V. Ya. DAVYDOV, A. V. KISELEV, V. I. LYGIN

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V. Ya. DAVYDOV, A. V. KISELEV, V. I. LYGIN

CHANGE IN THE SPECTRUM OF SURFACE HYDROXYL GROUPS AND THE HEAT OF ADSORPTION ON THE SURFACE OF SILICA

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Establishing the dependence between the spectral and energetic characteristics of various interactions, and in particular of the hydrogen bond, is very important for understanding their nature. There are studies of the dependence between the shift of the absorption band of a group entering into a hydrogen bond and the energy of formation of this bond in solutions ([1]). In this case, however, difficulties arise because of the low accuracy in estimating the enthalpy of the hydrogen bond, the contribution of van der Waals forces, and molecular association ([1]). In adsorbate–adsorbent systems, on the other hand, it is possible to measure with greater accuracy the heats of adsorption of various molecules on fairly homogeneous surfaces of known chemical structure in the absence of interaction with extraneous molecules and with weak adsorbate–adsorbate interaction. In our works ([2]) we made the first attempt to compare the results of calorimetric and spectral studies of adsorption. In the present work, the relation between the heats of adsorption and the magnitudes of the shift $\Delta\nu$ of the absorption band of the stretching vibrations of hydroxyl groups on the surface of silica has been investigated for adsorption of a number of different substances.

Spectral studies of the adsorption of diethylamine, benzene and its derivatives ([3]), and also ether ([4]), showed that these molecules interact strongly with the free hydroxyl groups of silica, which give a narrow absorption band at 3749 cm^{-1} ([5]). Van der Waals forces lead only to a small shift of the absorption band. The different shift of the absorption band of surface hydroxyl groups upon adsorption of nitrogen and argon ([6]) was explained by the interaction of the hydroxyl groups with the quadrupole of nitrogen molecules ([7]). Much larger changes are undergone by the vibrational spectrum in the case of still more specific interactions of the hydrogen-bond type ([1]). The absorption bands of the vibrations of OH, NH, and other functional-group bonds in this case undergo a considerable shift, broadening, and increase in integral intensity. In spectral studies of adsorption (see reviews ([5,8])), an increase was established in the perturbation of free hydroxyl groups on the surface of silica on going from nonpolar molecules to polar ones and to those capable of forming more specific bonds of the hydrogen-bond type.

The value of $\Delta\nu$ for surface hydroxyl groups depends comparatively weakly on the surface coverage θ. In the case of adsorption of benzene and its derivatives, $\Delta\nu$ changes upon filling of the monolayer only by 10-15% ([3]). The values of the differential heats of adsorption Q_a, however, are more sensitive to the geometric and chemical heterogeneity of the surface and to adsorbate–adsorbate interaction ([9]). Therefore, in order to establish the relation between the quantities $\Delta\nu$ and Q_a, it is very important, first, to choose close values of θ, and, second, to isolate the part of the molecule that interacts most specifically with the surface hydroxyls. In this work we have made an attempt at an approximate allowance for these factors. The values of $\Delta\nu$ and Q_a are given in Table 1.

Figure 1a gives the dependences of $\Delta\nu$ of the surface hydroxyl groups on the corresponding values of the differential heat of adsorption Q_a. To take into account the dependence of Q_a on θ, in Fig. 1a horizontal segments are drawn—

the ranges of variation of Q_a as θ increases from 0.25 to 0.75 are shown. With increasing Q_a, referred to one mole of adsorbate, the value of $\Delta\nu$ increases monotonically.

Such a representation of the dependence of $\Delta\nu$ and Q_a does not quite correctly reflect the nature of the relation between these quantities, since $\Delta\nu$ is an energetic characteristic of the action of adsorbed molecules on a hydroxyl group, whereas Q_a (referred to 1 mole of adsorbate) reflects the contributions of different forces to the total energy of the adsorption interaction and, for large molecules, corresponds to contact of the adsorbate molecule with different numbers of surface hydroxyl groups.

Table 1

Shifts of the absorption band of free hydroxyl groups on the surface of silicas ($\Delta\nu$) and differential heats of adsorption on the hydrated surface (at $\theta = 0.5$), referred to one mole of adsorbate (Q_a), to the area ω_m occupied by the whole adsorbate molecule on the surface (Q_s), and to the area ω'_m occupied by the "active" part of this molecule (Q'_s), as well as the differences of the heats of adsorption on the hydrated and dehydrated surfaces (ΔQ_a)

Adsorbate	$\Delta\nu$, cm^{-1}	Q_a, kcal/mol	ω_m, Å^2	Q_s, erg/cm^2	ω'_m, Å^2	Q'_s, erg/cm^2	ΔQ_a, kcal/mol
n-Hexane	45*	8.8 (10)	51 (10)	120	51	120	< 0.5 (16)
Benzene	110**	10.2 (11)	40 (11)	175	40	175	2.0 (16)
Toluene	130**	11.8 (11)	46 (11)	180	40	205	–
n-Xylene	146**	13.4 (11)	50 (11)	185	40	230	–
Mesitylene	160**	14.0 (11)	57 (11)	170	40	230	–

Adsorbate	$\Delta\nu$, cm^{-1}	Q_a, kcal/mol	ω_m, $Å^2$	Q_s, erg/cm^2	ω'_m, $Å^2$	Q'_s, erg/cm^2	ΔQ_a, kcal/mol
Water	330 (6)	12.5 (12)	25 (12)	345	25	345	–
Methanol	350 (6)	14.5 (9)	25 (15)	405	25	400	–
Trimethylcarbinol	435 (13)	18.0 (12)	40 (12)	310	25	415	–
Diethyl ether	450 (4)	15.0 (12)	51 (12)	225	25	500	6.5 (4)

* Our data.
** $\Delta\nu$ values taken from (3) for $\theta = 0.5$.

It is therefore of interest to refer the differential heat of adsorption to the area ω_m occupied by the molecule on the surface (12). Such a reference is made in Fig. 1b, and the adopted values of ω_m and the corresponding values $Q_s = Q_a/\omega_m$ (erg/cm^2) are given in Table 1. It is not difficult to see, however, that such a representation of the heat of adsorption for molecules having long hydrocarbon chains is not sufficiently definite, since in this case all the surface hydroxyl groups covered by the adsorbate molecule are considered equivalent. In fact, under such a reference the surface hydroxyl groups both forming hydrogen bonds with active atoms of the adsorbate molecule (for example, with oxygen atoms in alcohols, ketones, and ethers) and interacting mainly with side groups (for example, with CH_2 and CH_3 groups), which are adsorbed predominantly due to dispersion forces, are not distinguished. Fig. 1b indicates that such indefiniteness in the cases under consideration exists mainly for mesitylene and ether, i.e., for molecules possessing the largest number of CH_3 and CH_2 groups. When comparing with $\Delta\nu$, it is apparently more correct to single out the part of the heat of adsorption characteristic of interaction with surface hydroxyl groups, referring Q_a not to the entire area ω_m occupied by the adsorbate molecule, but only to the area of that part ω'_m which interacts more specifically with the surface hydroxyl groups.

The choice of the corresponding contribution to the heat of adsorption and of the corresponding part of the molecular area is, of course, quite difficult, although even now some approximations can be made using additive schemes for Q_a and ω_m (11,14). Taking into account the comparatively small magnitudes of the increments of the heats of adsorption of the CH_3 and CH_2 groups of hydrocarbons, we referred the heat of adsorption of the whole molecule to the area of that part ω'_m which is "active" with respect to hydroxyl groups. The value of ω'_m for alkylbenzenes was approximately taken to be the same as for benzene (40 $Å^2$ (11)), and

for alcohols, water, and ether, the value ω'_m was taken as equal to ω_m for the molecules of the smallest dimensions—water and methanol $\left(\omega_{m\,H_2O} \approx \omega_{m\,CH_3OH} \approx 25\ Å^2\right)$, obtained from the corresponding monolayer-

Fig. 1. Relation between the shift of the absorption band of free surface hydroxyl groups of silica gel $\Delta\nu$ and the differential heat of adsorption, referred to 1 mole of adsorbate Q_a (a), to the area occupied by the entire adsorbate molecule Q_s (b), and to the portion of the adsorbate molecule area active (with respect to specific interaction with surface hydroxyl groups) Q'_s (c), as well as to the difference in heats of adsorption on the hydrated and dehydrated surfaces of silica gel ΔQ (d). Horizontal segments denote the values of the change in Q_a from $\theta = 0.25$ to $\theta = 0.75$.

Figure 1: Fig. 1. Relation between the shift of the absorption band of free surface hydroxyl groups of silica gel $\Delta\nu$ and the differential heat of adsorption, referred to 1 mole of adsorbate Q_a (a), to the area occupied by the entire adsorbate molecule Q_s (b), and to the portion of the adsorbate molecule area active (with respect to specific interaction with surface hydroxyl groups) Q'_s (c), as well as to the difference in heats of adsorption on the hydrated and dehydrated surfaces of silica gel ΔQ (d). Horizontal segments denote the values of the change in Q_a from $\theta = 0.25$ to $\theta = 0.75$.

capacity values (^{15}) and from the values of the specific surface area determined from nitrogen adsorption isotherms*.

Fig. 1. Relation between the shift of the absorption band of free surface hydroxyl groups of silica gel $\Delta\nu$ and the differential heat of adsorption, referred to **1 mole** of adsorbate Q_a (a), to the area occupied by the entire adsorbate molecule Q_s (b), and to the portion of the adsorbate molecule area Q'_s (c) that is active (with respect to specific interaction with surface hydroxyl groups), as well as to the difference in heats of adsorption on the hydrated and dehydrated surfaces of silica gel ΔQ (d). Horizontal segments denote the magnitudes of the change in Q_a from $\theta = 0.25$ to $\theta = 0.75$.

Fig. 1c expresses the dependence between $\Delta\nu$ and the differential heat of adsorption Q'_s, referred to the area ω'_m selected in this way. The corresponding values of the area ω'_m and of the heats of adsorption $Q'_s = Q_a/\omega'_m$ (erg/cm^2) are also given in Table 1. As has already been noted, the parts of a complex adsorbate molecule that do not participate in hydrogen-bond formation also contribute to the adsorption energy, i.e., to the magnitudes of the shift $\Delta\nu$ and the heat of adsorption. However, the position in Fig. 1 of the point for hexane shows that this contribution is small. Such a very approximate reference of the heat of adsorption of complex molecules to the area corresponding to interaction of the active part of the molecule with surface hydroxyls (in our case—the aromatic nucleus of alkylbenzenes or the oxygen atom of water, alcohols, and ether) makes the relation between the quantities $\Delta\nu$ and the heat of adsorption especially simple. The corresponding dependence is fairly close to linear.

Another approximation to establishing the relation between the spectral and energetic manifestations of adsorption can be made by taking into account only that part of the heat of adsorption which is due to interaction with the surface hydroxyl groups. This part of the heat of adsorption can be approximately taken into account either as the difference between the heats of adsorption of the same substance on a hydroxylated and a dehydroxylated surface (1,2,9,12,16), or as the difference between the heats of adsorption of geometrically similar molecules that possess different local electronic structures (for example, diethyl ether and *n*-pentane (12)). In Fig. 1d the dependence of the value $\Delta\nu$ on the difference in heats of adsorption at $\theta = 0.5$ on the hydrated and dehydrated surfaces of silica gel, ΔQ_a, is presented. In this case we can for the time being use data relating only to those substances whose molecules form hydrogen bonds only with the surface hydroxyl groups, and not with one another (Table 1). From Fig. 1d it follows that $\Delta\nu$ is approximately proportional to ΔQ_a, which characterizes the interaction energy of the active part of the molecule with hydroxyl groups—of the surface groups. The closeness to linearity of the dependence of $\Delta\nu$ on the energy of hydrogen-bond formation has also been noted for solutions (1).

The insensitivity of the heat of adsorption of hexane to the degree of dehydration of the silica surface (16) indicates that its interaction with the surface, including with its hydroxyl groups, occurs mainly only through dispersion forces. Therefore, in the adsorption of hexane only a small shift of the absorption band of the hydroxyl groups is observed. A considerable increase in the value of $\Delta\nu$ and in the heat of adsorption Q_s, and especially Q'_s, is observed on passing to molecules possessing π-electron bonds (see Fig. 1). The significant sensitivity of the heat of adsorption of benzene to the degree of dehydration of the silica surface, as well as the excess of the heat of adsorption of benzene over the heat of adsorption of saturated hydrocarbons with the same number of carbon atoms in the molecule—for example, cyclohexane or *n*-hexane—points to a more specific interaction in this case (17). The large values of $\Delta\nu$ indicate that the hydroxyl groups of the surface play the determining role in this additional specific interaction. The change, upon adsorption, of vibrations in the benzene molecule itself that are associated with its π-electron bonds indicates participation of these bonds in the adsorption interaction (18). Calculation of the interaction energy of a benzene molecule with a hydroxyl group by the semiclassical method and by the molecular-orbital method (19) indicates its substantial contribution to the total adsorption energy. Finally, adsorption of molecules having an oxygen atom with lone pairs of electrons—namely molecules of H_2O, CH_3OH, $(CH_3)_3COH$, and $(C_2H_5)_2O$—is accompanied by the formation of a strong hydrogen bond and by large $\Delta\nu$.

Of course, the dependence outlined by us (Fig. 1) is not final, and not all molecules need obey this relation. Thus, the energy of hydrogen-bond formation with surface hydroxyl groups rigidly fixed in space is affected by steric hindrance, which prevents the most favorable orientation of the molecule with respect to

* In (12) an underestimated value was initially adopted, $\omega_{m\,\mathrm{H_2O}} = 10.6$ Å^2, corresponding to 1 water molecule in ice crystals, and not in the adsorption layer.

the hydroxyl groups. It is possible that, with more detailed experimental and theoretical investigation, more exact linear dependences will be found for similar compounds.

It is also of interest to compare the heats of adsorption with the change in the absorption coefficient of the surface hydroxyl groups and of the bonds of adsorbing molecules that interact with them, since this change is very sensitive to a change in the dipole moment of the bond, i.e., to the redistribution of charge determined by the interaction energy.

Chemical Faculty of Moscow
State University
named after M. V. Lomonosov

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CITED LITERATURE

1. G. C. Pimentel, A. L. Clellan, *The Hydrogen Bond*, San Francisco, London, 1960.
2. A. V. Kiselev, V. I. Lygin, *Kolloid. zhurn.*, **23**, 574 (1961); A. V. Kiselev, *ZhFKh*, **35**, 233 (1961).
3. M. R. Basila, *J. Chem. Phys.*, **35**, 1151 (1961).
4. B. Ya. Davydov, A. V. Kiselev, V. I. Lygin, *Kolloid. zhurn.*, **25**, No. 1 (1963).
5. A. N. Terenin, in: *Surface Chemical Compounds and Their Role in Adsorption*, Moscow, 1957, p. 206.
6. R. S. McDonald, *J. Am. Chem. Soc.*, **79**, 850 (1957).
7. G. J. C. Frohnsdorff, G. L. Kington, *Trans. Farad. Soc.*, **55**, 1173 (1959).
8. A. V. Kiselev, V. I. Lygin, *Usp. khim.*, **31**, 351 (1952).
9. A. V. Kiselev, *Vestn. Moskovsk. univ., ser. khim.*, No. 1, 3 (1962).
10. A. A. Isirikyan, A. V. Kiselev, *ZhFKh*, **31**, 2127 (1957); *J. Phys. Chem.*, **65**, 601 (1961).
11. A. V. Kiselev, B. A. Frolov, *Kinetika i kataliz*, **3**, No. 5 (1962).
12. O. M. Dzhigit, A. V. Kiselev, G. G. Muttik, *Kolloid. zhurn.*, **23**, 504, 553

(1961); **24**, 241 (1962).

13. B. Ya. Davydov, A. V. Kiselev, V. I. Lygin, *ZhFKh*, in press.

14. N. N. Avdul, G. I. Berezin et al., *Izv. AN SSSR, OKhN*, 1957, 1021; 1959, 787; 1961, 205; *Kolloid. zhurn.*, **23**, 513 (1961).

15. L. N. Soboleva, A. V. Kiselev, *ZhFKh*, **32**, 49 (1958).

16. L. D. Belyakova, A. V. Kiselev, in: *Preparation, Structure, and Properties of Sorbents*, 1959, p. 180.

17. A. V. Kiselev, *DAN*, **106**, 1046 (1956).

18. G. A. Galkin, A. V. Kiselev, V. I. Lygin, *ZhFKh*, **36**, 1764 (1962).

19. A. V. Kiselev, D. P. Poskus, *DAN*, **120**, 834 (1958); A. V. Kiselev, Ya. Koutecký, J. Čížek, *DAN*, **137**, 638 (1951).

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