The study of copper dissolution in aqueous and nonaqueous systems $DMSO—HX_{solv}$ (solv = H_2O, X = Br, Cl; solv = MeCN, $PhNO_2$; X = Cl) by resistometric method

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Copper dissolution in the aqueous systems $DMSO—HX_{solv}$ (solv = H_2O; X = Cl, Br) under the inert atmosphere and under aerobic conditions at different acid concentrations was studied by the resistometric method by measuring the resistance of a metal sample in the course of the reaction. The overall activity of the system decreases with a decrease in the concentration of the starting hydrohalic acid. The rate of copper dissolution in the extremum points also decreases. The process of the metallic copper dissolution in nonaqueous systems, such as $DMSO—HCl_{solv}$ (solv = MeCN, $PhNO_2$), was studied. In the latter systems, as opposed to aqueous systems, only one maximum in the plot of the copper dissolution rate *versus* the component ratio is observed. The change in the nature of the solvent in the donor-acceptor electron transport system $DMSO—HCl_{solv}$ (solv = H_2O, MeCN, $PhNO_2$) results in the change in the position of the maximum of the copper dissolution rate, as well as in the change in its value. The rate of copper dissolution in the above mentioned systems varies in the following series: H_2O < MeCN < $PhNO_2$.

Key words: dimethyl sulfoxide, hydrohalic acids, water, dipolar aprotic solvents, copper, oxidative dissolution, complexation, adsorption.

Comprehensive studies of organic and aqueous-organic donor-acceptor electron transport systems (DAET-systems) capable of oxidizing zero-valent transition metals along with noble metals are important for the optimal use of these systems for both the direct synthesis of coordination compounds of metals and the solution of the practical problems in the metal extraction from industrial waste and from different types of mineral raw materials, which contain precious metals and concomitant elements.[1]

The oxidative dissolution of metals in DAET-systems, such as $DMSO—HBr_{solv}$ (solv = H_2O, "Chernogolovskaya Vodka"),[2] occurs due to the formation of intermediate particles, which are the products of donor-acceptor interaction of the liquid phase components between each other and with the surface of the solid phase (*i.e.*, with the metal). The nature of the oxidants of aqua regia (HNO_3 + HCl) is well known and studied (NOCl, $Cl_2 \cdot H_2O$). The principle of the action of "Chernogolovskaya Vodka" is similar to that of aqua regia; the active particles are formed as a result of the reaction of the starting reagents (components of the liquid phase), which are inert toward the metal, between each other and with the surface of the solid phase (metal). As in the case of aqua regia one of the metal-oxidizing particles is a solvated halogen molecule ($Me_2S \cdot X_2$).[2]

Previously,[3—6] the resistometric method has been proposed for the study of the metal dissolution kinetics in DAET-systems. In this method, the metal dissolution rate (metal wire is used) is calculated from the change in its electric resistance in the course of the reaction. The study of the copper and gold dissolution in the system $DMSO—HX_{aq}$* (X = Br, Cl) by resistometric method showed that the dissolution rate depends on the DMSO to HX ratio, as well as on the concentration of the initial solution of hydrohalic acid (water content). The stronger the acid used in the experiment, the higher the reaction rate.[5,6] However, the dependence of the metal dissolution rate on the initial acid solution concentration was not yet studied systematically.

To establish the influence of the concentration of hydrohalic acid in the initial solution (the content of water introduced into the system together with the acid) on the rate of metal dissolution, in the present work the process of metallic copper dissolution (in the inert atmosphere as well as in air) in aqueous systems $DMSO—HX_{aq}$ (X = Cl, Br) was studied by resistometric method with

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* For $DMSO—HX_{solv}$ systems, where solv = H_2O, the notation $DMSO—HX_{aq}$ is used.

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varying the initial acid concentration. Taking into account the water concentration, which is introduced with the acid (*Z* coordinate), the three-dimensional surfaces of activities of the systems DMSO—HX_{aq} (X = Br, Cl) toward copper in 3D coordinates were built, which can be used to predict the behavior of the system in any point on the surface. In addition, to elucidate the role of water, the comparative study of the metallic copper dissolution was performed (in air) in the aqueous (DMSO—HCl_{aq}) as well as in the nonaqueous (DMSO—HCl_{solv}; solv = $PhNO_2$, MeCN) DAET-systems.

In organic nonaqueous systems, such as DMSO—HCl_{solv}, the dipolar aprotic solvents ($PhNO_2$ and MeCN) are not involved in the equilibrium reaction of DMSO with HCl, but act as solvents for the gaseous hydrogen chloride. The final purpose of this research is to develop DAET-systems in which the medium has no considerable influence on the equilibrium concentration of the reaction products of the DAET-system initial components, including the oxidizer formed in the system.

Experimental

Non-insulated copper wires with diameters of 100 and 180 μm (Cu 99.99%) (copper, which is the gold-related metal, can be used as a model metal for the improvement of the experimental procedures for the oxidative dissolution of noble metals in the above described systems) were used in the experiments. The organic solvents (DMSO, MeCN, and $PhNO_2$) were purified by known procedures.[7] Hydrochloric and hydrobromic acids (HX_{aq}) were distilled under reduced pressure; the concentration of the acids was controlled by the density measurement with an areometer (the accuracy of measurements is 0.001 g cm^{-3}).

When the experiment was conducted in the inert atmosphere, the oxygen was removed directly before the experiment by bubbling argon through the corresponding component of the system (DMSO or HX) for 30 min and subsequent flushing with argon. Argon of high purity was used as the inert gas.

Gaseous hydrogen chloride was obtained by the known procedure.[8] Solutions of HCl in MeCN and $PhNO_2$ (HCl_{solv}) were prepared by passing dry gaseous hydrogen chloride through the corresponding solvents. The maximum concentration of the resulting HCl solution in MeCN was 5 mol L^{-1}; of the HCl solution in $PhNO_2$, 0.6 mol L^{-1}. For the experiments the solution was diluted with the corresponding solvent. The HCl concentration in the solutions was determined by titration with the standard alkali solution (NaOH).

The rate of copper dissolution was determined by resistometric method from a change in the electric resistance *R* of the sample (a thin wire with the radius *r*) measured in the course of the reaction with the use of an improved automated unit. The description of the method, the scheme of the unit, the general procedure of the experiment, and the principles of calculation of the metal dissolution rate determined by resistometric method were described in detail in the paper.[4] Here we show only the final expression for the calculation of the metal dissolution rate

$$W = -(1/S)(dm/dt) = -\gamma(dr/dt),$$

where *W* is the rate of metal dissolution, g cm^{-2} s^{-1}; *S* is the surface area of the sample, cm^2; *m* is the weight of the sample, g; *t* is the time of dissolution, s; *r* is the wire radius, cm; γ is the metal density, g cm^{-3}.

In the present work, the rate of the process was expressed with the use of the unit of measure reflecting the number of atomic layers being dissolved in 1 s (at. layers s^{-1}), because it is considered as one of the most informative and convenient units for the comparison with the results of other experiments:

$$W = -[(\gamma/M)N_A]^{1/3}(dr/dt),$$

where *W* is rate of dissolution, at. layers s^{-1}; *M* is the molecular weight; N_A is Avogadro´s number.

The study of the dependence of the copper dissolution rate on the ratio of liquid phase components. One of the components was poured into a thermostated reactor, the sample (thin wire) was placed into the reactor, and the measurement was started. Then, while the sample was left in the solution, the second component was added portionwise. The measurements were conducted for 600 s for every ratio of the components after the stabilization of the temperature. The course of the reaction was monitored on the display, where the dependence $U = f(t)$ (where *t* is the time from the beginning of the experiment, s; *U* is the voltage of the resistance bridge unbalance, one arm of which is the sample, mV) was graphically plotted. From the experimental data $U = f(t)$, the resistance *R* and the radius *r* of the sample were calculated and the rate of metal dissolution for every region of the measurements with the different ratios of the liquid phase components was determined. Examples of both the graphical representation of the experiments (experimental dependence of $U = f(t)$, for the calculated radius of the sample $r = f(t)$) and the treatment of the experimental data were presented in the paper.[6] The time dependence of the change in the radius is linear, the reaction rate in every region is constant and proportional to the slope of the straight line.

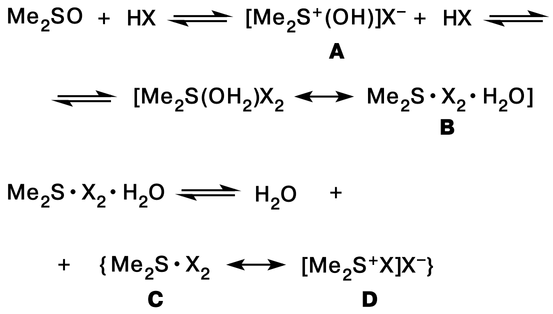
Taking into account the water concentration introduced with the acid (*Z* coordinate), the surfaces of activities of the systems DMSO—HX_{aq} ($T = 40$ (HBr) and 60 °C (HCl) in both the argon atmosphere and air) were built for copper in 3D coordinates *W*—$[H_2O]$—n_{HX}, where *W* is the rate of copper dissolution, at. layers s^{-1}; $[H_2O]$ is the water concentration, mol L^{-1}; n_{HX} is the molar fraction of HX_{aq} in the system, $n_{HX} = \nu_{HX}/(\nu_{HX} + \nu_{DMSO})$. The HCl concentration was 27, 30, 32, 35, and 37%; HBr, 33, 36, 41, 43.5, 45, and 46.6%.

Results and Discussion

Copper dissolution in aqueous systems DMSO—HX_{aq} (X = Br, Cl) in the argon atmosphere and in air. *The regions of activity of the system DMSO—HX_{aq} toward metallic copper in 3D coordinates.* In systems DMSO—HX_{aq} (X = Br, Cl) dimethyl sulfoxide and hydrohalic acid react in the absence of the metal, that can result in the accumulation of the products reactive toward the metallic surface in the bulk. Previously[5,9] the scheme of the sequential accumulation of the particles reactive in metal oxidation has been proposed (Scheme 1).

The behavior of the system depends on the nature of the halogen. When X = Br the reaction is in equilibrium.[10]

Scheme 1



$$Me_2SO + HX \rightleftharpoons \underset{\textbf{A}}{[Me_2S^+(OH)]X^-} + HX \rightleftharpoons$$

$$\rightleftharpoons \underset{\textbf{B}}{[Me_2S(OH_2)X_2 \longleftrightarrow Me_2S \cdot X_2 \cdot H_2O]}$$

$$Me_2S \cdot X_2 \cdot H_2O \rightleftharpoons H_2O \; +$$

$$+ \; \{\underset{\textbf{C}}{Me_2S \cdot X_2} \longleftrightarrow \underset{\textbf{D}}{[Me_2S^+X]X^-}\}$$

As it has been shown previously,[9] the equilibrium concentration of metal-oxidizing particles is achieved in five days after the mixing of the components of the system DMSO—HBr_{aq} at room temperature. Therefore, in the systems DMSO—HBr_{aq} stored for some time (from several hours to several days), the rates are considerably higher than in freshly prepared mixtures.[5] It should also be noted, that the activity of the system containing HBr («Chernogolovskaya vodka») remains unchanged for 5 years.

Oppositely, for the system DMSO—HCl_{aq} freshly prepared mixtures are active, while after keeping for some time (for more than one day) the system loses its oxidizing ability due to the intra- or intermolecular chlorination of the methyl group to form chlorodimethyl sulfide (Scheme 2).[5]

Scheme 2

$$[Me_2S^+(OH)]Cl^- \longrightarrow MeSCH_2Cl + H_2O$$

$$Me_2S + Cl_2 \longrightarrow MeSCH_2Cl + HCl$$

So, in the system DMSO—HCl_{aq}, unlike in DMSO—HBr_{aq} system, the polarized halogen molecule is not produced, and, consequently, the system oxidizes gold only to Au^I ([$(Me_2S)AuCl$] complex).[11]

The influence of the initial solution concentration of hydrohalic acid (the content of water introduced into the system along with the acid) on the rate of copper dissolution in the system DMSO—HX_{aq} was studied by resistometric method. The dependences of the copper dissolution rate on the molar fraction of HX_{aq} at the fixed temperature (in the air atmosphere) and at different concentrations of the initial acid are shown in Figs 1 ($[HBr]_{aq}$ = 33—47%) and 2 ($[HCl]_{aq}$ = 27—37%).

As can be seen from Figs 1 and 2, the total activity of the system decreases with a decrease in the initial hydrohalic acid concentration; the rate of copper dissolution decreases in the extrema (especially in the region of the big maximum, n_{HX} = 0.85—0.9). The strongest influence of the initial HX_{aq} concentration (content of water introduced along with the acid) on the rate of copper dissolution is observed for the system DMSO—HBr_{aq}; at [HBr] <36% (see Fig. 1, curves *1* and *2*) the rate of copper dissolution in the system approaches zero. This is probably specified by the fact that the system DMSO—HBr_{aq} is in equilibrium, and water in the system is not only the component of the system (the solvent) but is also formed during the equilibrium reaction of the starting reagents[12] and, thus, it influences the equilibrium concentration of the particles, which are produced in the system and are capable of oxidizing the metal.

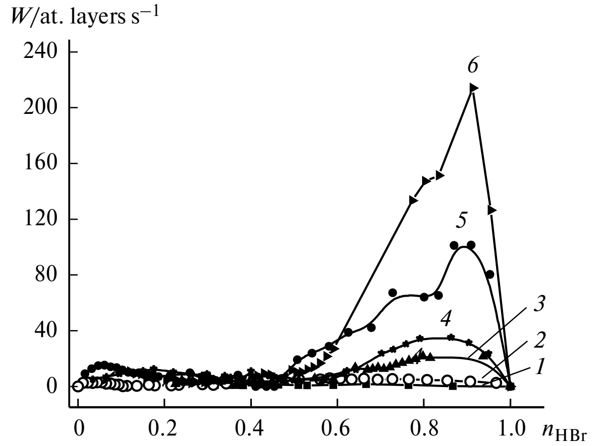


Fig. 1. The dependence of the rate of copper dissolution on the molar fraction of HBr_{aq} (n_{HBr}) (*T* = 40 °C, in air) at the initial acid concentrations 33 (*1*), 36 (*2*), 41 (*3*), 43.5 (*4*), 45 (*5*), and 46.6% (*6*).

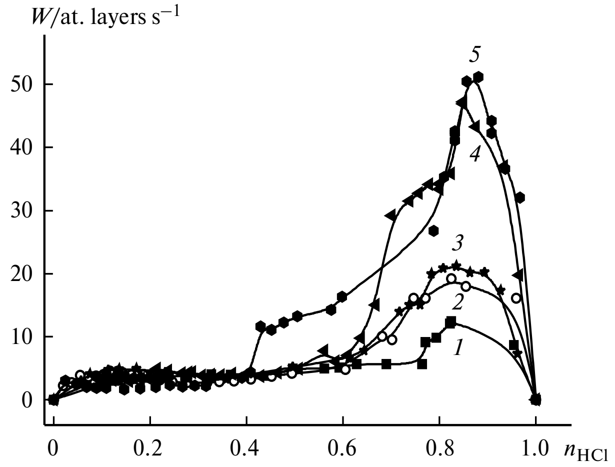


Fig. 2. The dependence of the rate of copper dissolution on the molar fraction of HCl_{aq} (n_{HCl}) (*T* = 60 °C, in air) at the initial acid concentrations 27 (*1*), 30 (*2*), 32 (*3*), 35 (*4*), and 37% (*5*).

$$Me_2SO + 2\,HBr \rightleftharpoons Me_2S + Br_2 + H_2O$$

Taking into account the concentration of water introduced with the acid (*Z* coordinate), the surfaces of activity toward metallic copper in the air atmosphere (Figs 3, *a* and 4, *a* for X = Br and Cl, correspondingly) and in the argon atmosphere (Figs 3, *b* and 4, *b* for X = Br and Cl, correspondingly) for the system DMSO—HX_{aq} were built at a fixed temperature in 3D coordinates W—[H_2O]—n_{HX}.

The analysis of the surfaces of activities of systems DMSO—HX_{aq} toward metallic copper shows that the metal-oxidizing particles appear in two regions of the component ratio: 1) at $n_{HX} = 0.05$ and 0.15 (an excess of Me_2SO and a relatively low water concentration); 2) at $n_{HX} = 0.8$ and 0.9 (an excess of HX (H_2O), *i.e.* under conditions when water comes to the system along with an increase n_{HX}).

The 3D surfaces of activity of the systems DMSO—HX_{aq} (X = Cl, Br) toward metallic copper allow predicting its behavior at any site on the surface.

Influence of the atmosphere (argon, air) on the rate of copper dissolution in aqueous systems DMSO—HX_{aq} (X = Br, Cl). If the system DMSO—HX_{aq} is exposed to air, it is necessary to consider the influence of molecular oxygen on the character of activity of DAET-systems. The analysis of the surface profiles shows that in the region of

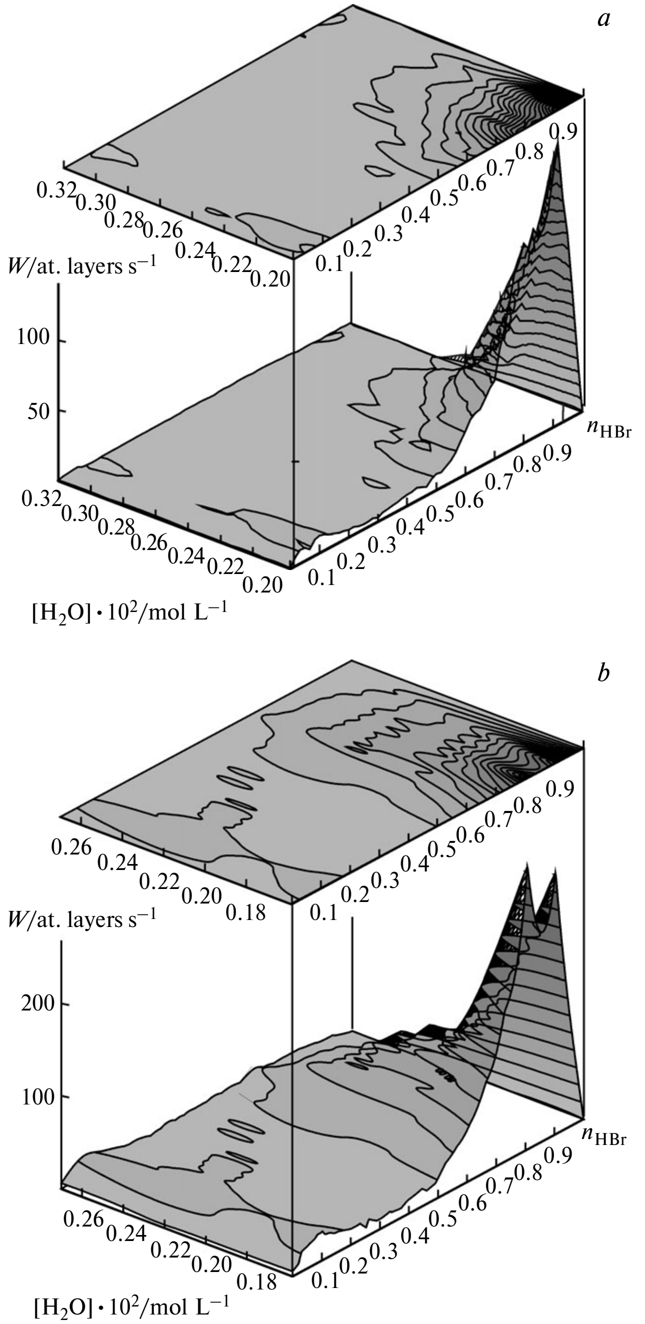


Fig. 3. The regions of activity of the system DMSO—HBr_{aq} upon copper dissolution (T = 40 °C) in the air atmosphere (*a*) and in an argon atmosphere (*b*).

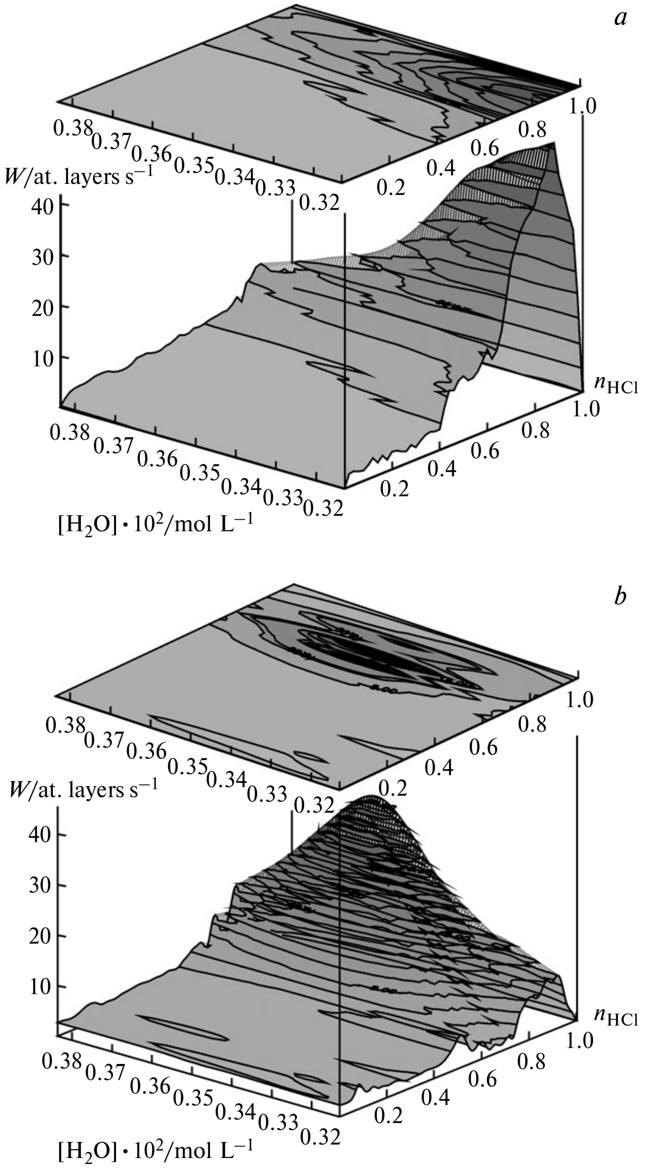


Fig. 4. The regions of activity of the system DMSO—HCl_{aq} upon copper dissolution (T = 60 °C) in the air atmosphere (*a*) and in an argon atmosphere (*b*).

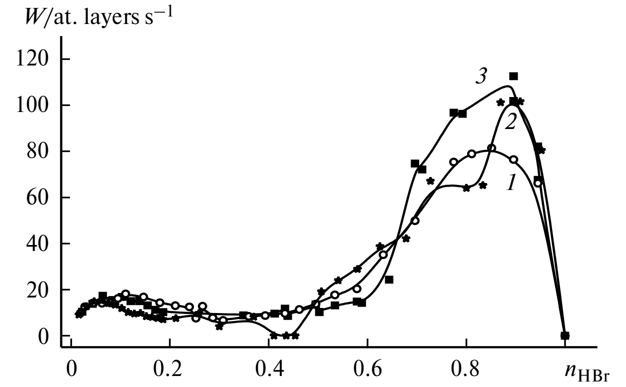


Fig. 5. The dependence of the rate of copper dissolution on the molar fraction of HBr_{aq} (n_{HBr}) ([HBr] = 45%), T = 40 °C) in an argon atmosphere (*1*), in the air atmosphere (*2*), and in the intensive air flow (*3*).

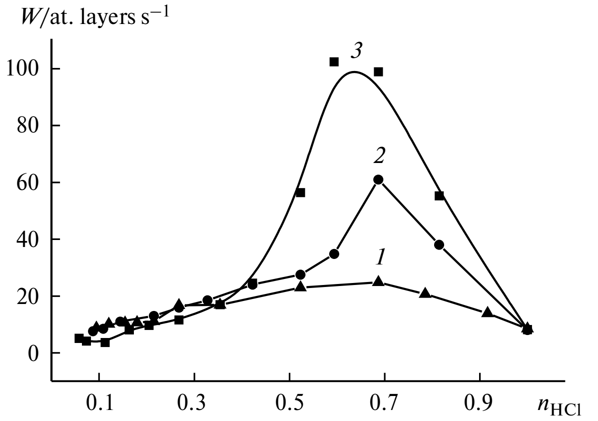


Fig. 6. The dependence of the rate of copper dissolution on the molar fraction of HCl_{solv} (n_{HCl}) (T = 40 °C, in air) in the system DMSO—HCl_{solv} (solv = $PhNO_2$) at different HCl concentrations in nitrobenzene: 0.3 (*1*), 0.45 (*2*), and 0.6 mol L^{-1} (*3*).

the big maximum (n_{HX} = 0.8—0.9) in the plot of the metal dissolution rate *versus* the molar fraction of the components of the media in the air atmosphere (see Figs 3, *a* and 4, *a*) a shoulder of variable intensity appears, which is absent when the reaction is carried out in the inert atmosphere (see Figs 3, *b* and 4, *b*). When copper is dissolved in the system DMSO—HBr_{aq} ([HBr] = 45%) at an intensive air flow, this shoulder (Fig. 5, curve *3*) is broadened and smoothed.

It can be assumed that the appearance of the shoulder on the big peak in the curve *2* (see Fig. 5) is due to the concurrent participation of molecular oxygen in the metal oxidation when the reaction is carried out in air.

Copper dissolution in nonaqueous DAET-systems DMSO—HCl_{solv} (solv = $PhNO_2$, MeCN). Two maxima in the plots of the reaction rate *versus* the component ratio at n_{HCl} = 0.15 and 0.85 are observed upon copper dissolution in the aqueous system DMSO—HCl_{aq}, which is indicative of the formation of two types of particles active in metal oxidation in the system.[5] Ascribing the presence of two maxima to the role of water, we tried to exclude its influence on the process of metal dissolution. For this purpose the copper dissolution in nonaqueous DAET-systems DMSO—HCl_{solv} (HCl_{solv} is the solution of the gaseous hydrogen chloride in the corresponding solvent) was studies. The dependence of the rate of copper dissolution in the systems DMSO—HCl_{solv} on the component ratio (molar fraction of HCl_{solv} (n_{HCl})) in the air atmosphere is shown in Figs 6 (solv = $PhNO_2$) and 7 (solv = MeCN).

As it is seen from Figs 6 and 7, the system which does not contain water has only one rate maximum. The rates of copper dissolution in organic media are an order of magnitude higher than those for the dissolution in aqueous media. Thus, despite instability of the solution of hydrogen chloride in nitrobenzene and its low concentration (not higher than 0.6 mol L^{-1}), as well as the limited solubility of the products in the media, the rates of copper dissolution are high: in the maximum (at n_{HCl} = 0.6) W = 105 at. layers s^{-1} (see Fig. 6).

In acetonitrile hydrogen chloride dissolves considerably better than in nitrobenzene; the maximum concentration of HCl in MeCN is 5 mol L^{-1}. Taking into account the difference in solubility of gaseous HCl, the system DMSO—HCl_{solv} (solv = MeCN) is intermediate in activity between aqueous and nitrobenzene media. The rate maximum is also intermediate in position (n_{HCl} = 0.75).

The aqueous system is the least active. Under these conditions, the rates of the process for the aqueous HCl solution with this concentration (0.6—5 mol L^{-1}) are at the limit of the method ($W \approx$ 1.5 at. layers s^{-1}). Therefore, water slows down the process of metal dissolution.

Comparing the studied systems, one can come to the conclusion that the solvent properties strongly influence

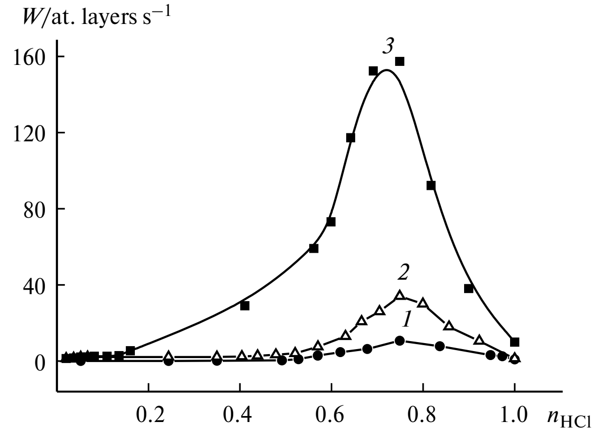


Fig. 7. The dependence of the rate of copper dissolution on the molar fraction of HCl_{solv} (n_{HCl}) (T = 40 °C, in air) in the system DMSO—HCl_{solv} (solv = MeCN) at different HCl concentrations in acetonitrile: 1.01 (*1*), 1.62 (*2*), and 2.52 mol L^{-1} (*3*).

the kinetics of metal dissolution. Despite the fact that polar media should be thermodynamically more favorable as a solvent of the products (copper complex compounds), the order of the kinetic activity is reversed. The rate of copper dissolution depending on the nature of the solvent changes in the following order: H_2O < MeCN < $PhNO_2$.

This difference in the activity of the systems DMSO—HCl_{solv} can be apparently attributed to the change in the absorbability of the reagents of the system on the metal surface upon using different solvents. It can be assumed that the lowest activity of the aqueous system in the solvents under study can be associated with the high absorbability of water on the metal surface[13] and with the probable competition between water and the reagent for the adsorption sites on the metal surface.

Summing up, the change in the nature of the solvent in DAET-systems DMSO—HCl_{solv} (solv = H_2O, MeCN, and $PhNO_2$) leads to both a change in the position of the maximum of the metal dissolution rate and to a change in its value. This makes it possible to design DAET-systems selective toward metals. For example, it was found that gold, unlike copper, is insoluble in the nonaqueous organic system DMSO—HCl_{solv}. This is a prerequisite for the design of systems for selective dissolution of gold and copper, for example, in the process of gold refinement.

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