EVALUATING ADSORBED-WATER STRUCTURE IN DISPERSED SYSTEMS BY NMR SPECTROSCOPY. Part 1. γ-Al_2O_3

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Nuclear magnetic resonance parameters are used to show that there is a special group of water molecules firmly bound to active centers and unlinked to the rest of the ensemble.

The vibrational frequencies of water molecules recorded in the infrared range have been used [1] with the force constants to show that there are three modes of interaction with active centers in γ-Al_2O_3. It was found that the adsorption energy for water molecules forming hydrogen bonds each to two oxygen atoms in the lattice is twice the adsorption energy for molecule whose oxygen atom interacts simultaneously with two OH groups, while one of the hydrogen atoms interacts with an oxygen atom in the lattice, and it is also three times larger than the adsorption energy for a molecule attached only via its oxygen atom to two OH groups on the surface of the γ-Al_2O_3. These data form the basis for studying the structure of adsorbed water by nuclear magnetic resonance (NMR).

The methods were as follows.

The γ-Al_2O_3 powder of known water content was placed in a special cell for nuclear magnetic resonance. The cells were dried in a desiccator at temperatures from 293 to 500°K, or else various water contents were produced in a high-pressure chamber under oscillating conditions. The measurements were made for water contents from 3 to 16%. See [1] on the calculation of the specific surface.

The NMR spectra were recorded with a VS-497 high-resolution spectrometer without the use of internal stabilization in the range 213-293°K. They were single broad absorption lines similar to Gaussian in shape (particularly at low water contents).

Figure 1 shows the temperature dependence of the line width (measured at half height) for certain water contents.

According to [2], the line width $\Delta\omega$ can be represented as

$$\Delta\omega^2 = S^{\mathrm{m}} \frac{2}{\pi} \operatorname{arctg}(\alpha \Delta\omega \tau_c), \tag{1}$$

where $\Delta\omega$ is the width measured at half height in Hz, $S^{(m)}$ is the second moment of the absorption line for adsorbed water molecules firmly bound to lattice active centers (at temperatures below 90°K) in Hz^2, τ_c is the correlation time in sec, and α is a dimensionless coefficient of the order of one.

The absorption line narrows because of motion of the hydrogen spins.

The physical explanation of the narrowing is [2] as follows. If the spins are in fast relative motion, the local field sensed by a spin fluctuates rapidly in time, and therefore one observes only the mean value over a time large by comparison with the duration of the fluctuations, where the mean field is less than the instantaneous field, which leads to line narrowing. The local-field fluctuation rates may be described by the correlation time τ_c.

We assume that an Arrhenius law applies:

$$\tau_c = \tau_0 \exp\left(\frac{E}{kT}\right), \tag{2}$$

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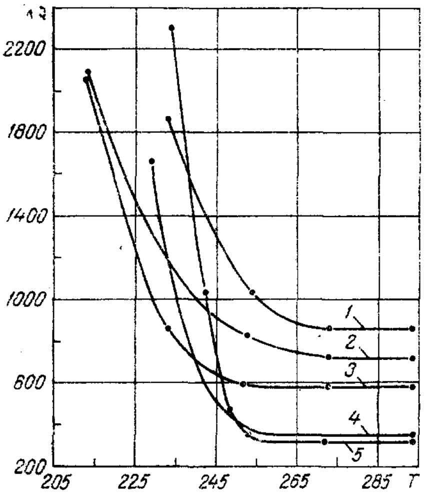

Fig. 1. Temperature dependence of the NMR line width Δω for water adsorbed on γ-Al_2O_3 for specimens with water contents in % as follows: 1) 3; 2) 4.8; 3) 7.3; 4) 10.5; 5) 15.8; Δν in Hz and T in °K.

where E is the activation energy for the motion, which corresponds approximately to the height of the potential barrier between two equivalent positions for a molecule, k is Boltzmann's constant, and T is absolute temperature.

At comparatively high temperatures, which correspond to small τ_c, (1) can be put as

$$\Delta\omega = S^{\mathrm{m}} \frac{2}{\pi} \alpha\tau_c. \tag{3}$$

However, (1) resembles (3) in applying to systems that can be characterized by single adsorption activation energies or single correlation times.

Adsorbed water does not fit this model at any stage in sorption. The water is heterogeneous from the NMR viewpoint in that molecules near different centers have different relaxation and correlation times and different activation energies.

According to the IR data, water adsorbed on γ-Al_2O_3 can be divided [1] into various parts, including molecules adsorbed only at lattice oxygen atoms (Fig. 2) in accordance with scheme I of [1] whose energies are 2-3 times those for the other molecules.

Then we have [3] for a heterogeneous system that

$$\Delta\omega = S_a^{\mathrm{m}} \frac{2}{\pi} \tau_0 \exp\left(\frac{E_a}{kT}\right) + S_b^{\mathrm{m}} \frac{2}{\pi} \tau_0 \exp\left(\frac{E_b}{kT}\right), \tag{4}$$

where $S_a^{(m)}$ and E_a, $S_b^{(m)}$ and E_b are correspondingly the second moments and activation energies for groups a and b.

Group a includes water molecules adsorbed in accordance with scheme I, while b includes all the others [1].

The second moment for group i may be calculated from Van Vleck's formula [4] with allowance for the contributions from the hydroxyl groups in the adsorbent (a and b):

$$S_{(i)}^{\mathrm{m}} = \frac{3}{5} \gamma^4 \hbar^2 J(J+1) N_i^{-1} \sum_{k=1}^{N_i} \sum_{l} r_{kl}^{-6}, \tag{5}$$

where N_i is the number of protons from water molecules in group i within the unit cell, γ is the gyromagnetic ratio in rad/sec·Oe, $\hbar$ is Planck's constant in Oe·sec/rad, r_{kl} is the distance between protons k and l in cm, and $\sum_l$ represents summation over all the protons.

TABLE 1. Values of the Second Moments, Activation Energies, and Correlation Times (at T = 293°K) for Groups *a* and b for Various Water Contents in γ-Al_2O_3

P, %	$S_a^{(M)}$, G^2	$S_b^{(M)}$, G^2	E_a, kcal/mole	E_b, kcal/mole	$\tau_{c(a)}$, 10^{-7} sec	$\tau_{c(b)}$, 10^{-8} sec
3,0	5,08	9,59	1,68	0,77	3,1	6,0
4,2	4,45	13,2	1,47	0,59	2,3	3,6
4,8	4,1	15,0	1,57	0,56	2,4	3,7
6,1	3,6	17,6	1,50	0,44	2,0	3,9
8,3	2,95	21,3	1,63	0,39	1,3	3,5
9,5	2,7	23,8	1,59	0,35	1,9	2,0
10,5	2,5	26,5	3,11	0,62	2,1	1,1
11,6	2,4	28,6	2,91	0,58	2,7	0,43

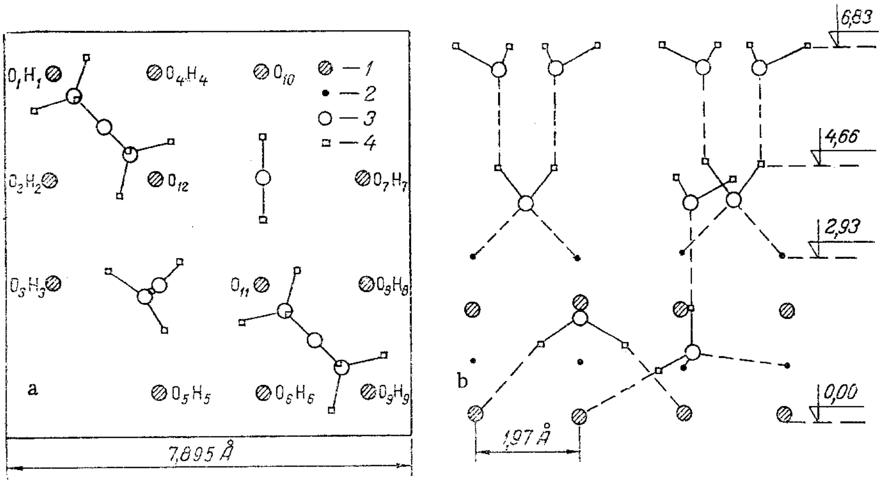

Fig. 2. Structure of the surface layer in γ-Al_2O_3: a) in projection on (001); b) in projection on (100): 1) oxygen; 2) hydrogen in the lattice surface; 3) oxygen; 4) hydrogen in adsorbed water molecules.

The distances between the protons are found from the coordinates of the hydrogen atoms in the water molecules adsorbed at active centers in accordance with the scheme in Fig. 2. Table 1 gives the second moments.

There are many papers such as [3, 5, 6] giving data on adsorption activation energies for water on various solids and various water contents. However, the energies are derived from experimental relationships and the method of calculation is not given.

In [7], there is a statistical derivation of the adsorption isotherm, and it is stated that the activation energy is proportional to the adsorption energy.

One can use the force constants for the hydrogen bonds from molecules of group *a* and the force constants for molecules of group b to derive E_a/E_b for any adsorbed water content.

When all the necessary parameters S_a, S_b, $\Delta\omega$, E_a/E_b are substituted into (4) for different temperatures (we used the limiting temperatures found by experiment), one can calculate the activation energy and correlation time as a function of water content. Table 1 gives the results. It is evident that the activation energy for group *a*, i.e., molecules attached to lattice oxygen atoms in γ-Al_2O_3, remains virtually constant over the content range 1-9.5%.

The water content P_m = 9.5% corresponds to all the active centers being covered by water molecules to form a double molecular layer. Therefore, one assumes that up to the P_m limit the molecules of group *a* are not related to the ensemble formed from the other water molecules.

We now derive the activation energies by a method independent of NMR.

According to [7], the activation energy in the kinetic approach is identical with the mean increment in the potential energy in the statistical approach:

$$E = u_a - u_g, \tag{6}$$

where u_a is the average potential energy of an adsorbed molecule and u_g is the mean potential energy of an isolated one.

TABLE 2. Activation Energies for Adsorbed Water Molecules Derived by Various Methods

P, %	E_a, kcal/mole		E_b, kcal/mole	
	from (6)	NMR	from (6)	NMR
3	1,91	1,68	0,65	0,77
4	1,91	1,51	0,61	0,62
5	1,91	1,56	0,60	0,52
6	1,91	1,51	0,59	0,46
7	1,91	—	0,58	—
8	1,91	1,60	0,57	0,39
9	1,91	1,61	0,57	0,35

In the general case, u_g can be put as

$$u_g = \frac{1}{2} \sum_{i,j}^{N} k_i^j q_i q_j, \tag{7}$$

where N is the number of natural vibrational coordinates, q_i, q_j; k_i^j being an element in the force-constant matrix.

The vibration amplitudes can be determined by calculating the eigenvalues and eigenvectors in the coefficient matrix for the complete interaction, where the eigenvectors are then normalized by multiplying them by normalization factors. We can calculate the potential energy of the vibrations of an adsorbed molecule from

$$u_a = \frac{1}{2} \sum_{i,j=1}^{N} k_i^j (q_i^a + \Delta r_i)(q_j^a + \Delta r_j), \tag{8}$$

where Δr_i and Δr_j are the increases in the bond lengths in the water molecule and $q_i{}^a$ and $q_j{}^a$ are the natural vibrational coordinates on adsorption.

According to [8], Δr_i or Δr_j may be determined as follows for weak hydrogen bonds:

$$4.72\,\Delta r = \frac{\Delta \nu}{\nu_0}, \tag{9}$$

where $\Delta\nu$ is the frequency shift in the stretching vibrations due to bond lengthening on adsorption and ν_0 is the vibrational frequency in an isolated molecule (mean frequencies may be used for symmetrical adsorbed complexes).

In our case we considered the frequencies of the D_2O molecule.

The bond stretching for molecules adsorbed under scheme I is 0.008 Å, the values for scheme II being 0.007 Å and 0.008 Å, and those for scheme III being 0.006 Å (see [1] for the schemes).

The hydrogen bonds formed on adsorption under scheme I are represented as average ones, and therefore the Δr derived from (9) is an underestimate, and estimation of Δr according to [1] gives 0.024 Å. We assumed a mean value of 0.016 Å.

We take the forms of vibration for molecules adsorbed in different ways in accordance with [9]. Then the mean potential energy in the vibration of a molecule of group a with the maximal natural coordinates is estimated as 6.04 kcal/mole, while that for group b is 4.87 kcal/mole (scheme II) or 4.68 kcal/mole (scheme III).

Table 2 gives the activation energies calculated from (6) and those derived from the NMR experiments.

The slight difference indicates that we have chosen the correct principle for calculating the activation energy and the correct scheme for the disposition of the water molecules in the crystal.

It therefore appears that there are two uncoupled ensembles of adsorbed water molecules with in the double molecular layer. However, Table 1 shows that there is a step by almost a factor two in E_a due to the formation of P_m, which is evidently due to an additional increase in the activation energy arising from the interaction of molecules of group a with those of group b on detachment or attachment at active centers.

See [3, 5, 6] for analogous behavior in the activation energy as the water content increases together with data on the correlation times.

This evidence for isolated molecules attached more rigidly to active centers and unrelated to the rest of the molecules has been used in evaluating the density of water adsorbed on γ-Al_2O_3.

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