

Rotational Degrees of Freedom in the Adsorption of Hydrocarbons on Aerosil

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A study has been made of the different contributions to the entropy of adsorption in Henry's zone of several hydrocarbons on Aerosil with different degrees of hydrophobicity. The statistical-mechanical interpretation of the experiments on the adsorption of isobutene on hydroxylated Aerosil shows that there is mobile adsorption with loss of one rotational degree of freedom.

A recent paper from this laboratory¹ reported the results of the adsorption of a series of saturated and unsaturated four-carbon hydrocarbons in the low-pressure region on the surface of Aerosil with different degrees of hydrophobicity, as defined by the concentration of OH groups on the surface. The confirmation of the fact that the experiments reached Henry's zone in every case allowed calculation of the heat of adsorption, $q_{st}(\theta \rightarrow 0)$, and the entropy of desorption, $\Delta S^\ominus(\theta \rightarrow 0)$, in the low-adsorption region ($\theta \rightarrow 0$) and discussion of the macroscopic behaviour of the system in that region, where phenomena such as lateral interactions and effects caused by the porosity of the solid can be excluded from the analysis.

This paper deals with the analysis of the entropic contributions to the different degrees of freedom of the adsorbate molecule. The following paper² gives calculations of the adsorption potential from the viewpoint of models of amorphous solids, such as these silicas.

CONTRIBUTIONS TO THE ENTROPY OF ADSORPTION

Table 1 gives details of the calculation of the different entropic contributions of the adsorbate molecule at 25 °C according to the ideas of Kemball³ and de Boer and Kruyer.⁴ The first three columns, which are the same as those reported previously,¹ correspond to the description of the system, the heat of adsorption, $q_{st}(\theta \rightarrow 0)$, and the experimental entropy of desorption, $\Delta S^\ominus(\theta \rightarrow 0)$, calculated from Henry's constant, K_H , using $P^\ominus = 1$ Torr as a reference for the gas phase and $\Pi^\ominus = 0.338$ dyn cm⁻² for the adsorbed phase, as suggested by de Boer.⁴ The nomenclature A110, A600 and A1000 refers to the treatment of Aerosil 200 (Degussa) under a pressure of 10⁻⁴ Torr at temperatures of 110, 600 and 1000 °C, respectively.

If it is assumed that in Henry's region the configurational entropy is negligible, the entropy of desorption of the adsorbed molecule may be interpreted as separable into contributions due to translation (ΔS_t), rotation (ΔS_r) and vibration normal to the surface (S_v), assuming that the internal molecular vibrations are not altered by the process of adsorption, *i.e.*

$$\Delta S^\ominus = \Delta S_t + \Delta S_r - S_v. \quad (1)$$

The fourth and fifth columns of table 1 show the values of the translational entropies of the gas phase, $S_t^{(g)}(P = P^\ominus)$, and the adsorbed phase, $S_t^{(s)}(\Pi = \Pi^\ominus)$, for the corresponding reference states, calculated from⁵

$$S_t^{(g)}(P = P^\ominus) = R \ln \left(\frac{(2\pi mkT)^{3/2} kT}{h^3 P^\ominus} \right) + \frac{5}{2}R \quad (2)$$

and

$$S_t^{(s)}(\Pi = \Pi^\ominus) = R \ln \left(\frac{(2\pi mkT) kT}{h^2 \Pi^\ominus} \right) + 2R \quad (3)$$

where m is the mass of one molecule of adsorbate, k is Boltzmann's constant, h is Planck's constant and T is the absolute temperature.

The variation of the rotational entropy shown in the last column of table 1 was calculated from the difference between eqn (1) and the assumption of mobile adsorption if

$$\Delta S_t = S_t^{(g)}(P = P^\ominus) - S_t^{(s)}(\Pi = \Pi^\ominus). \quad (4)$$

The vibrational entropy was calculated from

$$S_v = \frac{R\theta_v}{T[\exp(\theta_v/T) - 1]} - \ln[1 - \exp(-\theta_v/T)] \quad (5)$$

where $\theta_v = h\nu/k$. The frequency ν perpendicular to the surface was determined using the approximation of the classical harmonic oscillator, assuming that the adsorbate's internal rotational and vibrational degrees of freedom are not affected by the process of adsorption. In this case, Henry's constant K_H is given by⁶

$$K_H = \left(\frac{1}{2\pi mkTv^2} \right)^{1/2} \exp(-\varepsilon_{\min}/kT). \quad (6)$$

The frequency, ν , is thus derived directly from the position coefficient of the straight line that is obtained when $\ln K_H$ is plotted against $1/T$, assuming that the variation of the coefficient with temperature is negligible.

ROTATIONAL ENTROPY

The localized adsorption model of Kemball³ and de Boer and Kruyer⁴ assumes that $\Delta S_t = S_t^{(g)}(P = P^\ominus)$ and that the vibrational entropy is of the order of three times that of the mobile case. Therefore, from the values of table 1 it is evident that the systems considered correspond to mobile adsorption. The change in rotational entropy

$$\Delta S_r = S_r^{(g)} - S_r^{(s)} \quad (7)$$

that appears in the last column of table 1 corresponds to this assumption. Note that the values obtained are in agreement with those views presented in ref. (1) for all systems. Within the restrictions imposed by the experiment and by the theoretical calculations, only isobutene shows a significant rotational contribution. Therefore negative values should be interpreted as being equal to zero. An attempt will thus be made to analyse this variation in the light of statistical mechanics. As far as we are aware, this has been done only for the adsorption of simple molecules such as water^{7, 8} and not for the physisorption of more complex molecules.

Table 1. Thermodynamic parameters in Henry's region

	$q_{\text{at}}(\theta \rightarrow 0)$ /cal mol ⁻¹	ΔS^\ominus /cal K ⁻¹ mol ⁻¹	$S_i^{\text{(s)}}(\Pi = \Pi^\ominus)$ /cal K ⁻¹ mol ⁻¹	$S_i^{\text{(g)}}(P = P^\ominus)$ /cal K ⁻¹ mol ⁻¹	ν /s ⁻¹	S_v /cal K ⁻¹ mol ⁻¹	ΔS_r /cal K ⁻¹ mol ⁻¹
isobutene/A110	9694	19.4	26.0	38.0	1.14×10^{15}	0	7.40
buta-1,3-diene/A110	8005	13.8	26.0	37.9	7.38×10^{13}	0	1.90
isobutene/A600	6129	9.8	26.0	38.0	9.44×10^{12}	0.67	-1.53
n-butane/A600	6072	10.6	26.1	38.1	1.43×10^{13}	0.72	-0.68
isobutene/A1000	4312	4.7	26.0	38.0	7.44×10^{11}	6.20	-1.10

Table 2. Coordinates of the isobutene atoms of fig. 1

	C ₁	C ₂	C ₃	C ₄	H ₁	H ₂	H ₃	H ₄	H ₅	H ₆	H ₇	H ₈
x(i)	-0.6765	0.6765	1.4115	1.4115	-1.212	-1.212	0.7025	2.0387	2.0387	2.4841	1.1479	1.1479
x(i)	0	0	-1.2731	1.2731	0.9275	-0.9275	2.1023	1.3309	1.3309	-1.0737	-1.8452	-1.8452
z(i)	0	0	0	0	0	0	0	-0.6299	0.6299	0	-0.6299	0.6299

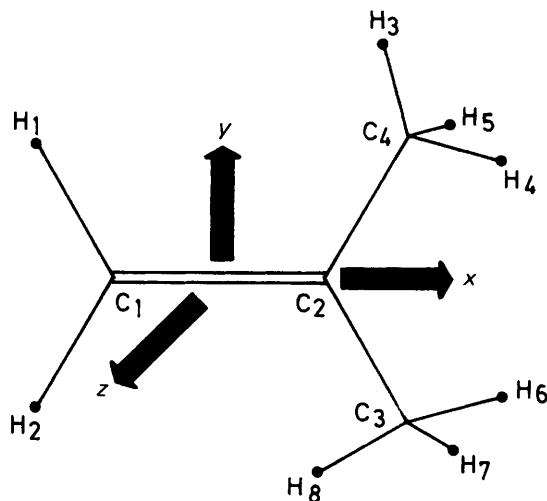


Fig. 1. Schematic diagram of the isobutene molecule.

Table 3. Rotational entropy at 25 °C

degrees of freedom, n	I_n	q_n	S_n^r (entropy units)
1	$22.638 \times 10^{-39} \text{ g cm}^2$	72.6	9.50
2	$14.809 \times 10^{-39} \text{ g cm}^2$	1 097.8	15.89
3	$144.283 \times 10^{-116} \text{ g}^3 \text{ cm}^6$	42 972.0	24.17

The following equations correspond to the rotational partition function, q_n^r , of a molecule with n degrees of rotational freedom:^{7, 8}

$$q_1^r = \pi^{1/2} \left(\frac{8\pi^2 kT}{h^2} \right)^{1/2} I_1^{-1/2} \quad (8)$$

$$q_2^r = \left(\frac{8\pi^2 kT}{h^2} \right) I_2^{-1} \quad (9)$$

$$q_3^r = \pi^{1/2} \left(\frac{8\pi^2 kT}{h^2} \right)^{3/2} I_3^{-3/2} \quad (10)$$

where the moments of inertia, I_n , are calculated with respect to the rotational axes in each case.

Fig. 1 is a schematic representation of the isobutene molecule showing a system of perpendicular cartesian coordinates in which the x axis coincides with the direction of the double bond and the origin of the coordinates is at its centre. Atoms H_1 , H_2 , H_3 , C_1 , C_2 and C_3 are on the xy plane, while the z axis is perpendicular to the plane of the paper. Table 2 includes the coordinates of all the atoms in the system, and it is then easy to calculate the centre of mass of the molecule, with $\bar{x} = 0.7325$, $\bar{y} = \bar{z} = 0$ and using 12.01 amu for the mass of the carbon atom and 1.008 amu for that of the hydrogen atom.

The partition function, q_3^r , corresponds to the isobutene molecule in the gas phase, when it has three rotational degrees of freedom. The calculation of q_3^r can be done using eqn (10), where

$$I_3 = I_a I_b I_c \quad (11)$$

if I_a , I_b and I_c are the moments of inertia for rotation about the three principal axes of rotation. If these are not known, the calculation can be performed using the expression

$$I_a I_b I_c = \begin{vmatrix} I_{xx} & -I_{xy} & -I_{xz} \\ -I_{xy} & I_{yy} & -I_{yz} \\ -I_{xz} & -I_{yz} & I_{zz} \end{vmatrix} \quad (12)$$

where

$$I_{xx} = \sum_i m_i (y_i^2 + z_i^2) \quad (13)$$

$$I_{yy} = \sum_i m_i (x_i^2 + z_i^2) \quad (14)$$

$$I_{zz} = \sum_i m_i (x_i^2 + y_i^2) \quad (15)$$

if the sums take into account all the atoms, i , in the molecule and the coordinates are considered relative to any set of mutually perpendicular axes that go through the centre of mass. The products of inertia, which cancel out if the axes are chosen as the principal axes of inertia, are calculated from

$$I_{xy} = \sum_i m_i x_i y_i \quad (16)$$

$$I_{xz} = \sum_i m_i x_i z_i \quad (17)$$

$$I_{yz} = \sum_i m_i y_i z_i. \quad (18)$$

The coordinates of the atoms that must be taken into account in the calculation of eqn (12)–(18) must have their origin at the centre of mass, so that after performing the translation $x_i = x_i + 0.7325$ of the coordinates corresponding to axis x , they will be those of table 2.

Table 3 includes, in addition to the results for the gas phase, two possibilities for the molecule in the adsorbed phase corresponding to one and two degrees of rotational freedom. In the first case, it is assumed that the molecule of adsorbate is rotating in the xy plane, parallel to the surface, with respect to the z axis that goes through the middle of the double bond. Physically, as was discussed in a macroscopic analysis of these systems,¹ this case takes into account the interaction of the molecule's double bond with the OH group on the surface of Aerosil. The calculation of q_1^r is performed using eqn (8), in which the moment of inertia is

$$I_1 = \sum_i m_i (x_i^2 + y_i^2) \quad (19)$$

if the coordinates are now those given in table 2.

The case of two degrees of freedom for the adsorbate takes into account the previous rotation together with the simultaneous rotation of the molecule with respect to the x axis. The calculation of q_2^r was made using eqn (9), where I_2 is obtained from

$$I_2 = \left[\left(\sum_i m_i (x_i^2 + y_i^2) \right) \left(\sum_i m_i (y_i^2 + z_i^2) \right) \right]^{\frac{1}{2}} \quad (20)$$

and the coordinates of table 2.

In all the cases, the entropy S_r^n , corresponding to n degrees of rotational freedom, was calculated from the expression:⁵

$$S_r^n = R \left(\frac{n}{2} + \ln q_n^r \right). \quad (21)$$

The results for the moments of inertia, partition functions and rotational entropies are shown in table 3.

CONCLUSIONS

Within the limitations imposed by the approximations and assumptions made in the calculations, we obtain a microscopic view of these systems, which were described macroscopically in a previous paper.¹ The adsorbates show behaviour associated with a mechanism of mobile adsorption, with no variation in the degrees of rotational freedom during the process of adsorption, except in the isobutene/A110 system, where the adsorbed molecule loses some of them as it goes from the gas phase to the adsorbed phase. This change of 7.40 entropy units in table 1 differs from the value of $S_3^r - S_1^r = 14.67$ entropy units, but, within experimental error, it agrees with the value of $S_3^r - S_2^r = 8.28$ entropy units if the values of table 3 are considered. The symmetry number σ has not been included in eqn (21). This does not affect the values of ΔS^r if we suppose that σ of the adsorbed molecule is equal to that of the gas phase. It could be stated, then, that in the adsorbed phase, even within the framework of mobile adsorption and as a result of the interactions between the double bond and the OH groups of Aerosil, when the isobutene molecule moves from site to site on the surface it still possesses two degrees of rotational freedom, having lost only one of those it had in the gas phase. We may thus view it as a rolling helix.

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