

INVESTIGATION ON THE ISOTHERM OF SILICA GEL+WATER SYSTEMS TG and volumetric methods

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Abstract

This article presents results of the experimental investigation on the adsorption of the water vapor on silica gel. Two independent experimental methods has been used, viz. the constant-volume-variable-pressure (CVVP) system and variable pressure thermogravimetry (TG). Results from these two methods are compared with each other. Also the isosteric heat of adsorption of this system has been determined from the equilibrium data. The silica gels investigated here are Fuji Davison type 'A' and type 'RD'. Adsorption isotherm of water vapor have been measured under a variety of conditions all referring to chiller operation cycles, i.e. temperatures from 303 to 358 K and pressures from 500 to 7000 Pa. The data collected from the two independent experiments compare very favorably with each other and their trends are consistent with those of the adsorption chiller manufacturer. This lends significant weight to our experimental data on silica gel+water systems as being valuable to the adsorption chiller manufacturers and the scientific community.

Keywords: adsorption isotherm, isosteric heat, silica gel, thermogravimetry, volumetric method

Introduction

The silica gel–water adsorption chiller is known to be an effective way to convert the low-grade heat source (typically at temperatures from 50 to 90°C, which are available in abundance in oil refineries and process industries) to useful cooling. The working pair, silica gel–water is environmentally benign, being made from harmless substances. The adsorbent, silica gel [1, 2], with a good thermal conductivity and a large pore surface area (typically in the region of 650–900 m² g⁻¹) has been proven as a good adsorbent for the commercialized chiller. The thermo-physical properties, isothermal data and isosteric heat of adsorption in the silica gel-water pair are essential data for the design of adsorption chillers. Despite much published work, both theoretical and experimental [3–5], there is still a dearth of experimental results that could be consistent with manufacturers' data. Thus, the motivation for the present study is to

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obtain accurate isotherm data and the isosteric heat of adsorption of the silica gel+water system. Recent experimental studies by Chua *et al.* [6], using the volumetric method (CVVP), are found to be consistent with the manufacturers' data in their trend but not in their magnitude.

In the present study, two independent methods, namely CVVP and thermogravimetry or TG were used to investigate the isothermal uptake of water vapour of Fuji Davison type 'A' and 'RD' silica gel. In terms of the chiller operation condition, we investigated the uptake of pure vapour (single-component) at isotherms ranging from 303 to 358 K, whilst the equilibrium pressures ranged from 500 to 7000 Pa. The experimental data from the two independent methods were compared with each other for checking the accuracy and reliability of each of the systems. For a chiller design purpose, the isosteric heat is calculated. Also the isotherm equation is found based on a correlation reported in the literature, namely, Tóth's isotherms, according to the experimental data. Furthermore, the experimental data were compared with the manufacturers' data that could provide more information to the manufacturer for cost-effective design.

Experimental

Physical properties

The adsorption performance of adsorbents is influenced by physical properties such as surface area, pore size and pore volume and pore distribution, porosity, and skeletal density. Yeh *et al.* [7] carried out a comprehensive literature survey on physical properties of silica gel; the manufacturer also provided data for the physical properties of Fuji Davison type 'A' and type 'RD' silica gels. To obtain accurate data, Chua *et al.* [6] experimentally investigated the physical properties by using a Micromeritics Gas Adsorption Analyzer-ASAP 2010 instrument, which is equipped with ASAP analysis software (Micromeritics Version 4) as summarized in Table 1. One could observe that the physical properties of the two types of silica gels are similar. However, the type 'RD' silica gel has a bigger surface area and higher thermal conductivity than type 'A' silica gel. This causes a significant difference to the vapour uptake of the silica gels, which is seen later in the experimental results.

CVVP system set-up and experiment

As shown in Fig. 1, the CVVP system mainly comprises a charging tank (material SS304) with a volume of $572.64 \pm 27 \text{ cm}^3$ inclusive of rated piping and valves, a dosing tank (material SS304) with volume of $698.47 \pm 32 \text{ cm}^3$ inclusive of rated piping and valves, an evaporator flask with a volume of 2000 cm^3 and vacuum system (a two-stage Edwards bubbler pump). 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 covered by the heat tape to enable in situ regeneration of the silica gel. The silica gel is placed in the big bottom plate and could be assumed to be in contact with the pure water vapour only, which closely resembled the actual condition in an adsorption

chiller. The detailed procedure and calibration for the system and components is found in our recent study [6], which conformed to national standards. The dry mass of silica gel was determined by the calibrated moisture balance (Sartorius MA40 moisture analyzer, uncertainty: 0.05% to DKD standard) at 413 K. For the two types of silica gel, type 'A' and type 'RD' used in our experiments, a mass of about 0.1 to 1.25 g was introduced into the charging tank at different pressures and temperatures. Prior to the experiment, the dosing tank, then charging tank plus related piping system, the so-called test system, must be purged by purified and dried argon and evacuated and subsequently isolated. Based on the 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 left over in the tanks was found to be very small and we had also adjusted the vapour partial pressure to avoid this small error due to the leftover argon after vacuuming.

Table 1 Thermophysical properties of silica gels*

Property	Value	
	type 'A'	type 'RD'
BET/N ₂ surface area ^c	716±3.3 m ² g ⁻¹	838±3.8 m ² g ⁻¹
BET constant ^c	293.8	258.6
BET volume STP ^c	164.5 cm ³ g ⁻¹	192.5 cm ³ g ⁻¹
Range of P _r ^c	0.05~0.19	0.05~0.23
Pore size ^c	0.8~5 nm	0.8~7.5 nm
Porous volume ^c	0.28 cm ³ g ⁻¹	0.37 cm ³ g ⁻¹
Micropore volume ^c	57%	49%
Mesopore volume ^c	43%	51%
Skeletal density ^d	2060 kg m ⁻³	2027 kg m ⁻³
Particle bulk density ^e	1306 kg m ⁻³	1158 kg m ⁻³
Surface area ^f	650 m ² g ⁻¹	720 m ² g ⁻¹
Average pore diameter ^f	2.2 nm	2.2 nm
Porous volume ^d	0.36 cm ³ g ⁻¹	0.4 cm ³ g ⁻¹
Apparent density ^{f**}	730 kg m ⁻³	700 kg m ⁻³
Mesh size ^f	10~40	10~20
pH ^f	5.0	4.0
Water content ^f	<2.0 mass%	
Specific heat capacity ^f	0.921 kJ kg ⁻¹ K ⁻¹	0.921 kJ kg ⁻¹ K ⁻¹
Thermal conductivity ^f	0.174 W m ⁻¹ K ⁻¹	0.198 W m ⁻¹ K ⁻¹

*Manufacturer's representative chemical composition (dry mass basis): SiO₂ (99.7%), Fe₂O₃ (0.008%), Al₂O₃ (0.025%), CaO (0.01%), Na₂O (0.05%); ^aRemarks ASAP 2010;

^dRemarks AccuPyc 1330; ^eRemarks computed; ^fRemarks Manufacturer;

**This value is inclusive of bed porosity

In order to maintain the system at constant temperature, the test system was immersed in a temperature-controlled bath (precision of control: ± 0.01 K). A two-stage rotary vane vacuum pump (Edwards bubbler pump) with a water vapour pumping rate of $315 \cdot 10^{-6} \text{ m}^3 \text{ s}^{-1}$ was equipped with this system for purging and vacuuming purposes. Argon with a purity of 99.9995% was passed through a column of packed calcium sulfate before being used to purge the vacuum system. Upon evacuation, a residual argon pressure of 100 Pa can be achieved in the set-up. The evaporator flask was immersed in a different temperature controlled bath (precision of control: ± 0.01 K). It was purged with argon with a purity of 99.9995% and evacuated by the vacuum pump before charging with distilled water. The temperature could be regulated to supply the water vapour at the desired pressure and an immersion magnetic stirrer was used to ensure uniformity of temperature inside the evaporator flask.

The dosing tank was first charged with water vapour. Prior to charging, the tank temperature was maintained initially at about (5~10) K higher than the evaporator temperature to avoid possible condensation. The effect of condensation would cause significant error in pressure reading. This would lead to significant error in calculating the actual mass of water vapour introduced 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 vapour was determined via pressure and temperature measurements, taking the effect of residual argon into account. Since the pressure transmitter was originally calibrated at room temperature, measuring the water vapour mass at this condition would ensure the maximum accuracy. The pressurized pneumatic inter-connecting valve between dosing tank and charging tank was opened once the whole test system reached thermodynamic equilibrium. Then by adjusting the water bath temperature, the water vapour inside the dosing tank and charging tank could achieve the thermodynamic equilibrium at the desired temperature. The temperatures and pressures

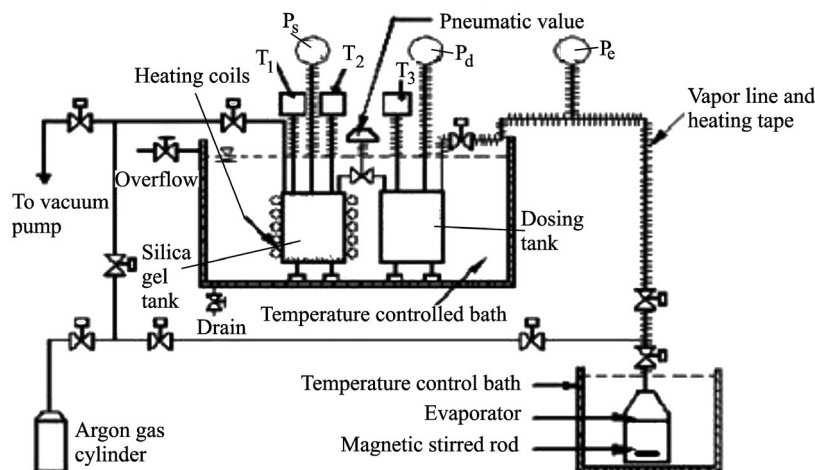


Fig. 1 A schematic diagram of the CVVP test facility: T_1, T_2, T_3 =resistance temperature detectors; P_s, P_d, P_e =capacitance manometers

inside the tanks could be monitored and recorded by the temperature and pressure sensors. Through pressures and temperature, the water vapour could be calculated by using the ideal gas equation before and after being adsorbed. The difference amounts to the uptake of the adsorbent. Since the above procedure was repeated for all the desired temperatures and pressures, the isotherm of the adsorbent could be deduced.

TG system set-up and experiment

The thermogravimetric analyzer, as shown in Fig. 2, comprises the Cahn TGA unit, an evaporator, a vacuum pumping subsystem and the helium gas supply subsystem. Water vapour is generated separately in a heater bath fitted with a PID controller. The pressure of the vapour is measured with a capacitance manometer, the Edwards barocel type 622 with 10 kPa span. The steam generator generates a flow of $(50\text{--}300)\text{ cm}^3\text{ min}^{-1}$. This flow rate is within the free delivery of the vacuum pump (about $3150\text{ cm}^3\text{ s}^{-1}$). The silica gel sample was put in the reaction chamber of the TG analyzer which has a radiant heater for maintaining constant sample temperature. Sufficient thermal insulation is incorporated to reduce heat loss. The changes of the sample mass were measured by the microbalance. A barocel pressure sensor was mounted at the bottom of the reaction chamber that reads the partial vacuum in the system. A RTD temperature sensor was inserted from the bottom of a 'tee-joint' and the whole glass tube was insulated. A vacuum pump was used for vacuuming and purging the system before test and maintaining the vapour testing condition in terms of the pressure and temperature during the experiment. The argon gas, for protection of the weighing bridge, was introduced from the top (from the inside) of double-walled tubing whilst the pure adsorbate is introduced upward to the silica gel sample which was contained within a quartz holder. The whole assembly is subjected to a pre-set pressure (P) and temperature (T). Isothermal environment of silica gel was maintained by direct radiant heating where the heaters are placed outside (non-vacuum) the reaction chamber. Cooling to the outside chamber (non-vacuum) is effected by passing cool air from a vortex chiller and external fan. By balancing the heating and the cooling effects (external to reaction chamber), a steady temperature environment for the silica gel was achieved readily.

In this experiment, we used the Fuji Davison type 'A' and type 'RD' silica gel as suitable adsorbents. The silica gel, about $(100\text{--}500)\text{ mg}$ was placed inside the quartz holder and the reaction chamber was then vacuum sealed and suitably insulated to prevent any possibility of condensation. The dry mass of silica gel was first measured by using the calibrated moisture balance (MA40) as that in the CVVP system. Thereafter, it was further confirmed within the reaction chamber of the TG analyzer, and the temperature of silica gel was held at 413 K for about 8 h. The dry mass was then read using the balance which is accurate to within $\pm 2\text{ }\mu\text{g}$. At the end of the regeneration process, the test system was purged by helium gas and evacuated. Thereafter, the reaction cell was continuously charged with water vapour and the vacuum pump kept pumping the vapour-gas mixture to maintain the desired vacuum

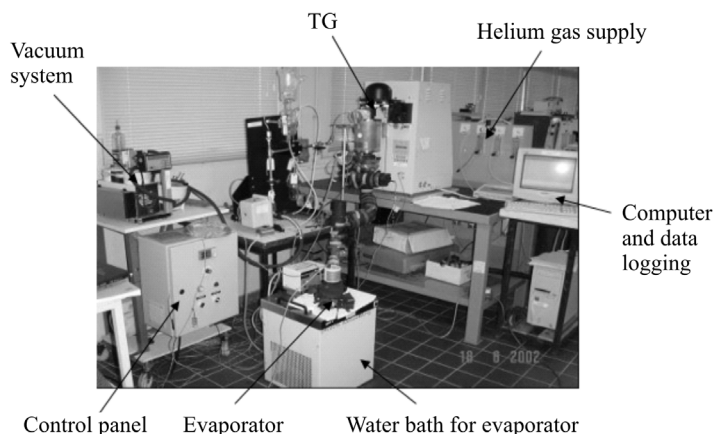


Fig. 2 The Cahn 2121 TGA unit with the LCD readout screen

and temperature conditions. Prior to the experiment, the Platinum standard mass was used to verify the TG system under the moisture environment.

To avoid condensation, the reaction cell and piping system were always kept at least (5~10) K higher than the saturated temperature of the vapour, which was achieved by wrapping heater tapes around the piping system and they were also well insulated to minimize heat loss. The system was deemed to be in thermodynamic equilibrium at desired pressure and temperature when the mass of the adsorbate remained unchanged for at least half an hour. The temperature was measured by one RTD sensor for data collection through the TG data recorder and one thermocouple for temperature control. The pressure and the mass of adsorbate were measured by the capacitance manometer and the TG balance, respectively. By repeating the above procedures, assorted range of tests were carried out under different settings of temperature and pressure. For every new test, the system checks were performed diligently, namely, (i) the system was evacuated, (ii) the silica gel was regenerated, and (iii) the chamber was purged with purified inert gas. Reproducibility of the measurements was checked by repeating the tests (at least three times). A fresh batch of the silica gel was always used for measurements.

Thermodynamics

The isosteric heat of adsorption [8] is a key parameter in the design of adsorption chillers, being a characteristic quantity of the adsorbent–adsorbate system. At a given specific surface loading, it can be calculated from isothermal equilibrium data at different temperatures using the Van't Hoff equation:

$$Q_{st} = RT^2 \left(\frac{d(\ln P)}{d(T)} \right)_q$$

The isosteric heat is related to the thermal equilibrium constant in analytical isotherm equation such as the Langmuir equation or the Tóth equation [9–11]. Therefore, its value is dependent on the isotherm equation by equilibrium data analytically correlated [12–14]. Chua *et al.* [6] demonstrated that the Tóth equation could fit the adsorption experimental data very well especially in the saturation region. Therefore it will be used here to find the isotherm parameters and the isosteric heats of adsorption. The form of the Tóth equation used in the present study is given as:

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

where q^* is the amount of adsorbate in the adsorbent under equilibrium conditions, q_m denotes the monolayer capacity, P , T are the equilibrium pressure and temperature of the adsorbate in the gas phase respectively, R is the universal constant, $\Delta_{\text{ads}}H$, Q_{st} are the isosteric enthalpy of adsorption, K_0 is a pre-exponential constant, and t is the dimensionless Tóth constant. Tóth observed that the empirical constant t was between zero and one in his experiments, but Valenzuela and Myers [12] reported that t actually could be greater than one. Chua *et al.* [6] reported that it is 10 in some cases.

Results and discussion

In this study, the temperatures and pressures ranged from 303 to 358 K and 500 to 7000 Pa, respectively. The uncertainty of pressure ranged from $\pm(10\text{--}200)$ Pa. It must be emphasized here that the conditions experienced in the adsorber are the same as the range of conditions to directly determine the cooling capacity.

Adsorption equilibrium data of water vapour on the above-mentioned silica gels were obtained from these two independent methods. Figure 3 shows the comparison between the isothermal data from two independent experimental methods and manufacturer's data. It is found that the equilibrium data resulting from two methods are consistent with each other and the trends are quite compatible with manufacturer's data which are not reported in other literature. Of course, the uncertainties of measurements are not available from the manufacture. The temperature range shows that the manufacturer is focusing more on the desorption conditions.

The isotherms covering the entire chiller operation range for the two types of silica gel are depicted in Figs 4, 5, respectively. One could observe that the equilibrium data from the two methods under different temperature and pressure are in very good agreement with each other. This strengthens the validity of the methods and the accuracy of the measurements. In Figs 4 and 5, the solid lines are experimental curve fits using Tóth's equation to fit the experimental data from the CVVP method. At the temperatures of 348 and 358 K, the data from Tóth's equation are in good agreement with the experimental data from TG. This further confirmed the accuracy of the experiments. One also observes that there is a significant difference between these two types of silica gels in their water vapour uptake characteristics. This is due to the different surface areas of the two types of silica gel. From Table 1, it is seen that the surface area of type 'RD' silica gel is much higher than that of type 'A' silica gel.

Therefore, the uptake of the vapour on the type 'RD' silica gel is much higher than that on the type 'A' silica gel.

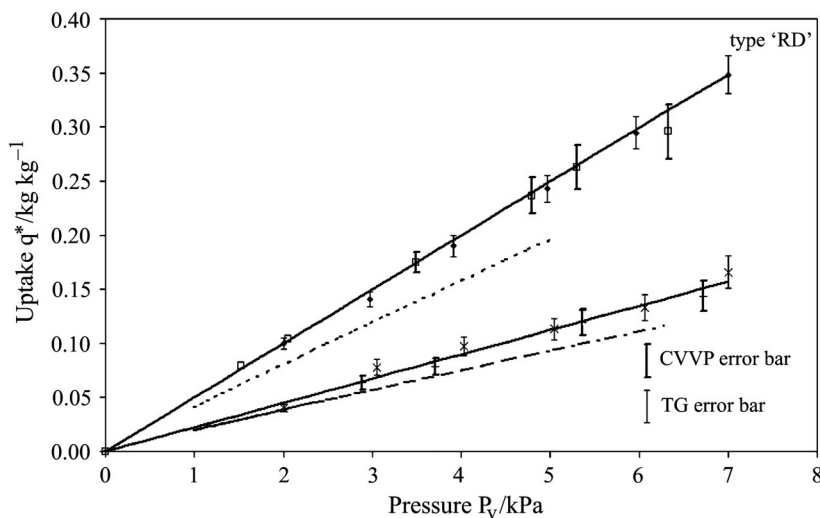


Fig. 3 Comparison of isotherm data for type 'RD' silica gel+water system. CVVP experimental data points: \square – $T=323$ K, $+$ – $T=338$ K; variable pressure TG experimental data points: \bullet – $T=323$ K, $*$ – $T=338$ K; solid lines are experimental curve fits using the Tóth's equation; a chiller manufacturer's data: --- – $T=323$ K, - - - – $T=338$ K

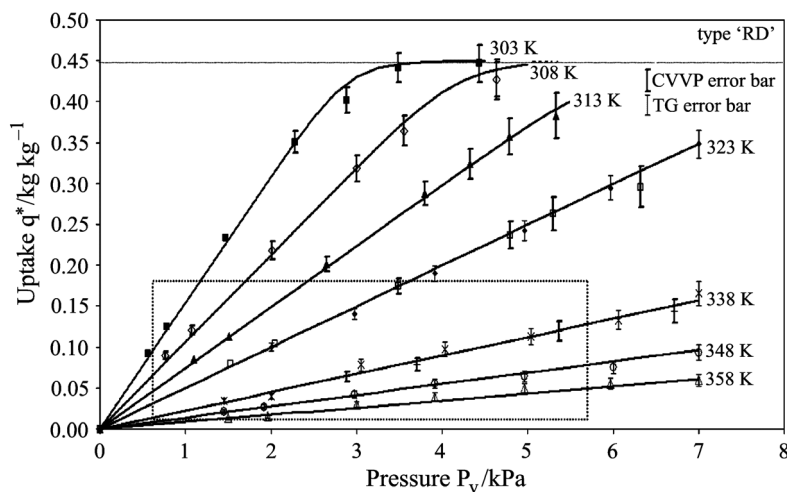


Fig. 4 Isotherm data for type 'RD' silica gel+water system. CVVP experimental data points: \blacksquare – $T=303$ K, \diamond – $T=308$ K, \blacktriangle – $T=313$ K, \square – $T=323$ K, $+$ – $T=338$ K; variable pressure TG experimental data points: \bullet – $T=323$ K, $*$ – $T=338$ K; \circ – $T=348$ K; \triangle – $T=358$ K; solid lines are experimental curve fits using Tóth's equation

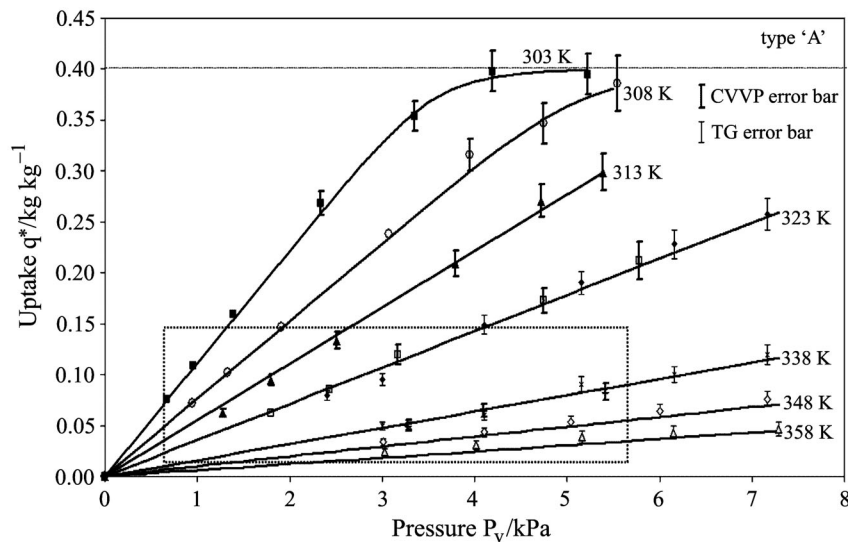


Fig. 5 Isotherm data for type 'A' silica gel+water system. CVVP experimental data points: ■ – $T=303$ K, ○ – $T=308$ K, ▲ – $T=313$ K, □ – $T=323$ K, + – $T=338$ K; variable pressure TG experimental data points: ● – $T=323$ K, * – $T=338$ K; ◇ – $T=348$ K; △ – $T=358$ K; solid lines are experimental curve fits using Tóth's equation

The rectangular areas in Figs 4 and 5 are the typical chiller operation regions. As demonstrated by Chua *et al.*, Tóth's equation fits the experimental data of both the type 'RD' and type 'A' silica gels well and is therefore used to find the isotherm parameters and isosteric heats of adsorption shown in Table 2. In the present study, $\Delta_{\text{ads}}H$ and q_m are significantly different from those reported by Chihara and Suzuki [4]. Cremer and Davis [15] first reported a value of $2.8 \cdot 10^3$ kJ kg⁻¹ for $\Delta_{\text{ads}}H$ and Sakoda and Suzuki [5] later reported a value of $2.8 \cdot 10^3$ kJ kg⁻¹ for $\Delta_{\text{ads}}H$. This could be easily explained according to the effects of the selected isothermal equation on the calculation of the isosteric heat. In the literature, the Henry equation or Langmuir equation is used mostly to fit isothermal data and calculate isosteric heat. As we studied, both the Henry equation and Langmuir equation could not fit the experimental data very well over the active region, especially in the saturation region. In addition, if only the chiller operation range was considered, both the Henry equation and the Langmuir equation can fit the experimental data. However, the constant coefficients in the isotherm equation could only be determined based on the experimental data in the chiller operation region which is not suitable for covering all the isotherm regions of the silica gel and water system. Therefore, the isosteric heat can only be calculated based on the experimental data within this region.

Table 2 Correlation coefficients for the two grades of Fuji Davison silica gel+water systems
(The error quoted refers to the 95% confidence interval of the least square regression of the experimental data)

Type	$K_0/\text{kg kg}^{-1} \text{ kPa}^{-1}$	$\Delta_{\text{ads}}H/\text{kJ kg}^{-1}$	$q_m/\text{kg kg}^{-1}$	t	Remarks
'A'	$(4.65 \pm 0.9) 10^{-10}$	$(2.71 \pm 0.1) 10^3$	0.4	10	by Tóth
'RD'	$(7.30 \pm 2) 10^{-10}$	$(2.693 \pm 0.1) 10^3$	0.45	12	by Tóth
'RD' (Manufacturer)	$2.0 10^{-9}$	$2.51 10^3$			by Henry Refs [2, 7]

Conclusions

Adsorption equilibrium studies of water vapour on the two Fuji Davison types of silica gels have been investigated independently by TG and CVVP methods. The conditions of our experiments were very similar to the actual conditions in an adsorption chiller process. The pressure and temperature ranges covered the typical operation range of an adsorption chiller. It was found that the experimental data in one method could be reproduced by the other independent method. This supports the reliability of our present study. In addition, Tóth's equation is used to describe the performance of the two types of silica gel with water vapour and to calculate the isosteric heat. This provides a good correlation for the simulation of an adsorption chiller system. Our computed values for $\Delta_{\text{ads}}H$, the isosteric enthalpy of adsorption in Tóth's equation, is lower than those of [15] and the monolayer capacity q_m is higher than those of [15]. However, our present investigation shows good consistency with chiller manufacturer's correlation in terms of the isotherm characteristics and the isosteric heats of adsorption of the type 'RD' silica gel with water vapor system.

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