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GRAVIMETRIC AND QUANTUM-CHEMICAL STUDY OF INTERACTION OF MONOETHANOLAMINE VAPOR WITH SILICA SURFACE

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Abstract

Kinetics of the monoethanolamine vapor adsorption on the surface of silica previously deposited onto quartz plate was examined by the piezoelectric microweighing. With the assumptions which are in accord with the experimental data, the kinetic equation of the process was obtained and thus the adsorption and desorption constants were found. The structure of the possible adsorption complexes was studied in the framework of the quantum-chemical MNDO method and the conclusion was made that the two-center adsorption of the monoethanolamine on the silica surface proceeds as a two-stage process with the participation of both functional groups. The bonding is mainly effected owing to the proton-acceptor properties of amine groups.

Keywords: adsorption mechanism, monoethanolamine, piezoelectric microweighing, silica

Introduction

For years piezoelectric crystals have already been used for the measurement of small variations in mass. As early as in 1959, Sauerbrey revealed that a change of the resonance frequency of a crystal caused by the deposition of thin uniform film of adsorbate on its surface is equal to a frequency decrease caused by a quartz layer of the same mass [1]. This observation is widely used in studies of gas adsorption [2, 3] and relative humidity [4], in measurements of thickness of deposited films [5], in design of gas chromatography detectors [6, 7], in qualitative revealing and quantitative determination of pollutants in air [8–10]. The theoretical estimation of the sensitivity of the method of piezoresonance microweighing gives a value 10^{-12} g [11], whereas in practice the maximum limit may be as much as 10^{-9} g [6]. The essential weakness of the method is its unselectivity: adsorption of any gas results in a change of mass and, hence, the resonance frequency. To attain the selectivity, as a rule, the previous chemical treatment of the surface of a piezoquartz crystal or a coating is needed in accord with the aim of investigation. On the coating of specific layers which provide

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their donor-acceptor bonds [12], H-bonds [13] or complexes with analyte [14], the selectivity increases and the selective sensors, relative to the chosen class of compounds can be developed. Currently, silica films are used as sorbent coatings, and chemically modified surfaces for covalent fixation of the desired compounds [15, 16].

Experimental

In this study, the surface of piezoquartz resonators was treated with a triethoxysilane solution with the resulting formation of a thin uniform silica film with terminal OH groups. The mass of the coated silica layer is varied from 40 to 70 μg providing efficient absorption of monoethanolamine (MEA) vapor. The availability of basic ($-NH_2$) and acidic (–OH) functional groups in MEA molecule causes the possibility of its two-center adsorption and a relatively large variety of surface complexes. In this connection, it is extremely important to determine the rates of MEA adsorption on the surface of dispersed silica (DS). This enables us to determine the rate constants of adsorption and desorption and to find the conditions for attainment of an adsorption equilibrium.

Results and discussion

Figure 1 illustrates the experimental time dependence of the MEA mass adsorbed on the DS surface. It is characterized by three sections. Section *a* represents the adsorption of MEA saturated vapor. When removing the sensor from the chamber, the mass sharply increases due to the water adsorption from air (section *b*); this evidences for the presence of hydrophylic adsorption complexes on the surface. The MEA desorption from the DS surface is represented by section *c*.

The kinetic equation of the process under study was obtained on the natural assumptions, namely: interaction of MEA with the surface is reversible; adsorption is

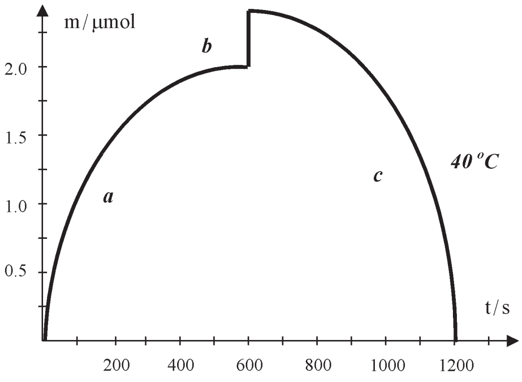

Fig. 1 Change of the mass of monoethanolamine adsorbed on the surface of silica grafted onto a piezoquartz plate

bimolecular process; desorption is monomolecular process; adsorbed molecules do not interact one another; all surface sites are equivalent. In this frame, the interaction of saturated MEA vapor with the DS surface is given by the stoichiometric equation:

$$\equiv\mathrm{SiOH}+\mathrm{HOCH_2CH_2NH_2}\overset{k_1}{\underset{k_2}{\rightleftarrows}}[\equiv\mathrm{SiOH}\text{---}\mathrm{H_2NCH_2CH_2OH}]$$

where k_1 (k_2) is the rate constant of adsorption (desorption) and the time (t) dependence of the mass (m) of the adsorbed substance is of the form

$$m=\frac{\alpha\beta(\mathrm{e}^{-2\mathrm{tk}_1\gamma}-1)}{\beta\mathrm{e}^{-2\mathrm{th}_1\gamma}-\alpha} \tag{1}$$

where $\gamma=\sqrt{p^2/4-a_{\mathrm{in}}b_{\mathrm{in}}}$; $\alpha=p/2+\gamma$; $\beta=p/2-\gamma$; $p=k+a_{\mathrm{in}}+b_{\mathrm{in}}$; a_{in} and b_{in} – masses (in μmol) of silica grafted onto the quartz plate and MEA vapor in the working volume of the chamber, respectively; $k=k_1/k_2$ – is the equilibrium constant.

The adsorption rate constant is expressed as

$$k_1=\frac{1}{2t\gamma}\ln\frac{\alpha\beta-m\alpha}{\alpha\beta-m\beta} \tag{2}$$

On the use of this equation, those values of t and m were taken, for which the mean square deviation between experimental data (Fig. 2, curve 1) and values found from Eq. (1) (Fig. 2, curve 2) is minimal.

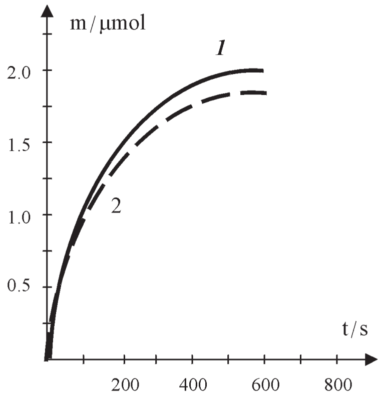

Fig. 2 Experimental (1) and calculated (2) dependencies of mass of adsorbed monoethanolamine as a function of time

As is clear from Fig. 2, the initial stages of adsorption are well described by Eq. (1). With saturation of active sites of the surface, there appear some discrepancies between experimental and calculated values. In our opinion, this occurs because the surface has active sites of various nature.

For section *a* the rate constant of the forward reaction was found to be $2.3\cdot10^{-2}$ (μmol s)$^{-1}$ and the rate constant of the reverse one is $1.2\cdot10^{-2}$ s^{-1}; for section *c* these constants are $1.4\cdot10^{-2}$ s^{-1} and $2.3\cdot10^{-2}$ (μmol s)$^{-1}$, respectively.

To establish the nature of the bonding of MEA molecule with silica surface, the quantum-chemical examination of relevant model clusters was performed by MNDO method [17]. A silica surface was represented by the segment of the (111) face of β-cristobalite with terminal OH groups (Fig. 3). According to the structural data used by us the distance between neighboring hydroxyl groups on the (111) face of the β-cristobalite surface is equal to 5.4 Å (Fig. 3) and characteristical sizes of a MEA molecule depending on its conformation are 5–6 Å. In view of the great flexibility of the HO–CH_2–CH_2–NH_2 chain, i.e. relatively small barriers of rotation about single bonds, it is possible to assume that two-site adsorption of a MEA molecule is the most probable on neighboring hydroxyl groups.

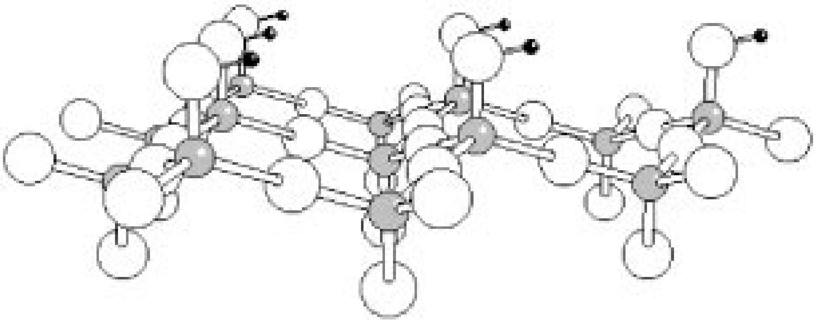

Fig. 3 Structure of a cluster modeling the (111) face of β-cristobalite with terminal groups

A recent book [18] demonstrates that the essential features of possible structure of adsorption complexes on the solid surface can be obtained from the corresponding distributions of electrostatic potential (ρ).

Figure 4 displays the electrostatic potential profile at the (111) face of β-cristobalite in the plane that passes through neighboring hydroxyl groups perpendicularly to the hexagonal ring plane. From this figure one can see that in the vicinity of oxygen atoms of hydroxyl groups there are relatively compact regions of negative ρ values that are the most favorable for localization of hydrogen atoms of amine and hydroxyl groups. In the vicinity of hydrogen atoms of terminal OH groups there are extended and diffuse regions of positive potential values, and during adsorption these regions are favorable for localization of unshared electron pairs of nitrogen and oxygen atoms.

First, let us consider constitution of surface complexes formed during one-site adsorption of MEA molecules. Our calculations showed that the most stable complex (K1) is formed with the aid of an unsymmetrical hydrogen bond O···H···N, in which a structural hydroxyl group of the surface acts as a proton donor. The energy of its bonding (E_{bnd}) is equal to –64.5 kJ mol^{-1}. In this situation, three-atom fragment O···H···N has a bent structure (<OHN=166.5°), which ensures localization of amine group protons in the negative ρ value region for the initial hydroxylated surface. Validity of the inference about such a constitution of the complex is also corroborated

by experimental data [19–21]. According to these data the chemisorption of MEA on pyrogenic silica containing mainly free structural silanol groups at 343 K is completed within 15 h [19]. In spectra for samples synthesized under such conditions there is no band at 3750 cm^{-1} (valence vibrations of silanol groups), but there is an intense absorption band in the range of the valence vibrations of N–H (3390 cm^{-1}) and C–H bonds (3330 cm^{-1}).

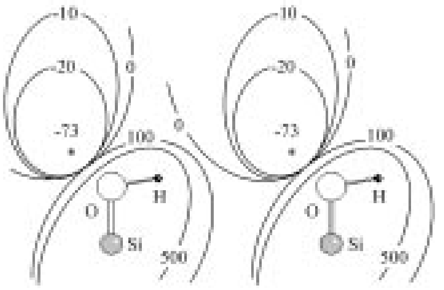

Fig. 4 Profile of the electrostatic potential (kJ mol^{-1}) in the vicinity of the (111) face of the β-cristobalite surface in the plane that passes through neighboring hydroxyl groups perpendicularly to the hexagonal ring plane

The formation of the next-in-stability surface complex (K2) (E_{bnd}= –41.2 kJ mol^{-1}) is also effected owing to an unsymmetrical hydrogen bond O···H···N, but in this case the role of the proton donor is performed by amine groups of MEA molecules. Localization of the proton that ensures bonding almost exactly coincides with the minimum of ρ for the starting hydroxylated surface. The surface complexes occurred because of the symmetrical hydrogen bond O···H···O proved to be less stable than those considered above. Moreover, for complex K3, in which the proton donor is a hydroxyl group of a MEA molecule, the binding energy is equal to –22.4 kJ mol^{-1}, which provides evidence for the possibility of formation of a bound state, while for complex K4, where the proton donor is a surface hydroxyl group, E_{bnd}= +56.0 kJ mol^{-1}. In the former case the stability is ensured by localization of the proton of an OH group of a MEA molecule in the region of the potential minimum for the starting hydroxylated surface. In the case of complex K4 such a stabilizing factor is absent. From Fig. 4 it is also seen that in the vicinity of surface silicon atoms there are continuous regions of positive potential values, which gives evidence for a general possibility of formation of surface complexes due to coordination of hydroxylated silicon atoms by unshared electron pairs of oxygen or nitrogen atoms of MEA molecules. However, the direct calculations showed that the binding energy for such complexes is positive, and they are not formed because of steric hindrances.

Now, let us turn to two-site adsorption. The calculations showed that the most stable was the complex (Fig. 5) whose formation involved an amine group of adsorbed molecule as an acceptor of the proton of a surface hydroxyl group and an OH group as a proton donor for the oxygen atom of the neighboring surface group. The binding energy for this complex is equal to –79.6 kJ mol^{-1}, i.e. the value which is slightly less than the sum of the binding energies for complexes K1 and K3. This difference, to our mind, is due to small conformational stresses developed in an MEA molecule during its two-site adsorption.

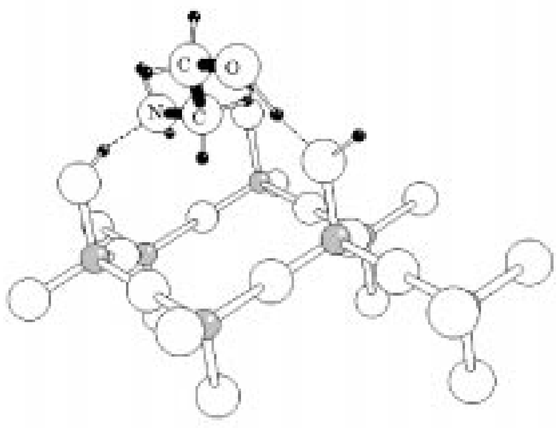

Fig. 5 Schematic representation of an adsorption complex formed during two-site adsorption of an MEA molecule by the dispersed silica surface. Chemical bonds in the cluster modeling a part of the (111) face of the β-cristobalite surface are shown by double lines, those in an MEA molecule are shown by bold lines; hydrogen bonds are shown by dotted lines

According to the available experimental data [22] sorption of MEA by the dispersed silica surface depends on its preliminary treatment, and as the temperature increases from 293 to 837 K the number of adsorbed molecules increases.

From our calculated data it is possible to suggest the following mechanism of adsorption of MEA by silica surface. At low temperatures dispersed silica adsorbs molecules as a result of hydrogen bonding with formation, mainly, of complexes K1 and K2 owing to unsymmetrical hydrogen bonds. As the temperature increases, low conformational barriers in a MEA molecule are overcome and an additional stabilization of complex K1 is effected due to formation of hydrogen bonds between protons of OH groups of adsorbed molecules and oxygen atoms of neighboring terminal hydroxyl groups of the surface.

Thus, two-site adsorption of monoethanolamine on dispersed silica proceeds as a two-stage process with participation of both functional groups. The bonding is mainly effected owing to proton-accepting properties of amine groups.

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