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PHYSICOCHEMICAL PROCESSES
AT THE INTERFACES

Adsorption of Vinyl Trimethoxysilane and Formation of Vinyl Siloxane Nanolayers on Zinc Surface from Aqueous Solution

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Abstract—The method of quartz crystal microbalance is used to study adsorption of vinyl trimethoxysilane (VS) on the surface of zinc from an aqueous solution. Adsorption isotherms are obtained. Approaches corresponding to the known adsorption isotherms are used for interpretation of adsorption data: Langmuir, BET, Flory–Huggins, Langmuir multicenter, Temkin, and Langmuir–Freundlich. It is shown that silanes are adsorbed on the surface of thermally deposited zinc from aqueous solutions and displace adsorbed water from the surface by occupying more than six adsorption sites on the surface. It is found that monolayer coverage of the zinc surface is reached at a concentration of the VS solution of 1×10^{-4} M. The neighboring adsorbate molecules can interact, forming siloxane dimers and trimers bound to the metal surface by either covalent or hydrogen bonds. Adsorption heats are calculated using different adsorption models. It is shown that VS is chemosorbed on the surface of zinc. An increase in the concentration of the VS solution up to 0.1 M results in formation of polycondensed siloxane oligomers on the surface with polycondensation degree $n = 8$–12. Oligomer surface fragments are connected with each other by hydrogen bonds and are connected with the surface by Zn–O–Si bridge bonds. The overall thickness of such a layer is 10–12 nm or ten molecular layers.

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INTRODUCTION

Modern technological progress provides a high rate of development of nonferrous metallurgy. Zinc occupies the third place after aluminum and copper in the overall production of industrial nonferrous metals and the overall production of zinc is more than 16% of the annual smelting of nonferrous metals. Zinc, zinc-based alloys, and different zinc compounds are widely applied for engineering and nonengineering targets owing to their special properties. In recent years, zinc-based alloys have been used for the manufacturing of cast protectors for corrosion protection of boats and metallic structures. Zinc is most widely used for coating metal sheets, manufacturing crude products and mold castings. Thus, about 45% of the world production of zinc is used for steel metallization. However, despite increased resistance, zinc undergoes corrosion degradation, which often results in loss of functional and decorative characteristics of products and coatings [1, 2]. Development of new methods of enhancing corrosion stability of zinc is a topical problem. One such method is to form nanosize functional layers on the metal surface [3, 4].

Organosilicon compounds (alkoxysilanes) with the general formula of $R_nSi(OC_2H_5)_{4-n}$ are environmentally friendly compounds and have shown good results as adhesion promotors, metal corrosion inhibitors, and coating (antiadhesion) layers in lithography and in a number of other fields [5–9] that can adsorb on the surface of inorganic substrates and form self-organizing siloxane nanolayers [10]. Alkoxysilane molecules are characterized by high affinity to a wide spectrum of inorganic substrates [5] and owing to their bifunctionality can, on the one hand, condense with hydroxyl surface groups forming strong and hydrolytically stable Me–O–Si bonds with the hydroxylated metal surface. On the other hand, neighboring silane molecules on the surface can undergo polycondensation with formation of surface self-organizing siloxane nanolayers [7] that can be used for different purposes. In addition, alkoxysilanes can be used for formation of functional nanolayers on the zinc surface [10–12].

Adsorption of alkoxysilane molecules on the metal surface is the first stage of formation of a self-organizing layer. Despite the intense research that has taken place on the formation and properties of self-organizing siloxane layers on the surface of inorganic materials, the mechanism of silane adsorption on the zinc surface has, in fact, not been studied. Vinyl trimethoxysilane $CH_2{=}CHSi(OCH_3)_3$ (VS) is an industrially available reagent capable of forming self-organizing nanolayers on the surface of nonferrous metals [13], which can be used for corrosion protection of zinc products.

In this connection, the aim of this work was to study the mechanism of adsorption of vinyl trimethoxysilane (VS) on the surface of zinc from an aqueous solution and evaluation of the effect of self-organizing VS-based layers on the physico-chemical behavior of the metal.

EXPERIMENTAL

Vinyl trimethoxysilane $CH_2{=}CHSi(OCH_3)_3$ (especially pure grade), solid zinc (TsV00 grade) with zinc content of 99.997 were used in the work [14].

Coatings of zinc and its alloys on the metal surface are obtained using a number of techniques, among which one can list plasma–electrochemical [15], galvanic [16], and physical methods of coating application [17]. Here, physical methods of vacuum thermal deposition are obviously best suited for model physico–chemical studies, which is related to the possibility of obtaining high–purity zinc coatings. Besides, the optimum choice of the mode of vacuum thermal deposition of metals allows obtaining metallic and metal–oxide nanocomposites with an ordered structure characterized by unique functional properties [17, 18].

Therefore, in order to ensure purity and reproducibility of adsorption studies, VS adsorption was studied on the surface of a zinc layer thermally deposited from vacuum. A zinc sample was placed into a tungsten evaporator and heated to the evaporation temperature by applying the 16 A current in vacuum (10^{-6} mm Hg) (a VUP 2 exhaust cart).

The supports used for application of a zinc layer were a quartz crystal resonator (QC-10-AuBU) with gold sputtering, AT-cut, with a basic frequency of 10 MHz, and silicate glass with a thickness of 2 mm, geometric size of 1.5 × 30 mm, and surface area of 4.5 cm^2. The support surface was degreased by alcohol, rinsed by water, and dried in air at the room temperature.

The metal layer thickness and amount of adsorbed VS was determined by quartz crystal microbalance [19] on an EQCN700 setup (Elchema, United States) by measuring variation of the quartz resonator frequency during the sputtering and calculating mass variation due to metal deposition:

$$\Delta m = -(N\rho S\Delta f / f_0^2),$$

where f_0 is the basic frequency, $f_0 = 10000$ kHz; Δm is the variation of the mass of silane (g); Δf is the variation of the piezo-quartz resonator frequency (kHz); N is the frequency constant (in the case of AT-cut crystals, $N = 1670$ kHz mm); ρ is the density of quartz, $\rho = 2.65$ g/cm^3; and S is the working area of quartz, $S = 0.72$ cm^2.

The deposited metal mass was used to calculate the layer thickness assuming uniform zinc distribution on the surface. The thickness of the obtained layer was 1.1 ± 0.1 μm.

After the end of deposition, the working volume was evacuated for 30 min, after which air was supplied, with samples then being removed and placed into a dessicator with dehydrated $CaCl_2$. Adsorption was studied 15 h after metal deposition. The true surface area was estimated by comparing the resistance of the sputtered metal layer with the tabulated value of zinc and the ratio of the true and visible surface area values were calculated. Comparison of the resistance of the sputtered metal layer with the tabulated value of specific electric resistance showed a 2.64-fold difference; i.e., the true surface area was 2.64 times larger than the visible surface area. All calculations were carried out taking into account the true metal surface area.

Adsorption of vinyl trimethoxysilane was studied using an in situ quartz crystal microbalance in the solution by measuring variation of the quartz resonator frequency after adding methoxysilane to the solution. After a constant frequency was established, the sample was conditioned in the solvent to remove reversible sorbed substance. The adsorbed silane mass was calculated according to the above formula.

Variation of the zinc surface state was characterized by an in situ quartz crystal microbalance and ex situ Fourier-transform infrared spectroscopy (FT–IR). Infrared spectra were obtained using a HYPERION-2000 IR microscope coupled with an IFS-66 v\s Bruker Fourier spectrometer (ZnSe crystal, 150 scan., resolution of 3 cm^{-1}, range of 4000–600 cm^{-1}).

RESULTS AND DISCUSSION

Previous works studied adsorption of VS on copper and aluminum and showed [7, 13] that modification of metal surfaces in aqueous VS solutions resulted in formation on the metal surface of self-organizing nanolayers. The thickness of such layers is determined by the concentration of the modifying solution. Adsorption of vinyl trimethoxysilane on the surface of zinc was determined by measurement of the frequency of a quartz resonator when the adsorbate is added to the solution. Figure 1 shows the adsorption isotherm of VS on the surface of zinc. The curve shape (Fig. 1) corresponds to polymolecular adsorption isotherms. Submonolayer surface coverage was observed at low concentrations (up to 1×10^{-4} M). Judging by the curve shape corresponding to the Langmuir isotherm at low concentrations, the monolayer coverage is reached at the concentration of the VS solution of 1×10^{-4} M. In addition, about 20 ng of vinyl trimethoxysilane are adsorbed on the surface, which corresponds to the surface coverage of 3 molecules per 1 nm^2. Calculation of the molecule geometry showed that compact monolayer package corresponds to 2.4 vinyl trimethoxysilane molecules per 1 nm^2 of the surface and 4.34 silanol molecules/nm^2 in the case of hydrolysis of silane observed in the aqueous solution. The thickness of the layer here was about 0.9 nm.

Additionally, it is found that, in the case of concentrations not exceeding 5×10^{-3} M, the adsorbed VS

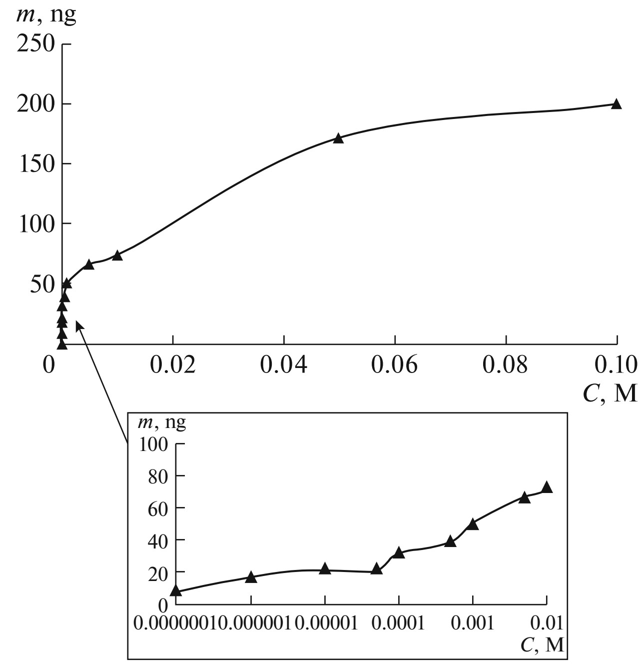

Fig. 1. Adsorption isotherm of VS on the surface of thermally deposited zinc. Quartz crystal microbalance.

layer consists of reversible and irreversible parts. The reversibly sorbed layer is easily removed from the surface by sample conditioning in pure water for 10 min (Fig. 2a). Here, the amount of reversibly adsorbed VS often exceeds the gain in the amount of irreversibly sorbed adsorbate. When the concentration of 1 × 10^{-2} M was reached, no decrease in the sample mass as a result of conditioning in water was observed (Fig. 2b). Apparently, silanol molecules enter polycondensation with the neighboring molecules at high solution concentrations, which hinders removal from the surface to the solution. Here, a "thick" siloxan layer, up to ten molecular layers, is used that can be considered irreversibly sorbed. Such irreversibly sorbed surface layers are stable under exposure to water for at least 4 h; in the meantime, the sample mass remains practically unchanged.

A Fourier–IR study of the sputtered metal surface was performed to research chemical processes occurring in the course of formation of vinyl siloxane nanolayers on the surface of zinc. Figure 3 shows FTIR spectra of VS applied from solutions of different concentration and attribution of band coordinates to the chemical composition of surface groups is presented in Table 1.

As seen in Fig. 3, infrared spectra obtained for surface VS nanolayers of different thicknesses are similar, which indicates a close chemical composition of the obtained layers. The most intense bands in the spectra are the bands of –OH valence vibrations (3450–3500 cm^{-1}) and H–O–H– deformation vibrations (1591, 1550 cm^{-1}) [20], which indicates the presence of hydroxyl groups on the surface of zinc. The FTIR spectrum of the zinc surface with applied VS layers (Fig. 3) contains bands attributed to the vinyl siloxane layer formed as a result of hydrolysis and polycondensation of silane molecules on the surface. Thus, the bands at 780 and 826 cm^{-1} and an intense wide band in the range of 1080–1090 cm^{-1} correspond to vibrations of the Si–O–Si fragment, while the bands at 1185 and 1203 cm^{-1} can be attributed to symmetric and asymmetric vibrations of the Si–O bonds of the Si–O–Si fragment [20–22]. The obtained data indicate the presence of a polycondensed siloxane layer on the surface that is formed already at the 1 × 10^{-6} M VS concentration in the solution. An increase in concentration from 1 × 10^{-6} to 1 × 10^{-4} M results in no enhancement of bands corresponding to the Si–O–Si group (Fig. 3, curves *1*, *2*); moreover, the intensity value even decreases. An increase in the solution concentration to 0.1 M leads to an increase in the intensity of the above bands (Fig. 3, curve *3*), which may point to the more complete occurrence of the polycondensation reaction. The spectra (Fig. 3) also contained bands corresponding to the organic radical in the silane molecule. Thus, the band at 1590 cm^{-1} is in the range close to vibrations of

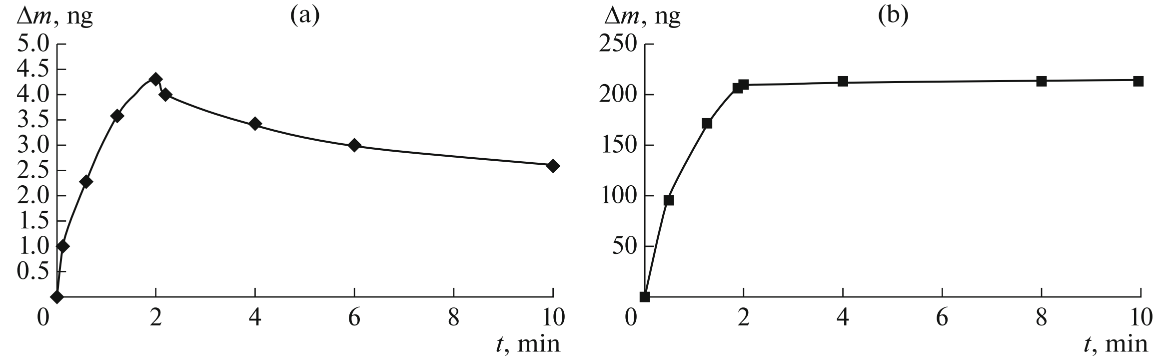

Fig. 2. Kinetics of variation of the amount of adsorbed VS in the course of sample conditioning in water after application of VS on the surface of zinc from the solution with the VS concentration of (a) 1 × 10^{-5}, (b) 5 × 10^{-1} M.

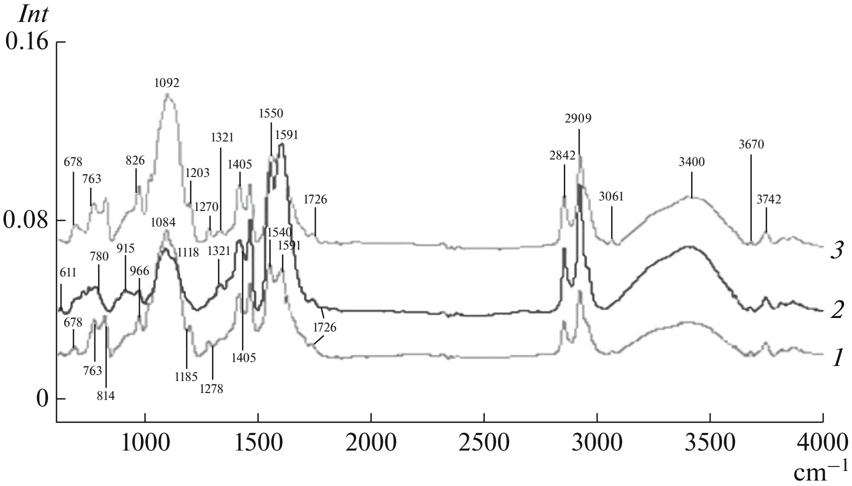

Fig. 3. FT–IR spectra of the surface of sprayed zinc coated by nanolayers based on VS applied from aqueous solutions with the VS concentration of: (*1*) 1×10^{-6} M (less than 1 VS monolayer), (*2*) 1×10^{-4} M (1 VS monolayer), and (*3*) 0.01 M (10 molecular layers of VS).

the $-CH=CH_2$ double bond; the bands at 2909 and 2842 cm^{-1} correspond to valence vibrations of the C–H bond; the band at 1456 cm^{-1} corresponds to deformation vibrations of the C–H bond [23]; and the bands at 763, 865, 1270 cm^{-1} correspond to vibrations of the Si–C bonds.

In all spectra, bands at 679, 696, 966 and 3740 cm^{-1} corresponding to the silanol group were observed [21, 24]. The band at 3670 cm^{-1} can be attributed to hydrogen bonds. In addition, surface layers formed in solutions with a low VS concentration (Fig. 3, curves *1*, *2*), manifested a band at 611 cm^{-1} absent in the layer obtained in the 0.1 M VS solution (Fig. 3, curve *3*). It can be attributed to the methoxy group of vinyl trimethoxysilane. All the obtained spectra (Fig. 3) contain weak bands in the range of 890–920 cm^{-1} that can be attributed to vibrations of the –Me–O–Si– surface groups [20, 24]. Thus, vinyl trimethoxysilane on the surface of sputtered zinc is hydrolyzed according to reaction (1) forming silanol; moreover, the hydrolysis reaction is not completed in the layers formed in low-concentration solutions and some molecules contain methoxyl groups. Apparently, these molecules do not

Table 1. Adsorption bands observed in FT–IR spectra of thermally deposited zinc with supported VS nanolayers

Band coordinate, cm^{-1}	Band attribution	Band coordinate, cm^{-1}	Band attribution
611	Vinyl trimethoxysilane SiOR	1118	Si–O–Si
679	Vinyl trimethoxysilane SiOH	1185	Symmetric and antisymmetric vibrations of the Si–O bond
696	Silanetriol	1203	Coordination bond Si–O in Si–O–Si
763	Vibrations of the –Si–C bond	1270	Si–C Si–CH_2
780	Si–O–Si	1405	Vibrations of $-CH_2=CH$
827	Si–O–Si	1456	Deformation vibrations of the C–H bond
865	Vibrations of the Si–C bond	1591	$CH=CH_2$
890–920	Si–O–Me	2842	Valence vibrations of the C–H bond
966	Si–OH	2910	Vibrations of –CH, $-CH_2$
1018	Vibrations of the Si–C bond	3061	Valence vibrations of the C–H bond
1051	Si–O–Si	3400	–OH, H–O–H
1084	Si–O–Si	3670	Hydrogen bond
1092	Si–O–Si	3742	–Si–OH

Table 2. Use of the known adsorption isotherms for description of VS adsorption on the surface of zinc from dilute aqueous solutions

No.	Isotherm	Correlation R	Monolayer capacity, ng/cm^2	Monolayer capacity, mol/nm^2	"Landing area" of the molecule, nm^2/mol	f (Temkin isotherm)	n (Langmuir multicenter adsorption isotherm)	x (Flory–Huggins isotherm)	h (Langmuir–Freundlich isotherm)	Interaction energy, kJ/mol
1	Langmuir	0.999	59.67	2.20	0.46					
2	BET	0.996	107.34	4.33	0.23					25.31
3	Temkin	0.934				17.65				55.47
4	Langmuir multicenter adsorption	0.901					6.90			48.59
5	Flory–Huggins	0.901						6.90		33.97
6	Langmuir–Freundlich	0.958							0.62	20.24

enter the polycondensation reaction. An increase in the concentration of the VS solution results in complete hydrolysis of all silane molecules and their entering the polycondensation reaction with formation of siloxane oligomers on the surface. Here, silanol molecules interact with hydroxyl groups on the metal surface forming Zn–O–Si bonds (reaction 2).

$$\begin{gathered}CH_2=CHSi(OCH_3)_{3aq}+H_2O\\ \rightarrow CH_2=CHSi(OH)_3,\end{gathered} \tag{1}$$

$$\begin{gathered}CH_2{=}CHSi(OH)_3+\ HO{-}Zn{-}\\ \rightarrow CH_2=CH(OH)_2Si{-}O{-}Zn{-}.\end{gathered} \tag{2}$$

Adsorption of vinyl trimethoxysilane from the aqueous solution was studied in more detail in order to understand the mechanism of surface layer formation. For this purpose, adsorption data (Fig. 1) were processed using the known adsorption isotherms: Langmuir [25], BET [25], Temkin [26], Flory–Huggins [27], Langmuir–Freundlich [28], and multicenter Langmuir isotherm [23]. Equations describing the corresponding isotherms are presented below (3)–(8):

—Langmuir (3):

$$1/C = 1/m_m + C^*(1/m_m b), \tag{3}$$

where C is the VS concentration (M); m is the adsorbed VS mass (ng); m_m is the monolayer capacity at compact coverage, ng; and b and k are constants.

—BET (4):

$$C/m^*(1 - C) = 1/m_m k + C^*(k - 1)/m_m k, \tag{4}$$

where C is the VS concentration (M); m is the adsorbed VS mass (ng); m_m is the monolayer capacity at compact coverage, ng; and b and k are constants.

—Flory–Huggins (5).

$$\ln(\theta/C) = x - 1 + \ln K + x\ln(1 - \theta), \tag{5}$$

where C is the concentration, θ is the surface coverage, x is the replacement factor (the amount of replaced water molecules), and K is the adsorption equilibrium constant.

—Temkin (6)

$$\theta = a + \frac{1}{f}\ln C, \tag{6}$$

where a is a constant used to calculate K and f is the metal surface nonuniformity factor.

—Langmuir–Freundlich (7):

$$\log\left[\frac{\theta}{(1-\theta)}\right] = h\log K + h\log C, \tag{7}$$

where C is the concentration, θ is the surface coverage, c is the number of adsorption centers occupied by the adsorbate molecule, K is the adsorption equilibrium constant, and h is the surface nonuniformity degree.

—Langmuir multicenter adsorption (8)

$$\log(\theta/C) = \log K + n\log(1 - \theta), \tag{8}$$

where C is the concentration, θ is the surface coverage, n is the number of adsorption centers occupied by the adsorbate molecule, and K is the adsorption equilibrium constant.

Adsorption heat ΔG°_{ads} is calculated by determining adsorption equilibrium constant K in (4)–(8) according to Eq. (9) [29]:

$$K = \frac{1}{55.5}\exp\left(\frac{\Delta G^\circ_{ads}}{RT}\right), \tag{9}$$

where R is the universal gas constant and T is the temperature.

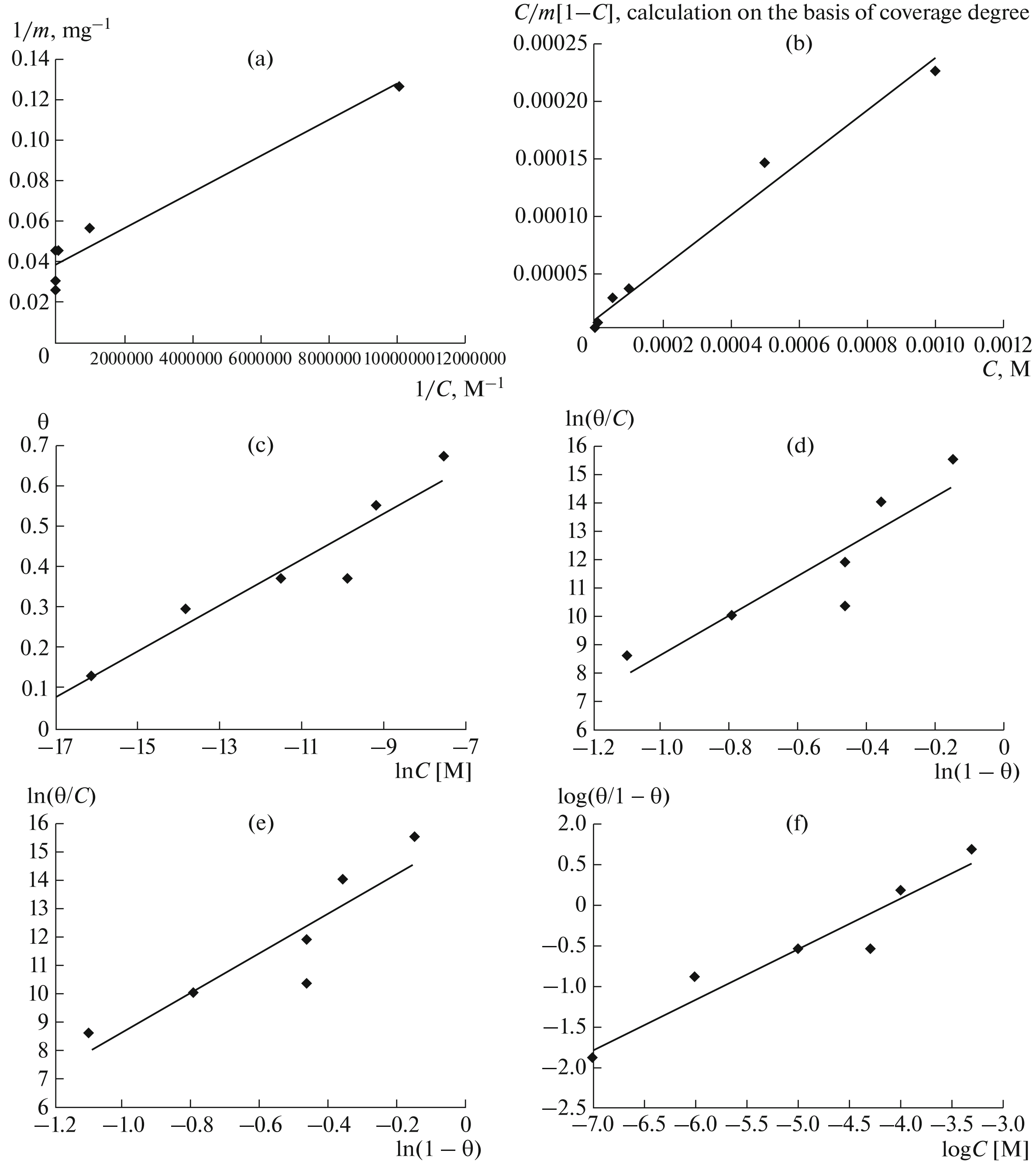

Fig. 4. Adsorption isotherm of vinylmethoxysilane on the surface of thermally deposited zinc in the coordinates of adsorption isotherms: (a) Langmuir, (b) BET, (c) Temkin, (d) Flory–Huggins, (e) Langmuir–Freundlich, and (f) Langmuir multicenter adsorption.

Parameters calculated on the basis of adsorption isotherms (3)–(8) for the vinyl siloxane layer adsorbed on the surface of zinc are presented in Table 2. It is found that adsorption of vinyl trimethoxysilane from solutions at the concentrations of up to 1×10^{-3} M on the surface of thermally deposited zinc is well described by the above isotherms (Fig. 4, Table 2).

Presenting the adsorption isotherm of VS in Langmuir (Eq. (3)) and BET (Eq. (4)) coordinates allows determining the value of monolayer capacity, which is 59.67 and 107.34 ng/cm^2 for calculation in the terms of Langmuir and BET, respectively. Recalculating monolayer capacity to surface coverage showed that 1 nm^2 of surface sorbs 2.4–4.3 molecules in the case of monolayer coverage, while the surface area occupied by 1 VS molecule is from 0.455 to 0.231 nm^2, respectively. Calculation of conventional radii of fragments –Si–O–C–H and –Si–O– based on the bond lengths and atomic radii yields 0.725 and 0.541 nm for methoxy and silanol groups, which corresponds to the following values of surface areas occupied by individual molecules: 0.413 and 0.229 nm^2 per molecule. Such surface areas correspond to coverage of 1 nm^2 of the surface of zinc by 2.42 vinyl silane molecules and 4.35 vinyl silanol molecules. Coincidence of the calculated and experimental coverage values allows assuming the vertical arrangement of molecules on the metal surface.

As shown by IR studies (Fig. 3), in the case of submonolayer coverage, the surface contains both vinyl silanol and vinyl silane (nonhydrolyzed) molecules (Fig. 5a). In the case of surface coverage below one monolayer, vinyl silanol molecules interact with each other and with hydroxyl surface groups forming siloxane fragments strongly bound to the surface (Fig. 5b). Processing adsorption data using Temkin isotherm (6) confirms that there is a strong bond to the surface, as nonuniformity factor *f* was 17.65 (Table 2), which is close in order of magnitude to the values of *f* calculated using isotherms of specific adsorption of anions on smooth platinum [26].

Calculation of adsorption heat according to (9) using different adsorption models (Table 2) shows that adsorption heat can reach 55 kJ/mol, which also confirms that there is formation of chemical bonds between adsorbed molecules and the surface.

Processing adsorption data using approaches employed for description of adsorption in liquid media (Eqs. (3)–(6)) shows that VS adsorption on zinc is based on displacement, i.e., the adsorption isotherm is described by Flory–Huggins equation (5) (Fig. 4d). Adsorption results in water displacement from the surface. Using Eq. (5) yields *x* equal to 6.9; i.e., VS displaces more than six water molecules from the surface of zinc in the course of adsorption. In addition, a silane molecule can occupy more than one adsorption site on the surface. Langmuir multicenter adsorption isotherm (8) was used to determine the amount of adsorption centers on the surface, where it is assumed that there are *n* adsorption sites on the surface. Plotting adsorption data in the coordinates of Eq. (6) yields a straight line with the correlation coefficient above 0.9, which indicates applicability of the Langmuir multicenter adsorption isotherm in the case of VS. The value of *n* is 6.9; i.e., each adsorbate molecule occupies on average 6.9 adsorption centers. This means that the density of adsorption centers on the surface of zinc is from 15 to 30 per 1 nm^2. These data are confirmed by the results of IR studies showing a wide intense band at 3400 cm^{-1} (Fig. 3) corresponding to hydroxyl surface groups remaining "free" after adsorption of vinyl silane; i.e., vinyl silanol interacts only with a fraction of hydroxyl groups and leaves most of them unaffected.

Thus, analysis of adsorption isotherms of VS shows that, at the initial stages, VS is adsorbed, displaces adsorbed water, and each silane or silanol molecule is adsorbed vertically and occupies more than six adsorption sites on the surface. The neighboring molecules interact with each other, forming siloxane fragments, most probably dimers and trimers, bound to the metal surface by either covalent or hydrogen bonds (Fig. 5b).

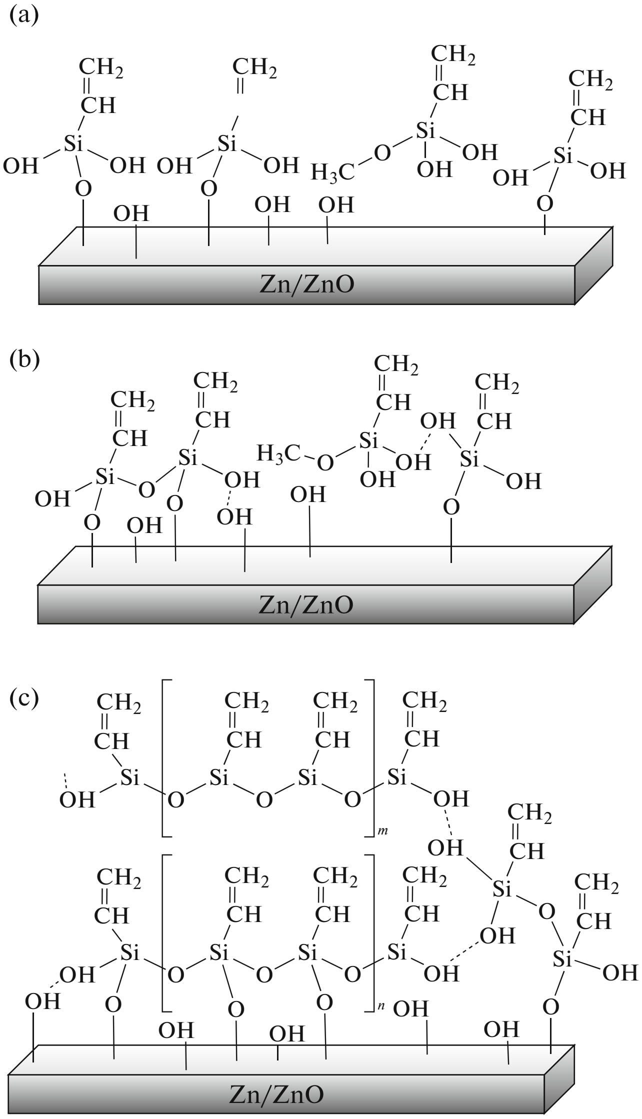

Fig. 5. Scheme of formation of a vinyl siloxane nanolayer on the surface of zinc. (a) Initial stage of adsorption, the concentration of VS solution is up to 1×10^{-4} M. (b) Monolayer formation, the concentration of VS solution is 1×10^{-4} M. (c) Formation of an ordered 10-nm-thick vinyl siloxane nanolayer, the concentration of VS solution is 0.1 M.

An increase in the concentration of VS solution to 0.1 M results in complete hydrolysis of adsorbate molecules on the surface and formation of an ordered nanolayer of polycondensed siloxane oligomers on the zinc surface. Oligomerization degree *n* determined on the basis of the ratio of intensities of the corresponding bands after 10 min of conditioning in the VS solution is 8–12. Oligomer surface fragments are connected with each other by hydrogen bonds, which is confirmed by the corresponding band in the IR spectrum (Fig. 3, Table 1), and they are connected with the zinc surface by Zn–O–Si bridge bonds (Fig. 5b). The overall thickness of such a layer is 10–12 nm or ten molecular layers.

CONCLUSIONS

1. It is shown that vinyl silane is adsorbed on the surface of thermally deposited zinc from aqueous solutions and displaces adsorbed water from the surface by occupying more than six adsorption sites on the surface.

2. It is found that monolayer coverage of the zinc surface is reached at the concentration of the VS solution of 1×10^{-4} M. The neighboring adsorbate molecules can interact forming siloxane dimers and trimers bound to the metal surface by either covalent or hydrogen bonds.

3. Adsorption heats are calculated using different adsorption models. It is shown that VS is chemosorbed on the surface of zinc.

4. An increase in the concentration of the VS solution up to 0.1 M results in formation of polycondensed siloxane oligomers on the surface with polycondensation degree $n = 8–12$. Oligomer surface fragments are connected with each other by hydrogen bonds and are connected with the surface by Zn–O–Si bridge bonds. The overall thickness of such a layer is 10–12 nm or ten molecular layers.

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