water vapor onto the type A silica gel: for experimental data points with (■) $T = 304$ K, (○) $T = 310$ K, (▲) $T = 316$ K, (□) $T = 323$ K, and (+) $T = 338$ K; for computed data points with solid lines for Tóth's equation; for one experimental data point with (◇) $T = 298$ K for the estimation of monolayer saturation uptake.

Table 3. Measured Isotherm Data for Type RD Silica Gels

T (K)	P_1 (kPa)	q^* (kg·kg ⁻¹)	P_1 (kPa)	q^* (kg·kg ⁻¹)
298.15	2.9512	0.4535		
304.15	0.5653	0.0916	2.8829	0.4018
	0.7774	0.1246	3.4849	0.4409
	1.4679	0.2331	4.4327	0.4465
	2.2804	0.3507		
310.15	0.7591	0.0897	3.5595	0.3640
	1.0747	0.1206	4.1266	0.4089
	2.0115	0.2182	4.6402	0.4270
	2.9984	0.3180		
316.15	1.0948	0.0853	4.3298	0.3235
	1.5080	0.1132	4.7023	0.3454
	2.6504	0.2012	4.7865	0.3572
	3.8004	0.2876	5.3335	0.3827
323.15	1.5294	0.0794	4.7954	0.2366
	2.0491	0.1037	5.3003	0.2630
	3.4923	0.1744		
338.15	2.8814	0.0638	5.3634	0.1191
	3.7069	0.0786		

pressures. Tóth's equation^{9,10} is found to fit the experimental data of both type RD and A silica gel–water systems well and is therefore used to find the isotherm parameters

and isosteric heats of adsorption (Table 4). The form of Tóth's equation we used is given as

$$q^* = K_0 \exp(\Delta_{\text{ads}}H/RT) P_1 / \{1 + [K_0/q_m \exp(\Delta_{\text{ads}}H/RT) P_1]^t\}^{1/t}$$

where q^* is the adsorbed quantity of adsorbate by the adsorbent under equilibrium conditions, q_m denotes the monolayer capacity, P_1 is the equilibrium pressure of the adsorbate in the gas phase, T is the equilibrium temperature of the gas-phase adsorbate, R is the universal gas constant, $\Delta_{\text{ads}}H$ is the isosteric enthalpies of adsorption, K_0 is the preexponential constant, and t is the dimensionless Tóth constant. Tóth¹⁰ observed that the empirical constant t was between the interval of 0 and 1 insofar as his experiments were concerned but t could actually be greater than 1 as reported by Valenzuela and Myers.¹¹ In addition to the choice of using Tóth's equation, we had considered the use of the Dubinin–Astakhov equation in describing the present isotherm data. However, the Dubinin–Astakhov equation was found to be unable to provide a good description of the data to within the experimental uncertainties.

The adsorption isotherm parameters and the isosteric enthalpies of adsorption for the two grades of silica gel (types RD and A) + water systems are summarized in Table 4. Cremer and Davis¹² first reported a value of 2.98×10^3 kJ·kg⁻¹ for $\Delta_{\text{ads}}H$, though neither the experimental uncertainty nor the grade of silica gel was reported. This value has since been widely used. While Chihara and Suzuki³ reported a $\Delta_{\text{ads}}H$ that ranged from (2.8×10^3 to 3.5×10^3) kJ·kg⁻¹ for the type A silica gel, Sakoda and Suzuki⁴ later adopted the value of 2.8×10^3 kJ·kg⁻¹. One can appreciate that the present thermodynamically consistent values for $\Delta_{\text{ads}}H$, insofar as the condition of the ideal vapor phase may be assumed in the isotherm equations, for the current type RD and A silica gel–water systems are lower than that of Cremer and Davis.¹²

It is instructive to compare the present findings with those of the published references.^{3–5} The Fuji Davison silica gel (6–10 mesh) used by Cho and Kim⁵ was also of the type RD, whereas that used by Chihara and Suzuki³ was Fuji Davison type A with a size ranging from (5 to 10) mesh. The data available from refs 3 and 4 were measured by the gravimetric method, and the correlation proposed was recommended for temperatures below $T = 393$ K. Figure 5 presents the isotherm comparisons for various types of silica gel–water systems proposed by various groups of researchers at both $T = 308$ K and 338 K. It is evident that the performance of the type RD silica gel, as presented by Cho and Kim,⁵ is much higher than those obtained by other researchers. However, details of the experimental method and procedures were not available.

With reference to Table 4, the derived monolayer capacity of the type A silica gel was estimated to be 0.4 kg·kg⁻¹, which is higher than the value, 0.346 kg·kg⁻¹, reported by Chihara and Suzuki.³ The derived monolayer capacity of the type RD silica gel was similarly estimated to be 0.45 kg kg⁻¹. We observe that there is a significant difference between the present measurements and those of refs 3 and 4 for the type A silica gel. Moreover, while Tóth's equation is employed to correlate the present experimental data, Freundlich's equation was used to correlate the data in the two said references. The present data for the type RD silica gel with water vapor show a good consistency with the chiller manufacturer's correlation.²

Table 4. Correlation Coefficients for the Two Grades of Fuji Davison Silica Gel + Water Systems^a

type	K_0 ($\text{kg}\cdot\text{kg}^{-1}\cdot\text{kPa}^{-1}$)	$\Delta_{\text{ads}}H$ ($\text{kJ}\cdot\text{kg}^{-1}$)	q_m ($\text{kg}\cdot\text{kg}^{-1}$)	t	remarks
A	$(4.65 \pm 0.9) \times 10^{-10}$	$(2.71 \pm 0.1) \times 10^3$	0.4	10	by Tóth
RD	$(7.30 \pm 2) \times 10^{-10}$	$(2.693 \pm 0.1) \times 10^3$	0.45	12	by Tóth
RD (manufacturer)	2.0×10^{-9}	2.51×10^3			by Henry in refs 2 and 7

^a The error quoted refers to the 95% confidence interval of the least-squares regression of the experimental data.

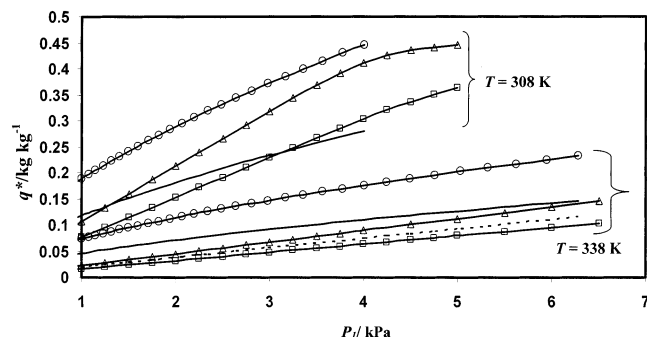


Figure 5. Isotherm data for water vapor with the silica gel by the present study and other researchers with (\square) type A by the present study, (\triangle) type A by Chihara and Suzuki,³ (\triangle) type RD by the present study, (\circ) type RD by Cho and Kim,⁵ and ($---$) type RD by NACC.²

Conclusion

Equilibrium studies of water vapor on the two Fuji Davison type silica gels had been investigated experimentally. The nature of our experiments was very similar to the actual condition in adsorption chillers, and the ranges of pressure and temperature also covered the typical operating range of adsorption chillers. The derived monolayer capacities for water vapor of the type A and RD silica gels had been calculated to be about (0.4 and 0.45) $\text{kg}\cdot\text{kg}^{-1}$, respectively. Tóth's equation is found to be able to sufficiently describe the performance of the type A and RD silica gels with water vapor. Our computed values of the isosteric heats of adsorption are lower than those found in the literature.^{3-5,12} This investigation, however, shows good

consistency with the chiller manufacturer's correlation² in terms of isotherm characteristics and isosteric heats of adsorption of the type RD silica gel with water vapor.

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