Adsorption Thermodynamics of Silica Gel−Water Systems[†]

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The thermodynamic property surfaces of silica gel + water systems have been developed and described from the rigor of chemical equilibria between adsorbed and gaseous phases, Maxwell relations, the entropy of the adsorbed phase, and experimentally measured adsorption isotherm data. These property fields compute the entropy, enthalpy, specific heat capacity, and isosteric heat of adsorption as a function of pressure, temperature, and the amount of adsorbate thoroughly, which are essential for calculating the energetic performances of adsorption cooling and desalination processes. In this paper, the properties of enthalpy and entropy data for the silica gel + water system at temperatures from (273 to 373) K and at different equilibrium pressures between (0.5 and 10) kPa are furnished. The specific heat capacity and the isosteric heat of adsorption obtained by the proposed property fields are also compared with experimental data.

Introduction

Thermodynamic properties of adsorbed phases are necessary for analysis of adsorption processes used in gas separation, purification, sorption cooling, and gas storage systems. For adsorption cooling and desalination applications,[1−6] silica gel + water as an adsorbent + adsorbate pair is being widely used as it is environmentally friendly and can be driven by low-grade thermal energy. Silica gel is an amorphous, highly porous, partially hydrated form of silica.[7] Water vapor is captured in a nonideal manner on its surface. The adsorption thermodynamics of water vapor on silica gel are essential in determining the energetic performances of adsorption chillers. From the viewpoint of fundamental design of adsorption chillers, the theoretical investigation of thermodynamic property fields, namely, energy, enthalpy, entropy, specific heat capacity,[8] and heat of adsorption,[9,10] of the silica gel + water system are pertinent for the purpose of adsorption system modeling.

The early theoretical models for physical adsorption systems are attributed largely to the works of Hill[11,12] and Everett,[13,14] and a more general approach to adsorption with an exchange of heat and work has been developed by Guggenheim.[15] Myers et al.[16,17] developed the thermodynamic functions such as Gibbs free energy, enthalpy, and entropy on the basis of the isothermal condition. Chua et al.[18] developed the thermodynamic property fields of the adsorbent + adsorbate system, which is based on the works of Feuerecker et al.[19] for absorption (liquid−vapor) systems. This method is based on the mass, energy, and entropy balances, which in turn led to the specific heat capacity expression for the adsorbent + adsorbate system as a function of pressure (P), temperature (T), and the amount of adsorbate uptake (c), which are roughly calculated.

In the above background,[11−19] the main objectives of this paper are (1) to develop the thermodynamic property surfaces, (2) to evaluate these thermodynamic quantities as a function of P, T, and c by temperature−entropy ($T-s$) and pressure−enthalpy ($P-h$) maps, and (3) to calculate accurately the specific heat capacity and the isosteric heat of adsorption of the silica gel + water system for various uptakes and to compare the results with experimental data.

Thermodynamic Framework

The physical adsorption system is an ensemble of adsorbed gas plus adsorbent enclosed by a surface. The extensive thermodynamic quantities such as entropy (s), internal energy (u), and enthalpy (h) of a single component adsorbent + adsorbate system at a given mass of adsorbent, M_s, are path independent, and their changes can be tracked by integrating in succession between the limits of P_o and P, T_o, and T and c_o ($c = 0$) and c with T, c; P, c, and P, T being held constant, respectively, for these integration processes. A graphical representation of the process of adsorption for any thermodynamic variable φ where the unsaturated state of an adsorbent + adsorbate system is depicted with an initial state (P_o, T_o, $c \approx 0$) to a final state (P, T, $c > 0$) is shown in Figure 1. The change of φ can be traced by a mathematical technique, and this is given by

$$\int_{\mathrm{i}}^{\mathrm{f}} \mathrm{d}\varphi = \int_{T_o}^{T}\left(\frac{\partial\varphi}{\partial T}\right)_{P,c}\mathrm{d}T + \int_{P_o}^{P}\left(\frac{\partial\varphi}{\partial P}\right)_{T,c}\mathrm{d}P + \int_{0}^{c}\left(\frac{\partial\varphi}{\partial c}\right)_{P,T}\mathrm{d}c \tag{1}$$

where i and f indicate the initial and final states. For a single component adsorbent + adsorbate system, the thermodynamic quantity of the final state φ^{f} is given by

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$$\varphi^{\mathrm{f}} = \varphi^{\mathrm{i}} + \int_{T_{\mathrm{o}}}^{T}\left(\frac{\partial \varphi_{\mathrm{s}}}{\partial T}\right)_{P,c}\mathrm{d}T + \int_{P_{\mathrm{o}}}^{P}\left(\frac{\partial \varphi_{\mathrm{s}}}{\partial P}\right)_{T,c}\mathrm{d}P + \int_{0}^{c}\left(\frac{\partial \varphi_{\mathrm{s}}}{\partial c}\right)_{P,T}\mathrm{d}c + \int_{T_{\mathrm{o}}}^{T}\left(\frac{\partial \varphi_{\mathrm{a}}}{\partial T}\right)_{P,c}\mathrm{d}T + \int_{P_{\mathrm{o}}}^{P}\left(\frac{\partial \varphi_{\mathrm{a}}}{\partial P}\right)_{T,c}\mathrm{d}P + \int_{0}^{c}\left(\frac{\partial \varphi_{\mathrm{a}}}{\partial c}\right)_{P,T}\mathrm{d}c \quad (2)$$

where the subscripts “s” and “a” indicate the solid and adsorbed phase, respectively. Neglecting the pressure and uptake dependence of solid-phase entropy with respect to the entropy of the adsorbent + adsorbate system is

$$s^{\mathrm{f}} = s^{\mathrm{i}} + \int_{T_{\mathrm{o}}}^{T}\left(\frac{\partial s_{\mathrm{s}}}{\partial T}\right)_{P,c}\mathrm{d}T + \int_{T_{\mathrm{o}}}^{T}\left(\frac{\partial s_{\mathrm{a}}}{\partial T}\right)_{P,c}\mathrm{d}T + \int_{P_{\mathrm{o}}}^{P}\left(\frac{\partial s_{\mathrm{a}}}{\partial P}\right)_{T,c}\mathrm{d}P + \int_{0}^{c}\left(\frac{\partial s_{\mathrm{a}}}{\partial c}\right)_{P,T}\mathrm{d}c \quad (3)$$

For a pure and incompressible solid adsorbent, $\int_{T_{\mathrm{o}}}^{T}(\partial s_{\mathrm{s}}/\partial T)_{P,c}\ \mathrm{d}T = \int_{T_{\mathrm{o}}}^{T}(c_{p,\mathrm{s}}/T)\ \mathrm{d}T$, where $c_{p,\mathrm{s}}$ is the specific heat capacity of the solid adsorbent. In the adsorbed phase, $\int_{T_{\mathrm{o}}}^{T}(\partial s_{\mathrm{a}}/\partial T)_{P,c}\ \mathrm{d}T = \int_{T_{\mathrm{o}}}^{T}(c_{p,\mathrm{a}}/T)\ \mathrm{d}T$, and $c_{p,a}$ is the specific heat capacity of the adsorbed phase. The mathematical model of $c_{p,\mathrm{a}}$ is described and analyzed by Chakraborty et al.[8] and is expressed as $c_{p,\mathrm{a}} = c_{p,\mathrm{g}} + Q_{\mathrm{st}}((1/T) - (1/v_{\mathrm{g}})(\mathrm{d}v_{\mathrm{g}}/\mathrm{d}T)) - (\partial Q_{\mathrm{st}}/\partial T)_P$, where v indicates the specific volume; Q_{st} defines the isosteric heat of adsorption; and the subscript “g” represents the gaseous phase. Invoking the Maxwell relations for the pressure integration, we have $\int_{P_0}^{P}(\partial s_{\mathrm{a}}/\partial P)_{T,c}\ \mathrm{d}P = -\int_{P_0}^{P}(\partial v_{\mathrm{a}}/\partial T)_{P,c}\ \mathrm{d}P$, where the subscript “a” indicates the adsorbed phase. The chemical potential of the adsorbed phase μ_{a} is a result of the partial change in internal energy u_{a} with the amount of adsorbate uptake c. The total differentials of chemical potential in adsorbed and gaseous phases can be written as $\mathrm{d}\mu_{\mathrm{a}} = -(\partial s_{\mathrm{a}}/\partial c)_{T,P}\ \mathrm{d}T + v_{\mathrm{a}}\mathrm{d}P + (\partial \mu_{\mathrm{a}}/\partial c)_{T,P}\mathrm{d}c$, and $\mathrm{d}\mu_{\mathrm{g}} = -s_{\mathrm{g}}\mathrm{d}T + v_{\mathrm{g}}\mathrm{d}P$, respectively.[9]

If the adsorbate is in equilibrium with the unadsorbed gas, $\mathrm{d}\mu_{\mathrm{a}} = \mathrm{d}\mu_{\mathrm{g}}$ or

$$\left(\frac{\partial s_{\mathrm{a}}}{\partial c}\right)_{T,P}\mathrm{d}T - v_{\mathrm{a}}\mathrm{d}P - \left(\frac{\partial \mu_{\mathrm{a}}}{\partial c}\right)_{T,P}\mathrm{d}c = s_{\mathrm{g}}\mathrm{d}T - v_{\mathrm{g}}\mathrm{d}P$$

At constant amount of adsorbate uptake, $(\partial\mu_{\mathrm{a}}/\partial c)_{T,P} = 0$. From these relationships, the entropy change with respect to the mass of adsorbate is given by

$$\left(\frac{\partial s_{\mathrm{a}}}{\partial c}\right)_{T,P} = s_{\mathrm{g}} - (v_{\mathrm{g}} - v_{\mathrm{a}})\frac{\mathrm{d}P}{\mathrm{d}T} \quad (4)$$

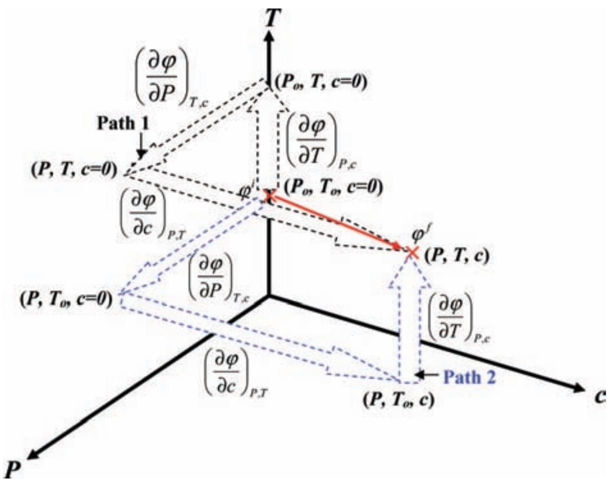

Figure 1. Thermodynamic paths for calculating extensive thermodynamic properties from the initial state to the final state (two possible paths are shown here).

Substituting the above-mentioned simplifications and neglecting the solid phase entropy at the initial state, the extensive entropy quantity is reduced to

$$s^{\mathrm{f}} = s_{\mathrm{a}}(P_{\mathrm{o}}, T_{\mathrm{o}}, c = 0) + \int_{T_{\mathrm{o}}}^{T}\frac{c_{p,\mathrm{s}}}{T}\mathrm{d}T + \int_{T_{\mathrm{o}}}^{T}\frac{c_{p,\mathrm{a}}}{T}\mathrm{d}T - \int_{P_0}^{P}\left(\frac{\partial v_{\mathrm{a}}}{\partial T}\right)_{P,x}\mathrm{d}P + \int_{0}^{c}\left\{s_{\mathrm{g}} - (v_{\mathrm{g}} - v_{\mathrm{a}})\frac{\mathrm{d}P}{\mathrm{d}T}\right\}\mathrm{d}c$$

or

$$s^{\mathrm{f}} = \int_{T_{\mathrm{o}}}^{T}\frac{c_{p,\mathrm{s}}}{T}\mathrm{d}T + s_{\mathrm{g}}(P, T) + \int_{0}^{c}\left\{s_{\mathrm{g}} - \frac{Q_{\mathrm{st}}}{T}\right\}\mathrm{d}c + \int_{T_{\mathrm{o}}}^{T}Q_{\mathrm{st}}\left(\frac{1}{T^2} - \frac{1}{Tv_{\mathrm{g}}}\frac{\mathrm{d}v_{\mathrm{g}}}{\mathrm{d}T}\right)\mathrm{d}T \quad (5)$$

where the definition $T(v_{\mathrm{g}} - v_{\mathrm{a}})(\mathrm{d}P)/(\mathrm{d}T) = Q_{\mathrm{st}}$ has been used for simplifying the equation of entropy in the adsorbent + adsorbed system.[9,10] By considering the effects of the nonideality of the gaseous phase, the heat of adsorption is represented as[10] $Q_{\mathrm{st}} = RT^2(\partial \ln P/\partial T)_c + Tv_{\mathrm{g}}(\mathrm{d}P)/(\mathrm{d}T)$, where the first term of the right-hand side indicates the form of Clausius−Clapeyron, and the second term occurs due to the nonideality of the gaseous phase.

Applying the Gibbs free energy equation, i.e., $\mathrm{d}h = T\mathrm{d}s + v\mathrm{d}P$, the thermodynamic property surface of enthalpy for the adsorbent + adsorbate system becomes

$$h^{\mathrm{f}} = \int_{T_{\mathrm{o}}}^{T}c_{p,\mathrm{s}}\mathrm{d}T + h_{\mathrm{g}}(P, T) + \int_{0}^{c}\{h_{\mathrm{g}} - Q_{\mathrm{st}}\}\mathrm{d}c + \int_{T_{\mathrm{o}}}^{T}Q_{\mathrm{st}}\left(\frac{1}{T} - \frac{1}{v_{\mathrm{g}}}\frac{\mathrm{d}v_{\mathrm{g}}}{\mathrm{d}T}\right)\mathrm{d}T \quad (6)$$

By definition, the internal energy ($u = h - Pv$) of the adsorbent + adsorbate system is given by

$$u^{\mathrm{f}} = \int_{T_{\mathrm{o}}}^{T}c_{p,\mathrm{s}}\mathrm{d}T + h_{\mathrm{g}}(P, T) + \int_{0}^{c}\{h_{\mathrm{g}} - Q_{\mathrm{st}}\}\mathrm{d}c + \int_{T_{\mathrm{o}}}^{T}Q_{\mathrm{st}}\left(\frac{1}{T} - \frac{1}{v_{\mathrm{g}}}\frac{\mathrm{d}v_{\mathrm{g}}}{\mathrm{d}T}\right)\mathrm{d}T - \int_{P_{\mathrm{o}}}^{P}v_{\mathrm{g}}\mathrm{d}P \quad (7)$$

The amount of adsorbate uptake (c) for a single-component adsorbent + adsorbate system is calculated from fits of experimental data to adsorption isotherm equations such as Langmuir, Tóth, Dubinin−Astakhov (D−A), Dubinin−Radushkevich, etc. The Tóth and Dubinin−Astakhov equations[20−24] as shown in Table 1 are used to calculate the adsorption isotherm parameters of the silica gel + water system in this particular case.

Intuitively, the c_{p} of the adsorbent + adsorbate system would have contributions from three parts, namely, (i) the specific heat capacity of solid adsorbent ($c_{p,\mathrm{s}}$), (ii) the partial contributions from the heat capacity of adsorbed phase to be considered as liquid phase ($c_{p,\mathrm{l}}$), and (iii) the gaseous phase ($c_{p,\mathrm{g}}$). The combined c_p of the adsorbent + adsorbate system then becomes

$$c_p = c_{p,\mathrm{s}} + \left[c_{p,\mathrm{g}} + \left\{\frac{1}{T} - \frac{1}{v_{\mathrm{g}}}\left(\frac{\partial v_{\mathrm{g}}}{\partial T}\right)_c\right\}Q_{\mathrm{st}} - \left(\frac{\partial Q_{\mathrm{st}}}{\partial T}\right)_P\right]c \quad (8)$$

The term $[\{(1/T) - (1/v_{\mathrm{g}})(\partial v_{\mathrm{g}}/\partial T)_P\}Q_{\mathrm{st}} - (\partial Q_{\mathrm{st}}/\partial T)_P]$ turns out to be significant because of the Q_{st} and the nonideality of the gaseous phase. The heat capacity of the gaseous phase is very close to the adsorbed phase when Q_{st} is not temperature

Table 1. Adsorption Isotherms in Calculating the Characteristics of Silica Gel (Type RD, $CaCl_2$–in–Silica Gel) + Water Systems

Adsorption isotherms Tóth: $c = c^o (KP)/\{1 + (KP)^t\}^{1/t}$; $K = K_o \exp(Q_{st}/RT)$	pre-exponential constant K_o (Pa^{1-})	Q_{st} (kJ·kg^{-1})	c^o (kg·kg^{-1})	Tóth constant t	source
silica gel type RD	$7.3 \cdot 10^{-13}$	2800	0.4	8	20
$CaCl_2$-in-silica gel	$2 \cdot 10^{-12}$	2800	0.8	1.1	21
Dubinin–Astakhov: $c = c^o \exp\{-[((RT)/E) \ln (P_s/P)]^n\}$	E (kJ·kg^{-1})	n	c^o (kg·kg^{-1})		source
silica gel type 125	220	1.29	0.33		22
$CaCl_2$-in-silica gel	305	1.75	0.65		23

Table 2. Thermodynamic Property Surfaces for Enthalpy (h_a) and Entropy (s_a) of the Silica Gel (type RD) + Water System When the Amount of Water Vapor on Silica Gel is 0.15 kg·kg^{-1}

T	P	h_g	s_g	s_a	h_a
K	kPa	kJ·kg^{-1}	kJ·kg^{-1}K^{-1}	kJ·kg^{-1}K^{-1}	kJ·kg^{-1}K^{-1}
290.15	0.3858	2532.9	9.48	9.60	2531.03
294.15	0.5126	2540.3	9.37	9.52	2543.29
298.15	0.6759	2547.7	9.27	9.44	2555.56
300.15	0.774	2551.4	9.22	9.40	2561.69
304.15	1.0094	2558.8	9.12	9.33	2573.98
308.15	1.3075	2566.2	9.03	9.26	2586.28
310.15	1.4843	2569.9	8.98	9.23	2592.43
314.15	1.9037	2577.3	8.89	9.17	2604.75
318.15	2.4264	2584.6	8.80	9.11	2617.07
320.15	2.7331	2588.3	8.76	9.08	2623.25
324.15	3.4524	2595.7	8.67	9.03	2635.61
328.15	4.3363	2603	8.59	8.97	2647.98
330.15	4.8498	2606.6	8.55	8.94	2654.17
334.15	6.0419	2614	8.47	8.90	2666.59
338.15	7.4881	2621.3	8.39	8.85	2679.03
340.15	8.3204	2624.9	8.35	8.83	2685.25
344.15	10.235	2632.1	8.28	8.78	2697.71
348.15	12.531	2639.4	8.21	8.74	2710.22
350.15	13.841	2643	8.17	8.72	2716.47
354.15	16.830	2650.1	8.11	8.68	2729.01
358.15	20.375	2657.3	8.04	8.64	2741.59
360.15	22.383	2660.8	8.01	8.62	2747.89

dependent. If the thermal expansion terms of the gaseous phase are neglected, the resulting equation becomes[25] $c_{p,a} = c_{p,g} - (\partial Q_{st}/\partial T)_c$. From the contributions of the D–A equation, the value of Q_{st} is given by

$$Q_{st} = h_{fg} + E\left(\ln \frac{c^o}{c}\right)^{1/n} + Tv_g\left(\frac{dP}{dT}\right)_{gas} \qquad (9)$$

where h_{fg} indicates the latent heat of vaporization; E is the characteristic energy of the adsorbent + adsorbate system; c^o denotes the maximum uptake; and n indicates the heterogeneity constant. The derivative $(dP/dT)_{gas}$ is calculated as a function of pressure and temperature from the National Institute of Standards and Technology (NIST) standard reference database.[26] Equation 7 can be written as

$$c_p = c_{p,s} + \left[c_{p,g}(P,T) + \left\{\frac{1}{T} - \frac{1}{v_g}\left(\frac{\partial v_g}{\partial T}\right)_P\right\}Q_{st} + c_{p,l}(T) - c_{p,g}(T) - v_g\left(\frac{dP}{dT}\right)_{gas} - Tv_g\frac{\partial^2 P}{\partial T^2}\right]c \qquad (10)$$

Results and Discussion

From Table 2, one could observe that the thermodynamic properties of the adsorbed phase are not similar to those of the gaseous phase. The enthalpy and the entropy of the adsorbed phase are higher than the values of gaseous phases for both silica gel + water systems. These results presented herein are based on the experimentally measured adsorption isotherm data.[20,23] In the present study, the temperatures and pressures range from (274 to 373) K and from (1 to 10) kPa, respectively. Emphasis is placed on the conditions experienced in the adsorption cooling cycle.

The entropy is an increasing function of pressure, temperature, and uptakes. The $T-s$ maps for the adsorption characteristics of silica gel (type RD) + water are shown in Figure 2 for various *pressures* and *concentrations*. From this graph, one can easily calculate the energetic performances of the adsorption cooling cycle in terms of entropy flow and also plot an ideal cooling cycle. During the regeneration phase (lines A–B–C), the pressure in the adsorber rises from P_{evap} to P_{cond} by heating the adsorber, and desorption of water vapor from the silica gel occurs by connecting the adsorber with the condenser. The amount of adsorbed uptake falls from c_{ads} to c_{des}, and the entropy rises from s_{ads} to s_{des}. On the other hand, during the adsorption phase (lines C–D–A), the adsorber is cooled, and the pressure falls from P_{cond} to P_{evap}. Then, the refrigerant vapor is adsorbed on the adsorbent and the amount adsorbed increases up to c_{ads}. The amount of energy required for the desorption process is $Q_{des} = \int T_{des} ds_{des}$.

The enthalpy of the silica gel (type RD) + water system is a decreasing function of pressure and the amount of water vapor uptake, and the $P-h$ map is shown in Figure 3, where one can observe that h increases when the temperature is increased and the uptake is decreased. The enthalpy approximately approaches a constant value when the filling of water vapor on silica gel becomes weaker, and the silica gel + water systems approach equilibrium. This indicates that silica gel has highly microporous surfaces. Such curves also represent the nature of adsorbents.

Figure 4 shows a comparison of the predicted values of c_p of the silica gel (type 125) + water system against two sets of experimental data, namely, the DSC and THS (transient hot

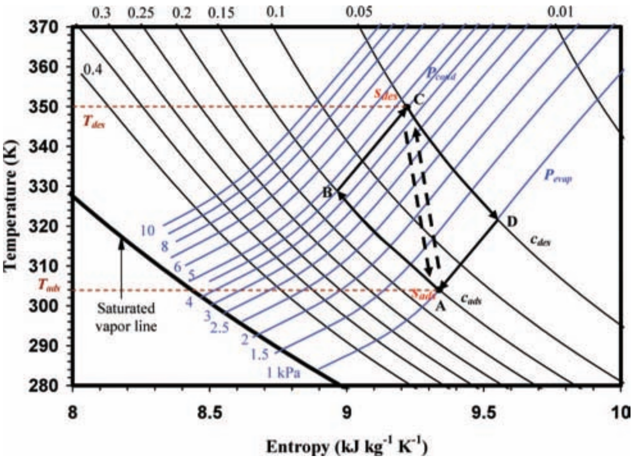

Figure 2. Temperature–entropy diagram of the silica gel (type RD) + water system for various pressures and uptakes. Here the subscripts "ads" defines adsorption, "des" indicates desorption, "cond" is the condenser, and "evap" refers to the evaporator.

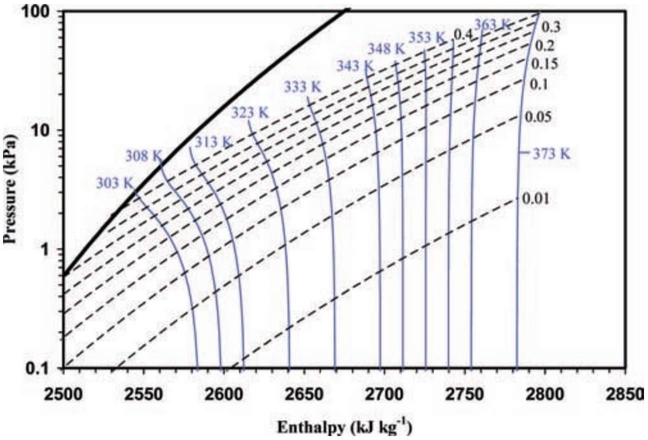

Figure 3. Pressure−enthalpy diagram of type RD silica gel + water system.

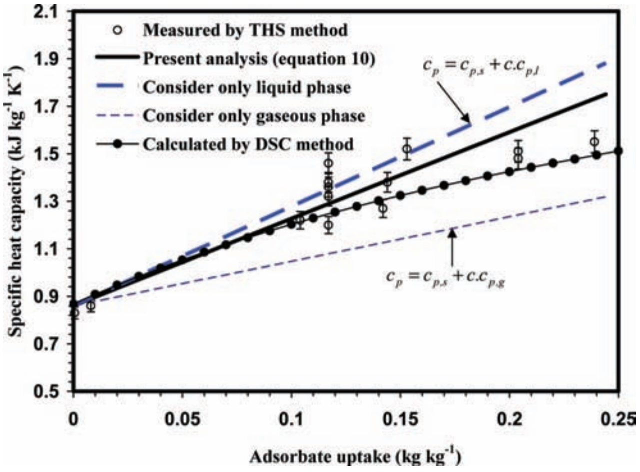

Figure 4. Specific heat capacity of the silica gel (type 125) + water system at 295 K.

strip) methods,[22] where the adsorbate uptake or coverage spans up to 32 % of the mass of silica gel, and these data are furnished in Table 3. In this analysis, adsorption isotherms were fitted to the D−A equation, where the isotherm parameters E, n, and c^o are calculated as 220 kJ·kg^{-1}, 1.29, and 0.33 kg·kg^{-1}, respectively. It is observed that most of the experimental data are found bounded in between the c_p of the liquid and gaseous phases. The predictions give better agreement, both in magnitude and trend, throughout the range of coverage when compared with the experimentally measured data.

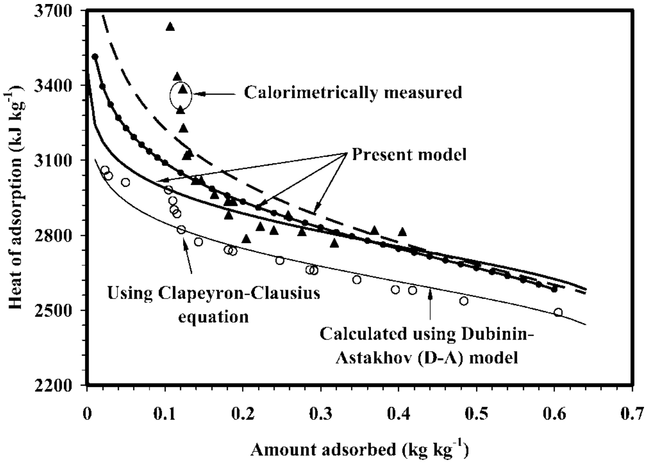

Figure 5. Isosteric heat of adsorption for the $CaCl_2$-in-silica gel + water system. The present model is compared with experimentally measured calorimetric heat of adsorption data. Hence: ▲, experimentally measured Q_{st} data; ○, the data measured by the Clausius−Clapeyron equation; dark line —, Q_{st} calculated by the present model where E = 305 kJ·kg^{-1}, n = 1.75, and c^o = 0.65; doted line ---, Q_{st} for E = 400 kJ·kg^{-1}, n = 1.2, and c^o = 0.64; and ●, the isosteric heat of adsorption for E = 350 kJ·kg^{-1}, n = 1.4, and c^o = 0.62. Here the adsorption isotherm equation of the $CaCl_2$-in-silica gel + water system calculated by using these parameters (E, n, and c^o for three different cases) is fitted well with the experimental data.

Table 4. Isosteric Heat of Adsorption for the $CaCl_2$-in-Silica Gel + Water System at 303 K and a Comparison between the $Q_{st}\{= RT^2(\partial \ln P)/(\partial T)|_c + Tv_g(dP/dT) = h_{fg} + E(\ln (c^o/c))^{1/n} + Tv_g(dP/dT)$ of the Present Model and the Calorimetrically Measured Q_{st} Data

uptake	v_g	dP/dT	present model	experimental[24]	by D−A equation
			Q_{st}	Q_{st}	Q_{st}
(kg·kg^{-1})	(m^3·kg^{-1})	kPa·K^{-1}	(kJ·kg^{-1})	(kJ·kg^{-1})	(kJ·kg^{-1})
0.140	543.51	0.00085	2942.69	3019.71	2802.78
0.150	514.25	0.000898	2934.95	3019.71	2795.04
0.165	457.51	0.001009	2918.61	2964.19	2778.69
0.1815	409.41	0.001128	2903.09	2936.44	2763.16
0.182	407.99	0.001132	2902.60	2880.93	2762.68
0.187	394	0.001172	2897.74	2936.42	2757.79
0.204	356.51	0.001296	2883.76	2786.56	2743.82
0.222	322.33	0.001433	2869.68	2836.52	2729.73
0.240	293.38	0.001575	2856.53	2819.87	2716.57
0.258	267.35	0.001728	2843.56	2880.93	2703.57
0.276	245.01	0.001886	2831.37	2814.32	2691.38
0.317	201.8	0.00229	2804.28	2769.91	2664.25
0.369	160.72	0.002876	2772.51	2819.87	2632.44
0.405	137.96	0.003352	2751.20	2814.32	2611.09

The isosteric heat of adsorption (Q_{st}) for water on $CaCl_2$-in-silica gel for various uptakes at 303 K is shown in Figure 5. These data are also furnished in Table 4. It is found from Figure 5 that the isosteric heat of adsorption decreases with the increase of the amount of adsorbate. The average value of Q_{st}, calculated from the Tóth model, is 2800 kJ·kg^{-1}. The calorimetrically measured experimental data[24] are also presented in Figure 5 for comparison. At lower surface coverage, the Q_{st} obtained by the proposed formalism is close to the data taken from the Clausius−Clapeyron formula, but at higher surface coverage,

Table 3. Specific Heat Capacity of the Silica Gel (Type 125) + Water System at 295 K

P	c	v_g	dP/dT	dv_g/dT	Q_{st}	c_p	c_p	c_p
kPa	kg·kg^{-1}	m^3·kg^{-1}	kPa·K^{-1}	m^3·kg^{-1}·K^{-1}	kJ·kg^{-1}	(DSC)	(THS)	(eq 10)
0.00272	0.0005	50077	9.216E-06	169.6664	3522.999	0.86	0.83	0.861
0.0303	0.008	4487.1	0.0001029	15.20424	3194.12	0.90	0.86	0.889
0.435	0.104	312.7	0.0014774	1.061025	2831.123	1.213	1.22	1.241
0.643	0.117	211.67	0.0021837	0.718749	2778.009	1.25	1.32	1.380
0.655	0.142	207.85	0.0022239	0.705785	2775.53	1.31	1.27	1.387
0.709	0.144	191.91	0.0024089	0.651808	2764.672	1.31	1.38	1.420
1.059	0.153	128.49	0.0036012	0.436962	2710.129	1.33	1.52	1.605
1.059	0.204	128.49	0.0036012	0.436962	2710.129	1.43	1.48	1.605
1.351	0.204	100.7	0.0045989	0.34286	2677.037	1.43	1.51	1.731
1.407	0.239	96.711	0.0047892	0.329348	2671.552	1.49	1.55	1.7532

the proposed Q_{st} matches well with the calorimetric measured Q_{st} values. The Dubinin−Astakhov isotherm model is also employed to evaluate the isosteric heat of adsorption. The D−A isotherm parameters such as E and n are sensitive to Q_{st} values. In Figure 5, three curves are plotted for three different values of E, n, and c^{o} using the present model. For higher E (= 400 kJ·kg^{-1}) and lower n (= 1.2), Q_{st} is nearer to calorimetrically measured Q_{st} data at lower surface coverage. On the other hand, the errors between the experimental data and the calculated Q_{st} values are small for lower E (= 305 kJ·kg^{-1}) and relatively bigger n (= 1.75) at medium and higher surface coverage. From Figure 5, one may observe that Q_{st} is found to be very high at lower loading or Henry's region compared to Q_{st} at higher uptakes. Silica gel consists mainly of micropores with different widths, and at first water vapor adsorbs rapidly onto sites of high energy, and molecules then adsorb onto sites of decreasing energy as adsorption progresses. The adsorbate molecules first penetrate into narrower pores and provide stronger interaction between the adsorbate and the adsorbent. This implies a higher value of Q_{st} at lower loadings. After completely filling the smaller pores, water molecules are gradually accommodated in larger pores, in which the adsorption affinity becomes weaker.

Conclusions

The temperature−entropy and pressure−enthalpy maps of water vapor on different silica gel samples have been developed and analyzed. The nature of these thermodynamic properties is evaluated in the ranges of pressure and temperature also covering the typical operating range of adsorption chillers. The specific heat capacity for water vapor of the type 125 silica gel has been calculated and compared with experimental data. It is found from the present analysis that the isosteric heat of adsorption plays an important role to calculate the thermodynamic property data in the adsorbed phase. It is also observed from the present analysis that the Clausius−Clapeyron (C−C) equation is not enough to explain the isosteric heat of adsorption completely, and the Q_{st} values obtained by the C−C equation are not fairly matched with the experimentally measured calorimetric Q_{st} values. The difference in the values of Q_{st} between the calorimetric and C−C may occur due to the nonideality of the gaseous phase, which is explained in this paper. The presented thermodynamic property fields of enthalpy and entropy, the specific heat capacity, and the isosteric heat of adsorption are used to improve the modeling of silica gel + water based adsorption cooling and desalination cycles more accurately.

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