

## ISOTHERMS OF WATER SORPTION ON COMPOSITE “CaCl<sub>2</sub> IN SILICA GEL”: EXPERIMENT AND APPROXIMATION

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### Abstract

In this work we present the isotherms of water vapour sorption on composite “CaCl<sub>2</sub> in silica gel” (SWS-1L) measured at T = 33.1, 49.0, 59.4 and 69.3 °C and vapour pressure P<sub>H<sub>2</sub>O</sub> = 6-80 mbar. New analytical equation was suggested for approximation of the experimental data. It is based on the Polyani invariant principle and contains only 3 fitting coefficients. This equation provides good description of whole set of sorption data experimentally obtained so far and allows calculation of isotherms, isobars and isosters of water sorption on SWS-1L at any T and P<sub>H<sub>2</sub>O</sub>. It can be used for plotting and analysing thermodynamic cycles of adsorption heat pump utilizing SWS-1L.

### KEYWORDS

Calcium chloride, silica gel, water vapour, sorption isotherm, approximation

### INTRODUCTION

The composite sorbent “CaCl<sub>2</sub> in silica gel” (SWS-1L) was invented in the Boreskov Institute of Catalysis (Novosibirsk, Russia) and studied in co-operation with ITAE/CNR (Messina, Italy) [1, 2]. Its sorption properties made it a promising material for adsorption cooling [3, 4]; this was confirmed by experimental testing of lab-scale chilling units with pelletised [5] and compact [6] adsorbent beds.

The analysis of the chilling cycle was based on the isosteric chart of SWS-1L, which was plotted in [1, 7] by section of the experimentally measured isobars at a constant water uptake *w* (Fig. 1). The isosteres were found to be straight lines

$$\ln P_{\text{H}_2\text{O}} = a(w) - b(w)/T, \quad (1)$$

where *a* and *b* are functions of the water uptake *w* [4, 7]. The coefficients *a* and *b* can be linked with the variation of the standard entropy Δ*S*<sup>0</sup> and enthalpy Δ*H*<sup>0</sup> of water sorption, *a*(*w*) = Δ*S*<sup>0</sup>(*w*)/*R* and *b*(*w*) = Δ*H*<sup>0</sup>(*w*)/*R*. The values of *a*, Δ*S*<sup>0</sup>, *b* and Δ*H*<sup>0</sup> obtained from the slope of as plotted isosteric lines, are displayed in Table 1 for uptakes *w* = 0.055-0.55 [7].

To approximate the dependencies *a*(*w*) and *b*(*w*), the polynomial expressions

$$a(w) = a_0 + a_1 w + a_2 w^2 + \dots \quad (2)$$

and

$$b(w) = b_0 + b_1 w + b_2 w^2 + \dots, \quad (3)$$

containing 8 [4] or 12 [7] fitting parameters (*a<sub>i</sub>* and *b<sub>i</sub>*) were used. Equations (1)-(3) with the tabulated *a<sub>i</sub>* and *b<sub>i</sub>* give satisfactory general description of the experimental data on water sorption by SWS-1L,

however, can not correctly describe the variation of  $\Delta S^\circ$  and  $\Delta H^\circ$  as a function of the water uptake (Table 1). In our opinion, a non-monotonous dependence of a and b (hence, of  $\Delta S^\circ$  and  $\Delta H^\circ$ ) on  $w$  has no physical meaning and results from inaccuracies accumulated during a) plotting isosters using data taken from the experimental isobars, and b) approximation of the isosters by equation (1). Thus, there is a room for improvement of the analytical description of the water sorption equilibrium on SWS-1L.

In order to make this improvement, we, first, amplified the set of experimentally obtained data by **direct measurement of isotherms** of water sorption, and, second, suggested new analytical equation for describing equilibrium of water sorption on SWS-1L.

## EXPERIMENTAL

The composite SWS-1L was prepared using a commercial silica gel of KSK type and calcium chloride according to the standard procedure described in [1].

Isotherms of the water sorption were measured at  $T=33.1, 49.0, 59.4$  and  $69.3^\circ\text{C}$  and vapour pressure  $P_{\text{H}_2\text{O}} = 0-80$  mbar using a CAHN-C2000 thermo-balance. First, the sample was dried at  $T = 150^\circ\text{C}$  under vacuum and its dry weight  $m_0$  was measured. Then, at constant temperature we increased the vapour pressure in small steps and measured the amount of sorbed water  $m$  as a function of  $T$  and  $P_{\text{H}_2\text{O}}$ . The uptake was calculated as  $w = m(T, P_{\text{H}_2\text{O}})/m_0$ . As it was previously shown [1], for SWS-1L it is reasonable to present the value of sorption as a ratio of moles  $N$  of water sorbed by one mole of  $\text{CaCl}_2$  in the sample  $N = (m \mu_1)/(m_0 \cdot c \cdot \mu_2)$ , where  $c = 0.337$  is the salt content in SWS-1L,  $\mu_1 = 111$  and  $\mu_2 = 18$  are the molecular weights of  $\text{CaCl}_2$  and water, respectively.

## RESULTS

The dependence of  $N$  on  $P_{\text{H}_2\text{O}}$  at various  $T$  is presented in Fig. 2. The value of  $N$  monotonously increases with the rise of vapour pressure and can reach  $N = 10-11$ , that corresponds to  $0.55-0.6$  g/g. At high uptakes ( $N > 4$ ), the sorption of water leads to the formation of an aqueous salt solution inside the pores [1], the sorption isotherms being almost linear (Fig. 2). At lower uptakes more sharp transition between calcium chloride dehydrate ( $N = 2$ ) and calcium chloride tetrahydrate ( $N=4$ ) is observed. Similar conclusion was made from the shape of isobars of water sorption in [1] (Fig. 1).

In ref. [2], the isotherms of water sorption on SWS-1L were calculated by making the section of the experimental isobars by lines corresponding to a constant temperature (vertical lines on Fig. 1). Fig. 3 demonstrates that as plotted isotherms are in agreement with those directly measured in this work, however, the number of points in the plotted isotherms is not sufficient for representing a detailed shape of isothermal curves.

As at low and high uptakes the mechanisms of water sorption quite differ, it is reasonable to consider different equations for analytical description of the experimental data at  $N > 4$  and  $2 < N < 4$ .

This description is based on the previous finding that only one parameter, namely, the free energy of sorption

$$\Delta F = -RT \ln(P_{\text{H}_2\text{O}}/P_s) \quad (4)$$

( $R$  is the universal gas constant,  $P_{\text{H}_2\text{O}}$  is the vapour pressure,  $P_s$  is the saturated pressure of ware vapour at fixed temperature  $T$ ) can be used instead of common two variables ( $T$  and  $P_{\text{H}_2\text{O}}$ ) [8].

Table 1. Coefficients a and b obtained in [7] from the experimental data and calculated in this work from equation (6) at various uptakes

w, g/g	N, mol/mol	Obtained in [7]		Calculated from equation (6)	
		a	b	a	b
0.055	1	23.85298	-7.61717	21.0048	-6.49859
0.11	2	18.26809	-5.24068	21.0048	-6.25791
0.165	3	18.2853	-5.05302	21.0048	-5.94504
0.22	4	19.48378	-5.36489	21.0048	-5.8608
0.275	5	20.12395	-5.50002	21.0048	-5.76453
0.33	6	20.16138	-5.42474	21.0048	-5.66826
0.385	7	20.26054	-5.37755	21.0048	-5.59606
0.44	8	20.80871	-5.49869	21.0048	-5.53589

0.495	9	20.92981	-5.45963	21.0048	-5.48776
0.55	10	17.49822	-4.09273	21.0048	-5.43962

Here we confirmed it ones more by plotting all the data on sorption isotherms as  $N$  vs.  $\Delta F$  graph, which does give the temperature-invariant curve of water sorption (Fig. 4). Again, this curve can be divided in two smooth parts which correspond to the two different mechanisms of water sorption: the absorption of water by the salt solution at  $\Delta F < 5,500$  J/mol ( $N > 4$ ) and the chemical reaction at  $5,500$  J/mol  $< \Delta F < 8,000$  J/mol ( $N < 4$ ), with the transition between these parts at  $\Delta F \approx 5,500$  J/mol.

For approximation of the dependence  $N(\Delta F)$  we used the polynomial expression [8, 9]

$$\ln(N) = a + b \cdot \Delta F + c \cdot \Delta F^2, \quad (5)$$

where  $a$ ,  $b$  and  $c$  are fitting coefficients, which have to be separately found for the two parts of the curve  $N$  vs.  $\Delta F$  (see Tables 2 and 3).

Table 2. Coefficients  $a$ ,  $b$  and  $c$ , providing the best fit to the experimental isotherms of water sorption on SWS-1L

Part	$N$ , mol/mol	$\Delta F$ , kJ/mol	$a$	$b$	$c$	SD
I	4 - 10	1.0 – 5.5	2.7948	$-3.2297 \cdot 10^{-4}$	$1.0940 \cdot 10^{-8}$	0.22
II	2 - 4	5.5 – 8.0	4.9586	$-9.5128 \cdot 10^{-4}$	$4.9565 \cdot 10^{-8}$	0.32

Table 3. Coefficients  $a$ ,  $b$  and  $c$ , providing the best fit to the experimental isobars of water sorption on SWS-1L measured in [1]

Part	$N$ , mol/mol	$\Delta F$ , kJ/mol	$a$	$b$	$c$	SD
I	4-10	1.0 ÷ 5.5	2.83378	$-3.0133 \cdot 10^{-4}$	$0.746702 \cdot 10^{-8}$	0.33
II	2-4	5.5 ÷ 9.0	5.80313	$-11.92 \cdot 10^{-4}$	$6.99054 \cdot 10^{-8}$	0.18

Fig. 2 demonstrates that the experimental isotherms and those calculated from eq. (5) with the fitting parameters tabulated in Table 2 are in good agreement. The standard deviation SD of approximation is not higher than 0.32. This equation provides approximation of the experimental isobars obtained in [1] (Fig. 1 and Table 3) and the temperature invariant curve of water sorption (Fig. 4) as well. Thus, equation (5) with only three fitting coefficients allows a) good description of whole available set of experimental data on equilibrium sorption of water on SWS-1L, and b) calculation of isotherms, isobars and temperature independent curves of water sorption on SWS-1L at any  $T$  and  $P_{H_2O}$ , which meet the condition  $1.0$  kJ/mol  $< \Delta F < 8.0$  kJ/mol.

Moreover, the isosteric chart of water sorption on SWS-1L, which can not be directly measured by a standard thermogravimetric method, may be calculated using equations (4) and (5). Indeed, for any fixed value of uptake  $N$  the dependence  $P_{H_2O}(T)$  along the appropriate isoster is given by the following equation

$$\ln[P(T)] = -\Delta F(N)/RT + \ln[P_s(T)], \quad (6)$$

where  $\Delta F(N)$  can be calculated from eq. (5). The calculated sorption isosters are somewhat different (Fig. 5) from those obtained by the section of experimental isobars as it is described in the Introduction and illustrated in Fig. 1. It is important, that the coefficient  $b(w)$  calculated from eq. (6) and, hence, the enthalpy of water sorption  $\Delta H^0 = b \cdot R$  decreases monotonously with the uptake increase, that is quite reasonable from physico-chemical point of view and is in line with the results of direct calorimetric measurements [10].

## CONCLUSIONS

The set of experimental data on sorption equilibrium of water vapour on composite "CaCl<sub>2</sub> in silica gel" was amplified by the direct measurement of sorption isotherms at T = 33.1, 49.0, 59.4 and 69.3 °C and vapour pressure  $P_{\text{H}_2\text{O}} = 0-80$  mbar. New analytical equation, containing only 3 fitting parameters, was suggested for approximation of the experimental data. This equation provides good description of whole set of sorption data experimentally obtained so far and allows calculation of isotherms, isobars and isosters of water sorption on SWS-1L at any T and  $P_{\text{H}_2\text{O}}$ , which meet the condition  $1.0 \text{ kJ/mol} < \Delta F < 8.0 \text{ kJ/mol}$ . It can be used for analysis of thermodynamic cycles of adsorption heat pumps and chilling units utilizing SWS-1L.

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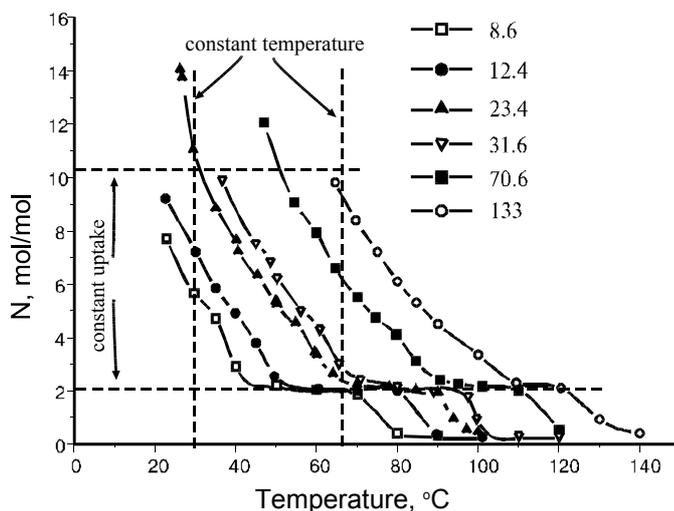


Fig. 1. Experimental isobars of water sorption on SWS-1L: a scheme of the calculation of sorption isotherms and isosters from experimental isobars

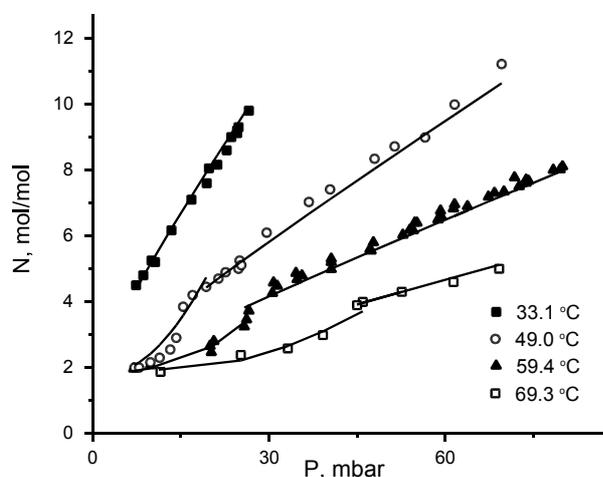


Fig. 2. Isotherms of water sorption on SWS-1L. Symbols – experimental data, lines – approximation by eq. (5)

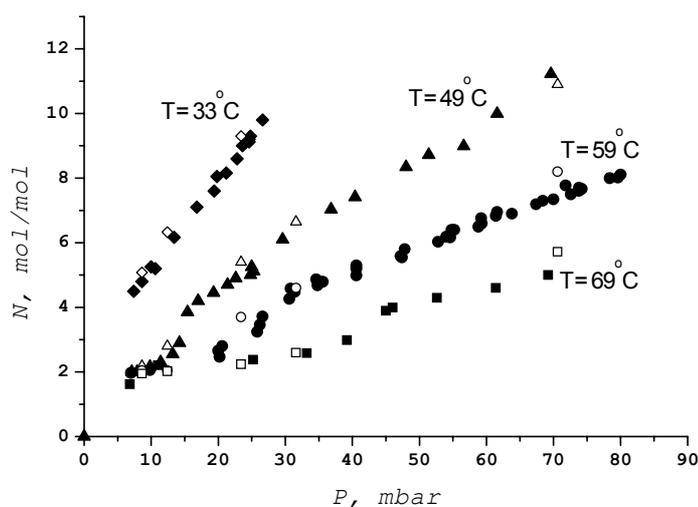


Fig. 3. Isotherms of water sorption on SWS-1L. Solid symbols – experimentally measured, open symbols – obtained by section of isobars in [2]

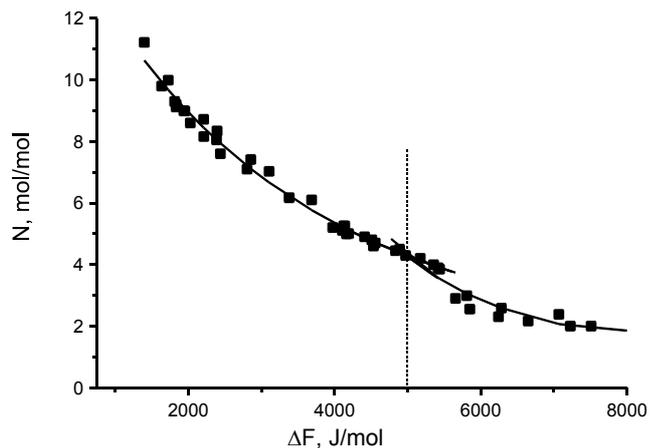


Fig. 4. Temperature-invariant curve of water sorption by SWS-1L. Symbols – experimental data, lines – approximation by eq. (5)

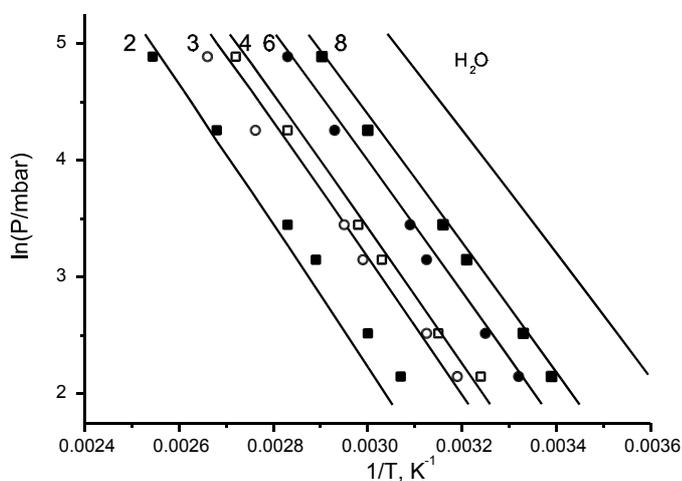


Fig. 5. Isosters of water sorption on SWS-1L calculated from equations (4) and (5) (lines) and obtained by the section of experimental isobars (symbols). Numbers indicate the value of uptake  $N$ , mol/mol