I. F. Abdrahmanova and Corresponding Member of the Academy of Sciences of the USSR B. V. Deryagin

1958

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

I. F. Abdrahmanova and Corresponding Member of the Academy of Sciences of the USSR B. V. Deryagin

SURFACE CONDUCTIVITY OF QUARTZ IN THE PRESENCE OF ADSORBED LAYERS

Introduction. The double layer formed when glass comes into contact with polymer films, which usually become negatively charged, indicates the donor properties of surface atoms. At the same time, the charge of the double layer determines the strength of the adhesive bond that is formed. One method for studying it may be the determination of the changes undergone by surface conductivity when the surface is coated with layers of other molecules, beginning with monolayers and ending with polymolecular layers. Thus, for example, an increase in surface electrical conductivity may indicate the transition of electrons to new energy levels, which also play a role in the formation of the double layer. (Of course, the mechanism of the increase in electrical conductivity may also be different.)

The surface conductivity of quartz and various glasses has been studied in the presence of water vapor, but there are no data on the effect upon it of the adsorption of organic compounds. Zechnowitzer (^{1}), in 1929, while studying the surface electrical conductivity of rock-salt crystals, found that whereas the conductivity in vacuum at room temperature is $10^{-15}\ \Omega^{-1}$, in the presence of benzene vapor it increases to $10^{-12}\ \Omega^{-1}$.

Studies by N. Chirkov (^{2}) showed that the conductivity of a mica plate treated with HCl increases in the presence of ethyl alcohol vapor in comparison with the conductivity in vacuum. These data indirectly indicate that adsorption of vapors of organic compounds should also influence the surface conductivity of quartz.

Method. In the present work the surface electrical conductivity of quartz was studied in vapors of water, benzene, CCl_4, and alcohols.

The apparatus for studying surface electrical conductivity (Fig. 1) was made of quartz glass. Into test tube 1 was poured the substance whose vapor adsorption was being studied. In the middle part of the apparatus a specimen 2, in the form of a rod with a platinum lead-in to the apparatus, was fastened; 4—a guard ring, 3—a mercury seal. A voltage was applied to one lead-in of the apparatus, while the other lead-in was connected to the grid of the electrometer tube of the amplifier. The amplifier was assembled in a bridge circuit (^{3}) using an

Fig. 1. Apparatus for studying surface electrical conductivity in vacuum. Fig. 2. Kinetics of the surface electrical conductivity of quartz during adsorption; a —water, b—ethyl, v—butyl, g—hexyl alcohols.

Figure 1: Fig. 1. Apparatus for studying surface electrical conductivity in vacuum. Fig. 2. Kinetics of the surface electrical conductivity of quartz during adsorption; a—water, b—ethyl, v—butyl, g—hexyl alcohols.

electrometer tube and made it possible to measure a minimum current of 10^{-13} A.

Specimens in the form of rods 1-3 mm in diameter were drawn in a burner flame from cylinders of optical quartz. After repeated boiling in fresh portions of distilled water, electrodes were applied to the specimens by firing on silver paste. This method of applying electrodes had previously been used by G. I. Skanavi (^{4}) and M. S. Aslanova (^{5}), whose experiments showed that silver electrodes obtained by firing on paste provide firm contact and give the most stable results.

Before measurements, the apparatus was evacuated with a two-stage fractionating pump operating on "Octoil 5"oil. The pressure was measured with a McLeod manometer. To prevent oil vapors from entering, the trap located directly in front of the apparatus was immersed in a Dewar vessel with liquid nitrogen, and the liquid in test tube 1 was frozen. After the pressure in the apparatus had fallen to 10^{-5} mm Hg, it was sealed off from the vacuum system.

Different vapor pressures were obtained by setting the temperature difference between sample 2, thermostated at a constant temperature T_c, and the liquid in test tube 1. By setting different temperatures T in the test tube with the liquid, the vapor pressure in the instrument was varied, while the saturated vapor pressure near the surface of the sample remained constant.

Fig. 1. Apparatus for studying surface electrical conductivity in vacuum

Fig. 2. Kinetics of the surface electrical conductivity of quartz during adsorption; *a*—water, *b*—ethyl, *v*—butyl, *g*—hexyl alcohols

Thus, any relative pressure p/p_s could be set, where p and p_s (the saturated vapor pressures at temperatures T and T_c, respectively) were calculated from tabulated data using the usual interpolation formula

$$\lg p = A + \frac{B}{T},$$

where A and B are constants.

Sample 2 was thermostated by passing water from a thermostat at temperature T_c through jacket 6. The test tube with the liquid under study was placed in another thermostat 5, in which the temperature T was varied.

Fig. 3. Isotherms of the surface electrical conductivity of quartz during adsorption; *a*—water, *b*—butyl, *c*—hexyl, *d*—octyl alcohols

Figure 2: Fig. 3. Isotherms of the surface electrical conductivity of quartz during adsorption; *a*—water, *b*—butyl, *c*—hexyl, *d*—octyl alcohols

The temperatures T and T_c were measured with Beckmann thermometers with a scale division of 0.01°. To determine how well the temperature difference read from the Beckmann thermometers corresponded to the actual difference between the temperature of the sample and the temperature of the liquid in the test tube, a check was carried out using a differential thermocouple, one junction of which was placed at the position of the sample and the other in the test tube. The accuracy of measuring the temperature difference was 0.01°. The temperature differences read from the thermometers and measured by the thermocouple differed by no more than 0.01°.

Before the experiment, the quartz apparatus for measuring surface electrical conductivity was washed with chromic mixture and then treated in hot steam for 5-6 hours. The quartz sample was heated to white heat. For comparison, several samples were cleaned by treatment in a glow discharge according to the method developed in the Laboratory of Surface Phenomena of the Institute of Physical Chemistry, Academy of Sciences of the USSR, by V. V. Karasev ([8]).

Results of measurements. Both for samples treated in a glow discharge and for quartz cleaned by ignition, the surface conductivity in vacuum proved to be below the sensitivity of the method, i.e., less than 10^{-17} Ω^{-1}.

At the beginning of each experiment the surface conductivity of the specimen was measured at temperature T_c with the substance frozen, i.e., at $p/p_s = 0$. In the case of optical-quartz specimens the surface conductivity was always less than 10^{-17} Ω^{-1}. Then the substance was thawed and test tube 1 was lowered into thermostat 5. At the same time, at a constant relative pressure p/p_s, the surface conductivity at first increases rapidly, reaches a maximum, then gradually decreases and after 10-20 min assumes an unchanging value corresponding to the given p/p_s. Such kinetic curves were obtained for all the substances studied except benzene and carbon tetrachloride, even saturated vapors of which did not change the surface conductivity of quartz (to an accuracy of 10^{-17} Ω^{-1}).

Fig. 3. Isotherms of the surface electrical conductivity of quartz during adsorption; *a*—water, *b*—butyl, *c*—hexyl, *d*—octyl alcohols.

Analogous kinetics of the conductivity of adsorbed water layers was observed in [9]. The authors explain these maxima by the transition of the initially amorphous layer of adsorbed water into the crystalline state.

Figure 2 presents kinetic curves for water, ethyl, butyl, and hexyl alcohols. The maxima observed here are obtained only when the first point of the isotherm of surface electrical conductivity is taken in a given experiment, i.e., when there are no adsorbed molecules of the substance under study on the quartz surface.

Figure 3 presents isotherms of the surface electrical conductivity for water, butyl, hexyl, and octyl alcohols. For the measurements, water twice distilled in a quartz apparatus was used. The remaining preparations were from Kahlbaum and, for dehydration before the experiment, were boiled in vacuum with shavings of metallic calcium in the apparatus for measuring surface conductivity. Table 1 gives the values of the surface conductivity of quartz in the absence of adsorption and when saturated with vapors of various substances.

Table 1

Substance adsorbed on quartz	$x_{p/p_s=0}$, Ω^{-1}	$x_{p/p_s=1}$, Ω^{-1}
Water	$< 1 \cdot 10^{-17}$	$\sim 1 \cdot 10^{-11}$
Ethyl alcohol	$< 1 \cdot 10^{-17}$	$\sim 5 \cdot 10^{-12}$
Butyl alcohol	$< 1 \cdot 10^{-17}$	$\sim 5 \cdot 10^{-14}$
Hexyl alcohol	$< 1 \cdot 10^{-17}$	$\sim 1 \cdot 10^{-15}$
Heptyl alcohol	$< 1 \cdot 10^{-17}$	$\sim 5 \cdot 10^{-15}$
Octyl alcohol	$< 1 \cdot 10^{-17}$	$\sim 5 \cdot 10^{-15}$
Carbon tetrachloride	$< 1 \cdot 10^{-17}$	$< 1 \cdot 10^{-17}$
Benzene	$< 1 \cdot 10^{-17}$	$< 1 \cdot 10^{-17}$

Discussion of results. The surface conductivity of optical quartz was measured in vapors of water, benzene, carbon tetrachloride, ethyl, butyl, hexyl, heptyl, and octyl alcohols. The isotherms obtained show that in the range of relative pressures 0.8-1, for the alcohols the surface conductivity changes by a factor of 2-3; only for ethyl alcohol is this increase considerably greater.

and the isotherm is similar in form to the isotherm of the surface conductivity of water. For benzene and carbon tetrachloride, surface conductivity was absent within the sensitivity limits of the method (10^{-17} Ω^{-1}), even at saturation and supersaturation, although, as shown in the work of B. V. Deryagin and Z. M. Zorin ([6,7]), for these substances near saturation the thickness of the adsorption layer reaches values even greater than for the polar substances investigated.

Comparison of the growth of the surface electrical conductivity of the substances studied with the growth of the thickness of the films formed by them during adsorption reveals a quantitative discrepancy: over the same interval of variation of relative pressures, the film thickness increases faster than the conductivity.

The second result of the work is the observed kinetics of the surface conductivity of the substances studied during adsorption on a clean surface of optical quartz. Apparently, in the initial moments an nonequilibrium adsorption layer is formed on the quartz surface, the molecules of which, first, do not have the equilibrium orientation and, second, occupy sites not necessarily having the maximum adsorption energy (owing to the inhomogeneity of the surface), which corresponds to an increased surface conductivity. This is followed by orientation of the adsorbed molecules and their transition to sites with greater adsorption energy.

The process of orientation propagates from the lower layers to the upper ones, as a result of which an adsorbed layer is formed with firmly adsorbed molecules and an ordered structure, possessing a constant, considerably lower conductivity corresponding to the given relative pressure. When the subsequent points of the isotherm of surface electrical conductivity are taken, newly arriving molecules either are adsorbed at vacant sites from which they can no longer pass to others with lower energy levels, since these are occupied, or else are oriented by the already existing ordered layer; and the surface conductivity reaches the value corresponding to the new relative pressure more rapidly and without exhibiting sharply elevated values at the initial moments of time.

The results obtained do not yet make it possible to state with confidence which mechanism of surface conductivity is brought into operation by adsorbed layers of molecules—electronic or ionic.

Laboratory of Surface Phenomena
Institute of Physical Chemistry
Academy of Sciences of the USSR

Received
21 I 1958

CITED LITERATURE

1. E. V. Tsekhnovitser, ZhRFKhO, phys. part, **61**, No. 5, 487 (1929).
2. N. M. Chirkov, ZhFKh, **21**, issue 11, 1303 (1947).
3. G. I. Berleev, *Uspekhi fizicheskikh nauk*, **49**, issue 1, 93 (1953).
4. G. I. Skanavi, *Dielectric Polarization and Losses in Glasses and Ceramic Materials with High Dielectric Permittivity*, 1952.
5. M. S. Aslanova, Doctoral dissertation, Moscow, 1954.
6. B. V. Deryagin, Z. M. Zorin, DAN, **98**, 93 (1954).
7. B. V. Deryagin, Z. M. Zorin, ZhFKh, **29**, issue 6 (1955); **29**, issue 10 (1955).
8. V. Karasev, G. I. Izmailova, ZhTF, **24**, 871 (1954).
9. Sh. Kurosaki, Sh. Saito, G. Sato. *J. Chem. Phys.*, **23**, No. 10 (1955).