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INTERACTIONS BETWEEN PAPER AND ADSORBED MOLECULES
A preliminary study and some experimental results

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Abstract

We have studied the geometry and energy involved in the interactions between adsorbed molecules and paper substrate, over a wide range of partial pressures. A two-dimensional virial equation of state was employed to evaluate the extent of interactions by the compressibility factor (Z). Data of H-bonded molecules (water and butan-1-ol) and of more weakly interacting ones (*n*-decane and dioxane) were selected from the literature. At low surface coverage, the compressibility factor Z exceeds 1, showing a deviation from ideality due to interactions, and reaches a maximum at a value close to the BET monolayer.

As preliminary results we have measured by means of a differential microcalorimeter (Calvet) at 25°C the energy of interactions of water and *n*-heptane vapor on chromatographic grade Whatman paper.

At very low coverage, the differential heats of adsorption of water on paper are higher than those of *n*-heptane adsorption on paper: 114 kJ $\text{mol}^{-1} > 77$ kJ mol^{-1}. During the whole process of adsorption, in the first case, the specific interaction predominates, while in the second non-specific interactions predominate i.e. the dispersion or Van der Waals forces.

Keywords: adsorption of water and *n*-heptane on paper, BET theory, compressibility factor, microcalorimetry

Introduction

The degradation of books, archival materials and drawings mainly involves the interaction between gaseous substances (oxygen, pollution, water vapor) and the heterogeneous cellulosic substrate.

Although the extent to which gaseous molecules interact with cellulose has been subjected to several studies [1], much less work has been done in the field of paper

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conservation science, where sizing materials (gelatin, rosin), inks and colors play a very important role.

Similarly, new trends in restoration procedures, such as mass deacidification and gaseous disinfection, require a deeper understanding of the physical and chemical processes which occur in these heterogeneous environments.

Referring to physical processes, two main aspects are of interest, namely i) the geometry of adsorption, and ii) the energy of interactions.

For the purpose of measuring these properties, the so-called BET theory [2] is widely accepted and applied to adsorption isotherms.

BET theory postulates that increasing values of vapor pressure (P/P°) give rise to the formation of a monolayer of adsorbed species, which saturates the accessible surface, followed by a multi-layer structure. Near saturation ($P/P^\circ \sim 1$), a singularity in the number of adsorbed layers, which tends to infinity, reveals that the properties of adsorbed molecules approach those of bulk liquid.

Taking into account the BET equation, i.e.

$$\frac{n}{n_{\mathrm{m}}} = \frac{c\sum_{\mathrm{i}} x^{\mathrm{i}}}{1 + c\sum_{\mathrm{i}} x^{\mathrm{i}}}$$

$i = 0, 1, \ldots\ldots\ldots m$ number of layers, n = amount of adsorbed molecules, n_{m} = monolayer value, x = vapor pressure (P/P°)
and its classical transformation (Y)

$$Y = \frac{x}{[n(1-x)]}$$

the constants c and n_{m} can be easily evaluated from the linear domain ($x < 0.4$) of an Y-x plot since the ratio [(slope-intercept)/intercept)] yields c and [1/(c-intercept)] yields n_{m}.

While the accessible surface can be evaluated from the value of n_{m} and the constant c roughly accounts for the vapor-substrate interaction energy [$E = RT\ln(c)$], BET logic does not highlight easily the multilayer–bulk liquid transition which appears to be a very important feature in paper conservation science.

In water–paper interactions, this transaction at $P/P^\circ < 1$ might, for instance, be a threshold value for biological attack or ink migration over the paper sheet. In the field of mass deacidification, the non-aqueous vapor used as carrier might reach this threshold value with dangerous effects on water-resistant colors.

In order to evaluate the multilayer–bulk liquid transition, we developed a two-dimensional equation of state by introducing a two-dimensional pressure (π) and area (A), related to the amount of adsorbed vapor (n) using the Gibbs adsorption equation:

$$\frac{\mathrm{d}\pi}{\mathrm{d}n} = \frac{nRT}{A}\frac{\mathrm{d}\ln(P/P^0)}{\mathrm{d}n}$$

The correlation between $\ln(P/P^\circ)$ and n can be drawn from adsorption isotherms by means of the virial equation, the theoretical grounds for which have been well established [3], i.e.

$$n(P/P^\circ) = \ln(n) + \sum c_j\, n^{j-1} \qquad j = 1, 2, \ldots\ldots\ldots M$$

from which we obtain

$$\frac{\pi A}{nRT} = 1 + \sum[(j-1)/j]c_j n^{j-1}$$

As in the three-dimensional case, the right term of the last equation is the so called compressibility factor (Z), which accounts for the deviations from the ideal case.

Analysis of some isotherms from the literature

In order to verify whether the deviations from the ideal case ($Z \neq 1$) map the substrate-vapor interactions [$RT\ln(c_{\mathrm{BET}})$], we selected adsorption isotherms of four sorbates (data from Refs [4, 5]:

n-decane,	weakly interacting with cellulose by Van der Waals forces
dioxane,	acceptor of H-bonds from cellulose
butan-1-ol,	acceptor and donor of H-bonds
water,	strongly interacting with cellulose

and c_j parameters were determined by applying Davidon's algorithm [6] for increasing values of j until a minimum value of χ^2 was reached (typically $j=5$ to 7).

As shown in Fig. 1, a general feature of these sorbates is a positive deviation from ideal law, at least from low to moderate values of P/P°. The compressibility factor Z reaches a maximum at values close to the monolayer completion as determined by BET theory. The height of this maximum is consistent with surface–sorbate attraction ($RT\ln(c_{\mathrm{BET}})$ in Table 1). As P/P° increases, the attractive forces between sorbate molecules produce a decrease of Z, which recrosses 1, as also reported in Table 1.

Table 1 Influence of sorbates on the compressibility factor Z

Sorbate	T/°C	Z_{max} values/ P/P°	Z_{max} values/ Z	$RT\ln c_{\mathrm{BET}}$/ kJ mol^{-1}	P/P° at which Z recrosses 1
n-decane	30	0.30	1.15	4.28	0.58
dioxane	25	0.17	1.50	5.27	(0.75)
butan-1-ol	35	0.25	1.67	6.65	(0.96)
water	24.6	0.29	1.73	7.25	(0.94)

Data between brackets were extrapolated from Fig. 1. Z was expressed in arbitrary units: the actual value dependends on the integration constant.

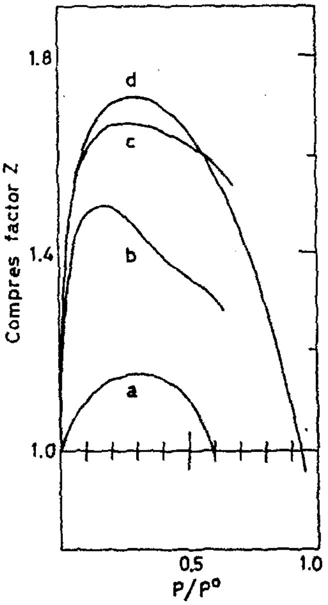

Fig. 1 Compressibility factor Z *vs.* $P/P°$: a) *n*-decane, b) dioxane, c) butan-1-ol, d) water

The values of $P/P°$ in which $Z=Z(\max)$ and Z recrosses 1 seem to be transition points from monolayer to multilayer and from multilayer to bulk liquid. The latter finding is consistent with some literature data on water–cellulose interactions [7, 8] and other theoretical approaches [9].

Nevertheless, the virial approach does not allow the quantitative determination of energetic interactions, since the calculation of ΔH by the integration of Clausius-Clapeyron equation is too rough an approximation in the presence of strong deviations from ideal gases law like those reported in this paper. To this purpose, we planned some calorimetric analyses, and we report some preliminary results here.

Experimental

Materials

The sample of paper utilized (about 100 mg) was chromatographic grade Whatman paper. The paper was introduced into a microcalorimetric cell as little twisted strips. The water was bidistilled and the *n*-heptane was supplied by E. Merck (Darmstadt, F. R. Germany). Afterwards, it was passed through a molecular sieve 3 A and successively the two liquids were rendered gas free by several "freeze-pump-thaw" cycles.

Microcalorimetric apparatus

The microcalorimetric assembly was composed of a heat flow microcalorimeter connected to a volumetric apparatus to evaluate the adsorption. In this way we can measure simultaneously both the heat evolved after the introduction of every dose of water or *n*-heptane vapor and the m mol respectively adsorbed on the paper surface. The measurements were carried out at 25°C. The reference cell and the laboratory cell were made of pyrex glass introduced into both stainless steel cells by means of teflon junctions. Between the pyrex cell and the stainless steel we put mercury to obtain the best heat conduction. The whole was placed into the microcalorimeter and connected to a volumetric vacuum line, after activation the sample of paper under vacuum of 10^{-5} torr and at 90°C for 5 h in an oven at controlled temperature to eliminate physisorbed water. The microcalorimeter calibration was performed by means of the Joule effect, using a pyrex cell with resistance of manganin, simulating the experimental arrangement as already published [10].

The integral heats (Q_i) accumulated for successive increments are fitted analytically to an appropriate model. The differential heats, q_{diff}, are then obtained by differentiation of the integral function with respect to the amount (m mol) of water and *n*-heptane vapor adsorbed respectively. All the measurements were carried out using an IBM-AT computer, interfaced with an A/D converter. The apparatus scheme is shown elsewhere [11].

Results and discussion

In Fig. 2, we report an example of the heat emission peaks of water (a) and of *n*-heptane vapor (b) on paper surface. The different shapes of the two peaks for the different interactions of water and *n*-heptane on the same adsorbent are evident. Interaction like hydrogen bond in the first case (specific adsorption) (acute shape of the peak) predominates and in the second case the contribution of "non-specific" adsorption is present, where only dispersion and repulsive forces are involved (rounded shape of the peak) [12].

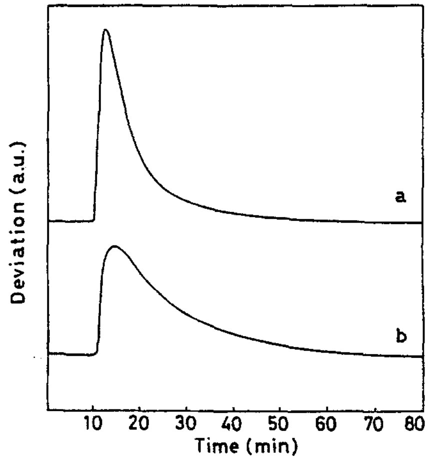

Fig. 2 Example of heat emission peaks: a) water adsorption on paper, b) *n*-heptane adsorption on paper

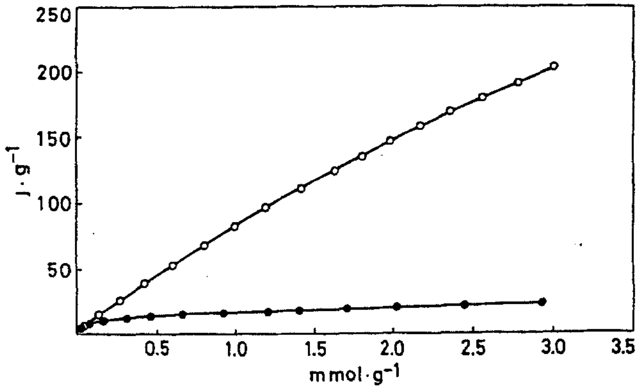

Fig. 3 Integral heats of adsorption (Q_{int}/j g^{-1}) as a function of m mol g^{-1} water adsorbed on paper (white points) and integral heats of adsorption (Q_{int}/j g^{-1}) as a function of m mol g^{-1} n-heptane adsorbed on paper (black points)

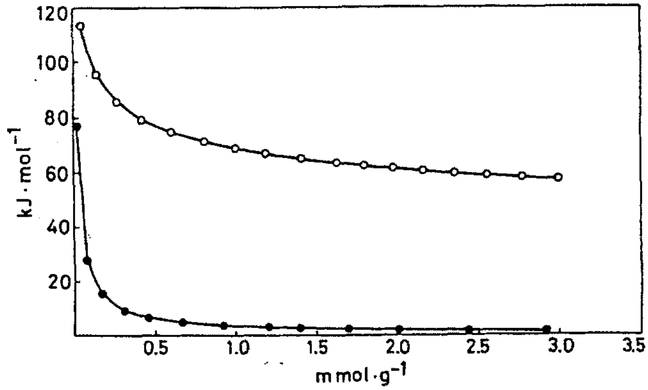

Fig. 4 Differential heats of adsorption (q_{diff}/kJ mol^{-1}) as a function of m mol g^{-1} water adsorbed on paper (white points) and differential heats of adsorption (q_{diff}/kJ mol^{-1}) as a function of m mol g^{-1} n-heptane adsorbed on paper (black points)

In Fig. 3, we show the trends of integral heats (Q_{int}/j g^{-1}) as a function of m mol g^{-1} of water (white points) and of n-heptane vapor (black points). In Fig. 4, we show the trends of differential heats of adsorption (kJ mol^{-1}) as a function of m mol g^{-1} adsorbed of water (white points) and n-heptane (black points) respectively. The discussion about the different trends of differential heats of adsorption of two adsorbates is very interesting. We note that the differences are:

a) the values of differential heats of interaction of water on paper which is made above all by cellulose (all components are made up of glucose units linked by oxygen bridges) are always higher than those of interaction of n-heptane. For example, at the same very low coverage, for water we have measured : 114–95 kJ mol^{-1} > 77–27 kJ mol^{-1} for n-heptane;

b) the decreasing trend of differential heats for water adsorption on paper is different from that of *n*-heptane.

In the case of water adsorption, the decrease is very slow, passing from high values of strong hydrogen bond between water molecules (polar molecule) and hydrogen and hydroxyls of cellulose until the value of 53 kJ mol^{-1}. Considering that such interaction is specific [12], these values of heats always remain high and the water molecule probably cannot penetrate into the bulk of the cellulose, also due to the chemical stability of its fibers thanks to the structure of micelles. Moreover we note that the differential heats, also slowly decreasing, are always above 53 kJ mol^{-1}, in a similar way to the interaction of water- SiO_2 [13]. As the heat of liquefaction or condensation has the value of 43.8 kJ mol^{-1} [14], we conclude that the paper surface is weakly hydrophilic in our experimental conditions.

On the contrary, in the case of *n*-heptane adsorption, the values of differential heats, at very low coverage, rapidly decrease from 77 kJ mol^{-1} to 15 kJ mol^{-1} becoming almost constant and reaching the value of 3.5 kJ mol^{-1}, at coverage higher than 1.0 m mol g^{-1} of *n*-heptane adsorbed.

It is possible, that as the dipole moment of *n*-heptane being negligible with respect to that of water, it is able (not affecting by lateral interactions) to interact deeply into the layers of the cellulose to form hydrogen bonds with inner oxygen bridges. But we note that these bonds are less strong than hydrogen bonds formed by water molecule and in smaller amounts. In fact just the amounts of *n*-heptane adsorbed increase, the interactions prevalent are those represented by dispersion and repulsive forces ("non-specific" adsorption).

Conclusions

The BET applied to solid materials allows us to know the surface reactivity in special conditions and adsorption microcalorimetry allows us to directly measure the energy of physisorption and chemisorption between the adsorbent and the adsorbate. From these experimental data, it is possible later, in the specific case of library paper, to pretreat such materials with suitable compounds to decrease its surface reactivity and consequently to decrease its degradation.

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