

APPLICATION OF THERMAL ANALYSIS FOR DETERMINATION OF FILM PRESSURE AND FILM SURFACE ENERGY ON SILICA GEL SURFACE

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The results of dynamic and quasi-isothermal thermodesorption of water from a silica gel surface at low furnace heating rates in the temperature range 20–125° are presented. From the experimental results, the water film pressure π on silica gel surface, the activation energy ΔE and the evaporation heat ΔH were calculated. An interpretation of π changes in relation to the film thickness and wetting process has been proposed. It is concluded that the characteristic film pressure values correspond to the work of spreading, and immersional, adhesional and adhesional-cohesional wetting. From the determined film pressure values, the average value of the silica gel polar component, γ_s^p , was calculated to be 114.67 mJ/m².

The role of water and its properties in adsorption and chromatographic processes has not been completely explained, despite many investigations [1–5]. It is known that the presence of water on a silica gel surface decreases its adsorption properties [6]. Even trace amounts of moisture cause a blockade of the chromatographic column packing and changes in its resolution. As a result, irreproducible data are obtained for the thermodynamic values characterizing the separation processes [7]. This is caused by different properties of the vicinal water [2, 5].

Thermal investigations of the properties of water adsorbed on silica gel at temperatures above 100° are presented in the papers [8–13]. From these investigations it appears that during water thermodesorption from a silica gel surface, physically adsorbed water is removed first, followed by water formed as a product of the bound hydroxyl groups (water chemically adsorbed) and water contained in the interior of the xerogel skeleton. On the other hand, the thermodesorption of water physically adsorbed on silica gel and the mechanism of surface wetting at temperatures below 125° and at a low evaporation rate have not been exactly investigated so far.

The wetting process may be characterized by spreading, and immersional or adhesional wetting work values. Each wetting process corresponds to another free surface energy drop, determined by the amount of water adsorbed on the surface. Investigations of the wetting of a silica gel surface by water and the energy changes accompanying this process were therefore undertaken.

Experimental

Silica gel (0.15–0.3 mm fractions of 150 m²/g surface area, Machery Nagel and Co., Germany) applied in chromatographic columns was used in our experiments. The samples investigated were wetted with double distilled water until complete surface saturation (49%) had been obtained. Water thermodesorption was studied using a Q-1500 D derivatograph (MOM, Hungary). Classical dynamic measurements (T, TG, DTG and DTA changes in time) were made at a furnace heating rate of 1.25 degree/min. Quasi-isothermal measurements were also made at a furnace heating rate of 0.6 degree/min, when the given process took place at a constant temperature.

Results and discussion

Figure 1 presents thermal analysis curves of water thermodesorption from silica gel. Three low-temperature endothermic peaks are seen in the DTA curve. These peaks correspond to analogous peaks in the DTG curve, which account for stepwise water removal from the silica gel surface as the temperature increases. From the TG curve it results that 20.2 mmol/g (peak I), 13.36 mmol/g (peak II) and 2.25 mmol/g (peak III) of water are adsorbed on the silica gel surface. Assuming that the surface occupied by one water molecule is 7.065 Å², the numbers of statistical water layers adsorbed on silica gel for each peak in the DTA and DTG curves were calculated: 5.74, 3.8 and 0.64 layers for peaks I, II and III, respectively. These numbers of statistical water layers correspond to hydration values of 13.46 · 10⁻², 8.9 · 10⁻² and 1.5 · 10⁻² mmol/m² for peak I, II and III, respectively.

The film pressure π characterizing the wetting process was calculated in the following way. The Gibbs–Duhem equation for the surface layer assumes the following form [14]:

$$(S_m^s - S_m) dT + (V_m - V_m^s) dp + \frac{d\gamma}{a^s} = 0 \quad (1)$$

where S_m^s is the molar entropy of the adsorbed gas (water vapour), S_m is the liquid (water) molar entropy, V_m is the molar volume of water vapour in the bulk phase, V_m^s is the molar volume of the adsorbed gas (water vapour), a^s is the amount of water per surface unit in the surface layer, and γ is the interfacial tension in the silica gel–water system corresponding to film pressure π on the surface.

Transformation of Eq. (1) gives:

$$d\gamma = -a^s(V_m - V_m^s) dp - a^s(S_m^s - S_m) dT \quad (2)$$

Assuming that $V_m \gg V_m^s$, and $pV_m = RT_n$, Eq. (2) will assume the following form for the given temperature T_n :

$$\gamma_{T_n} = -RT_n \int_{P_1}^{P_2} a^s d \ln p \quad (3)$$

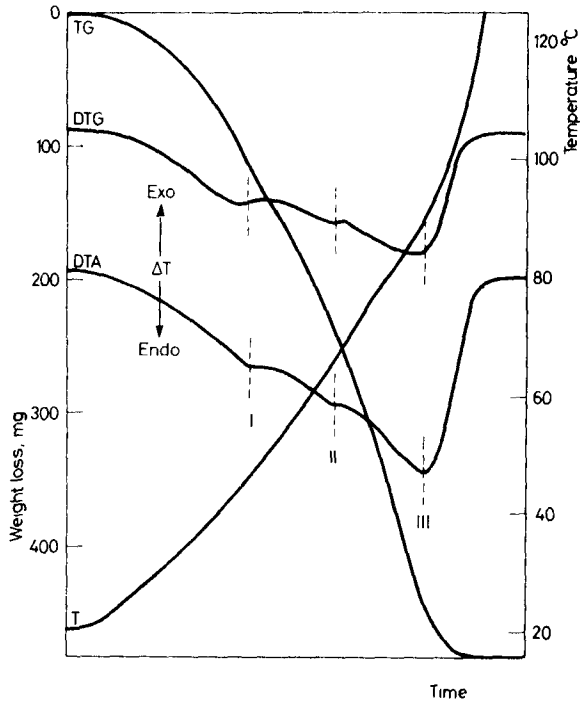


Fig. 1 Dynamic thermal curves of the water thermodesorption from the silica gel

On the other hand, if $d\gamma = 0$, then:

$$\Delta S_{m,\gamma}^s = (S_m^s - S_m) = -RT_n \left(\frac{d \ln p}{dT_n} \right)_\gamma \tag{4}$$

Thus:

$$dT_n \Delta S_{m,\gamma}^s = dT_n (S_m^s - S_m) = -RT_n (d \ln p) \tag{5}$$

where $\Delta S_{m,\gamma}^s$ is the differential gas (water vapour) molar entropy corresponding to the entropy change during the transfer of one gas (water vapour) mole from the gas phase to the surface layer (in thermal analysis $\Delta S_{m,\gamma}^s$ has a negative sign, because water is evaporated from the surface layer).

Since the temperature, the interfacial tension and the amount of water on the silica gel surface change in the thermal analysis, Eqs (3) and (5) must be taken into consideration in calculations of the film pressure. The calculations of γ_{T_n} were made in the following way. The amounts of water a^s desorbed at the given temperatures T_n were determined from the TG curves. Next, the saturated water vapour pressures p_n corresponding to temperatures T_n were read from the tables. The relationship $a^s = f(\ln p_n)$ was then plotted, and the values of γ_{T_n} corresponding to the tem-

peratures T_n were calculated through graphical integration. The values obtained are presented in Table 1.

From the tables, the entropy changes corresponding to the transfer of one water mole from the vapour to the liquid phase were read off, and it was calculated that when the temperature changed by 1° the entropy change was 0.5145 mJ/m^2 . Taking into account that amount of desorbed water a^s and the temperature changes $\Delta T_n = 125 - T_n$, the $\Delta T_n \Delta S_{m,\gamma}^s$ values were calculated; they are given in Table 1.

Table 1 Table containing the data on which base one have calculated water film pressure

T_n , °C	a^s , mmol/g	Statistical amounts of water layers	$\rho_n^{\text{H}_2\text{O}}$, mm Hg	γ_{T_n} , mJ/m ²	$\Delta T_n \Delta S_{m,\gamma}^s$, mJ/m ²	π_n , mJ/m ²
125	0	0	1740	0	0	0
101	2.52	0.71	787.6	15.6	31.1	15.5
97	3.89	1.1	682.1	25.2	56.0	30.8
94	5.73	1.62	610.0	36.5	91.4	54.9
90	7.56	2.14	525.7	54.3	136.1	81.8
86	9.16	2.6	450.9	76.6	183.8	107.2
83	10.77	3.05	400.9	98.6	232.7	134.1
79	12.14	3.44	341.0	131.7	287.3	155.6
75	13.74	3.89	289.1	167.9	353.5	185.6
71	14.66	4.15	243.9	211.3	407.3	196.0
69	16.04	4.54	223.7	239.2	462.1	222.9
65	16.96	4.8	187.5	290.8	523.6	232.8
61.5	18.1	5.13	160.1	358.1	591.3	232.7
57.5	19.02	5.39	132.9	388.0	660.5	272.5
54.5	20.16	5.71	115.2	434.2	731.2	297.0
51	20.85	5.91	97.2	496.0	793.8	297.8
49	21.31	6.04	88.0	530.8	833.3	302.5
48	22.22	6.3	83.7	552.3	891.7	339.4
45	23.14	6.56	71.8	603.5	952.4	348.9
43	24.06	6.82	64.8	650.5	1015.1	365.6
39.5	24.97	7.08	53.8	712.3	1098.4	386.1
37	25.43	7.21	47.0	767.0	1151.4	384.4
34.5	24.89	7.34	41.0	835.5	1205.5	370.0
32	26.35	7.47	35.66	891.6	1260.8	369.2
20	27.49	7.79	17.5	1177.8	1485.1	307.3

The water film pressure π_n on the silica gel surface at temperature T_n was calculated on the basis of the modified Gibbs–Duhem equation (2) from the following relationship:

$$\pi_n = -\gamma_{T_n} + \Delta T_n \Delta S_{m,\gamma}^s \quad (6)$$

The values calculated in this way are listed in Table 1. Figure 2 presents the film pressure π_n in relation to the amount of desorbed water a^s . The statistical water

layers are denoted in this figure by dashed lines. It can be seen in Fig. 2 that the relationship between π_n and a^s shows some inflection. The first inflection is observed when one water monolayer is present on the silica gel surface. The second inflection occurs when the surface is covered with 2 monolayers and $\pi_s = 82.7 \text{ mJ/m}^2$. The changes in π_n in the range 0–2 statistical water monolayers indicate that the particles on the surface are closely packed; peak III in Fig. 1 (DTA curve) corresponds to this situation. Further inflections are observed at 4 monolayers ($\pi_I = 182.7 \text{ mJ/m}^2$) and at 5 water monolayers ($\pi_A = 230.7 \text{ mJ/m}^2$); this situation is illustrated by peak II in Fig. 1. The area between 2 and 5 statistical monolayers corresponds to the film of water bonded to the silica gel surface, and to the bulk water film in which the particles possess limited possibilities to change their orientation. The suggestion relating to the structure of the first five adsorbed statistical water monolayers is confirmed by activation energy ΔE calculations made for the water molecules on the basis of the Piloyan equation [15]:

$$\ln \Delta T = C - \frac{\Delta E}{RT} \quad (7)$$

where ΔT is the deviation of the DTA curve from the base line and C is a constant.

Determining the ΔT values for various temperature ranges between the start and the minimum point, and plotting $\ln \Delta T$ as a functions of $1/T$, we determined a straight line with a slope of $\Delta E/R$, which permitted determination of the activation energy. In this method it is not necessary to know the sample mass, the apparatus parameters and the specific heats, and it is sufficient to plot only one DTA curve.

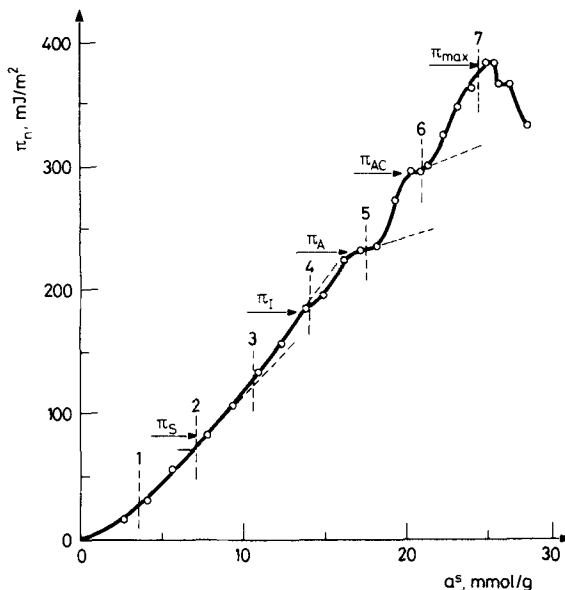


Fig. 2 The dependence water film pressure on the amount of desorbed water

The calculated ΔE values of water molecules adsorbed on the silica gel surface corresponding to peaks II and III are 40.13 and 36.37 kJ/mol, respectively. These energies are higher than that necessary to disrupt the hydrogen-bonds existing in bulk water, which, according to the literature [3], is 25.08 kJ/mol. Thus, peaks II and III correspond to the film of water bonded to the silica gel surface. Water molecules corresponding to peak II are adsorbed in the capillaries and on active centres of the silica gel, which are represented by free and bonded hydroxyl groups. The particles of this physically adsorbed water form structures with various bonding energies per molecule [3]. Disruption of these structures during water thermodesorption from the sample requires a greater energy than during evaporation of bulk water. The surface centres adsorbing water molecules, corresponding to peak III, are more active. These centres can be reactive OH groups, in which the proton of the bonded hydroxyl groups does not participate in hydrogen-bonding due to the spatial configuration [16]. The activity of these reactive OH groups is greater than those of free groups and bonded groups. Water molecules adsorbed on these groups are more resistant to dehydration.

Another inflection occurs in Fig. 2 when the surface is covered with 6 monolayers $\pi_{AC} = 296$ mJ/m². The maximum value of $\pi_{max} = 386$ mJ/m² is obtained when the silica gel surface is covered with 7 statistical monolayers. It should be noted that the sums $\pi_A + \gamma_w = 303.5$ mJ/m² and $\pi_A + 2\gamma_w = 376.3$ mJ/m² are nearly equal to π_{AC} and π_{max} . Thus, it can be concluded that:

$$W_{AC} = \pi_{AC} = \pi_A + \gamma_w = W_a + \gamma_w \quad (8)$$

and

$$\pi_{max} = W_A + 2\gamma_w = W_A + W_C \quad (9)$$

where W_{AC} is the adhesional-cohesional water wetting work, W_A is the adhesional water wetting work and γ_w is the water surface tension.

Thus, the π_{max} value corresponds to the formation on the silica gel surface of water layers possessing the properties of the bulk phase, and it is related to peak I in Fig. 1. In order to confirm this fact, the TG and DTG curves were used to calculate the heat of water evaporation, ΔH , for peak I from the relationship based on the Clausius-Clapeyron equation, according to the method given by Topor [17] and to the equation

$$\ln \frac{dx}{dt} = -\frac{\Delta H}{RT} + C \quad (10)$$

where dx/dt is the evaporation heat.

The obtained value is 42.3 kJ/mol and is near the water molar condensation heat of 43.89 kJ/mol.

The individual peaks in Fig. 1, to which the individual inflections in Fig. 2 are assigned, correspond to the inflections obtained from quasi-isothermal measurements. Figure 3 presents the curve obtained from these measurements, in which the numbers of water monolayers on the silica gel surface and the film pressure values correspond-

ing to the individual wetting processes are noted. From this figure it appears that in the initial stage of thermodesorption the bulk water evaporates from the silica gel surface (curve *ABC*). Inflection, *CD* corresponding to the adhesional-cohesional wetting process, is related to energy changes in the water molecules, which in turn are influenced by the silica gel surface properties. Thus, it can be assumed that the region of "bonded water" begins from 6th monolayer on, i.e. from the adhesional-cohesional wetting. Furthermore, a section of the straight line *DE* is a transition region [2], representing an unordered transition between the ordered vicinal water structure and the bulk phase containing various forms of structural water. The last section (*EFG*) of the curve (two monolayers of vicinal water) is related to water molecules physically bonded more strongly to the surface; evaporation of this water requires a greater amount of energy.

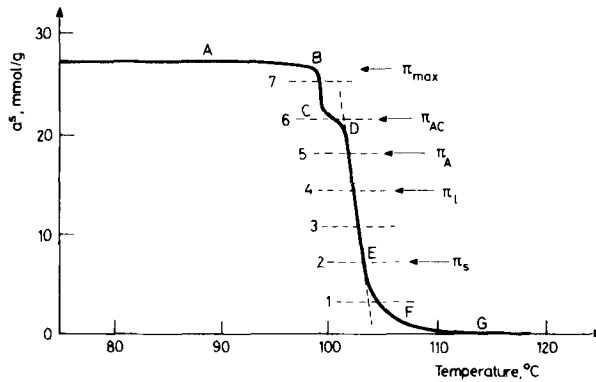


Fig. 3 Quasi-isothermal curve of the water desorption from the silica gel

Kisielew [18] has shown that the adsorption properties of silica gel and quartz are similar. Measurements of water adsorption on quartz showed that the water film pressure values may be correlated with the film thickness and wetting work values [19]. The film pressure values determined from the adsorption isotherm correspond to spreading, adhesion and immersion, respectively. Table 2 lists the values of water film pressure on silica gel and quartz corresponding to the individual types of wetting work, and the surface coverage values (numbers of water monolayers) for which these processes take place. From the data listed in this table it is seen that the values obtained are very similar.

From the energy changes (water film pressures corresponding to the individual types of wetting work), the polar component of the free surface energy of silica gel was calculated. It is shown that the energy changes are expressed by spreading (W_s), immersional (W_I), adhesional (W_A) and adhesional-cohesional (W_{AC}) wetting work, where $W_s < W_I < W_A < W_{AC}$, and thus the characteristic points in the curve in Fig. 2 correspond to the individual values of wetting work. According to Fowkes [20] the

interfacial energy in the silica gel–water system is expressed by means of geometrical mean values of dispersive and polar interactions, using the following equations:

$$W_s = \pi_s = 2\sqrt{\gamma_s^d \gamma_w^d} + 2\sqrt{\gamma_s^p \gamma_w^p} - 2\gamma_w \quad (11)$$

$$W_I = \pi_I = 2\sqrt{\gamma_s^d \gamma_w^d} + 2\sqrt{\gamma_s^p \gamma_w^p} - \gamma_w \quad (12)$$

$$W_A = \pi_A = 2\sqrt{\gamma_s^d \gamma_w^d} + 2\sqrt{\gamma_s^p \gamma_w^p} \quad (13)$$

where γ_s^d and γ_w^d are the dispersion components of the free surface energy of silica gel and water, respectively, while γ_s^p and γ_w^p are the polar components.

From Eqs (11, 12, 13) and (8, 9) the polar component of the free surface energy of silica gel was calculated for $\gamma_s^d = 76 \text{ mJ/m}^2$, $\gamma_w^d = 21.8 \text{ mJ/m}^2$ and $\gamma_w^p = 51 \text{ mJ/m}^2$. The values calculated (in mJ/m^2) were: 104.2, 146.38, 107.65, 93.03 and 122.1. The average value of γ_s^p is 114.67 mJ/m^2 , which shows very good agreement with the corresponding value obtained for quartz, 115 mJ/m^2 (Table 2).

Table 2 Comparison of the results calculated of water film pressure and of average value of polar component of surface free energy of silica gel and of quartz

Thermal analysis (silica gel)		Step profile method [19] (quartz)	
Water film pressure, mJ/m^2	Statistical amounts of water layers	Water film pressure, mJ/m^2	Statistical amounts of water layers
$\pi_s = 82.7$	2	$\pi_s = 96$	2
$\pi_I = 182.7$	4	$\pi_I = 162$	3
$\pi_A = 230.7$	5	$\pi_A = 227$	4
$\pi_{\max} = 386.1$	7.8	$\pi_{\max} = 380$	10.7
γ_s^p (average) = 114.67 mJ/m^2		γ_Q^p (average) = 115 mJ/m^2	

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Zusammenfassung — Die Ergebnisse der Untersuchung der dynamischen und quasi-isothermen Thermodesorption von Wasser von einer Kieselgeloberfläche im Temperaturbereich von 20–125° und bei niedrigen Ofenaufheizgeschwindigkeiten werden mitgeteilt. Der Wasserfilmdruck π an der Kieselgeloberfläche, die Aktivierungsenergie ΔE und die Verdampfungswärme ΔH wurden aus Versuchsdaten berechnet. Veränderungen von π werden im Zusammenhang mit der Filmdicke und dem Benetzungsprozeß interpretiert. Es wird geschlossen, daß die charakteristischen Filmdruckwerte der Arbeit der Spreitung, und der Immersions-, Adhäsions- und Adhäsion-Kohäsion-Benetzung entsprechen. Von den bestimmten Werten des Filmdruckes wurde der Durchschnittswert der polaren Komponente γ_s^D des Kieselgels zu 114.67 mJ/m² berechnet.

Резюме — Представлены результаты динамической и квази-изотермической термодесорбции воды с поверхности силикагеля при низких скоростях нагрева в области температур 20–125°. На основе экспериментальных результатов вычислены давление пленочной воды (π) на поверхности силикагеля, энергия активации ΔE и теплота испарения ΔH . Предложена интерпретация изменений величины π в зависимости от толщины пленки и процесса смачивания. Сделан вывод, что значения пленочного давления соответствуют работе растягивания и иммерсионному, адгезионному и адгезионно-когезионному смачиванию. Из найденных значений пленочного давления было вычислено среднее значение полярной компоненты силикагеля (γ_s^D) равное 114,67 мдж/м².