

Control of Kinetic Parameters and Rate-Determining Step Nature of Hydrogen Evolution Reaction on Iron

V.I. Vigdorovich^a, L.E. Tsygankova^{b*}, N.V. Shel^c, D.V. Balybin^b, D.V. Kryilskiy^d

^a *All-Russian Scientific Research Institute of Use of Machinery and Oil Products in Agriculture,
28, Novorubezhnyiy Per., Tambov, 392022, Russia*

^b *Tambov State University named after G.R. Derzhavin, 33, Internatsionalnaya St., Tambov, 392000, Russia*

^c *Department of Chemistry and Chemical Technology, Tambov State Technical University,
1, Leningradskaya St., Tambov, 392000, Russia*

^d *Research Institute of Applied Acoustics, 7A, 9 Maya St., Dubna, Moscow Region, 141981, Russia*

* Corresponding author: Tel.: +7 (4752) 72 36 55. E-mail: vits21@mail.ru

Abstract

Influence of nature and concentration (1–10 mM) of surface-active substances (SAS) – phenylbiguanidine and m-nitrophenylbiguanidine – on hydrogen evolution reaction (HER) kinetics on iron has been studied in acidic chloride solutions with constant ionic strength equal to 1. The rate-determining stage of HER changes depending on SAS nature and concentration according to the consequence: discharge → chemical recombination → surface diffusion → discharge. With some SAS concentrations, two consecutive stages proceed at commensurable rates.

The possibility of discharge or chemical recombination stage proceeding on ad-atoms or adsorbate molecules forming the first monolayer is considered.

Keywords

Hydrogen; iron; phenylbiguanidine; m-nitrophenylbiguanidine; rate-determining step; control.

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Introduction

A large number of works are devoted to the study of kinetics and mechanism of hydrogen evolution reaction (HER) on different metals, including those which have been published recently [1–8].

The results of the previous research have been generalized in a number of reviews [9–12]. In most cases the HER mechanism is only specified by kinetics research and estimation of kinetic parameters of phasic process in slightly changed conditions of the experiment.

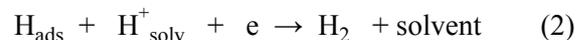
It is undoubtedly interesting to study the possibilities of managing kinetic parameters and rate-determining step nature of hydrogen evolution reaction on iron.

Assuming the quasi-equilibrium molecular hydrogen gas bubbles formation, the HER is usually considered as a two-stage process with the first stage of solvated hydrogen ions discharge in acidic media [1, 2, 7–12]



where solvent is a solvent molecule.

The subsequent removal of adsorbed hydrogen atoms can proceed according to the Heyrovsky electrochemical desorption reaction



or the Tafel chemical recombination reaction



that replace each other in some cases at the corresponding change of electrode potential in the cathodic polarization conditions [12].

Each of (1), (2) and (3) reactions can be rate-determining and their nature can be changed in the presence of surface active substances (SAS) or at the change of the mixed binary solvent composition. Therefore, the presence of Na₂HAsO₄ in acidic chloride medium leads to the replacement of rate-determining step (rds) of discharge on iron by limiting chemical

recombination (3) [13]. In the ethanol HCl solutions, addition of water leads to the reverse replacement of rds [14]. However, the process can be more complicated. Adding *o*-fluorophenylbiguanidine (***o*-FPBG**) to acidic aqueous chloride solutions and changing their concentration permits not only to replace the rds (1) by rds (3) on iron, but induces greater subsequent changes according to the consequence: discharge rds \rightarrow recombination rds \rightarrow surface diffusion rds \rightarrow repeated discharge rds [7]. Meanwhile the preceding steps are quasi equilibrium ones. Thus, the change of *o*-FPBG concentration in the solution permits to change the HER rds nature on iron deliberately. Nevertheless, such an approach must be proved.

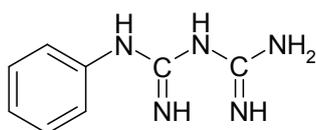
The aim of the present paper is to study phenylbiguanidine and *m*-nitrophenylbiguanidine influence on the HER kinetics and rds nature on iron in the same conditions of the experiment and the same range of c_{SAS} .

Experimental

The preparation of the working electrode, electrochemical polarization and impedance spectroscopy measurements (Solartron 1255 FRA and potentiostat 1287) were carried out according to [7].

Phenylbiguanidine (Scheme 1) and *m*-nitrophenylbiguanidine were obtained by target synthesis in specialized laboratory with purity up to 96 %.

The experimental data statistic processing was conducted according to the small sample method [15] with confidential probability of 0.95 and Student coefficient of 2.447.



Scheme 1. Phenylbiguanidine formula

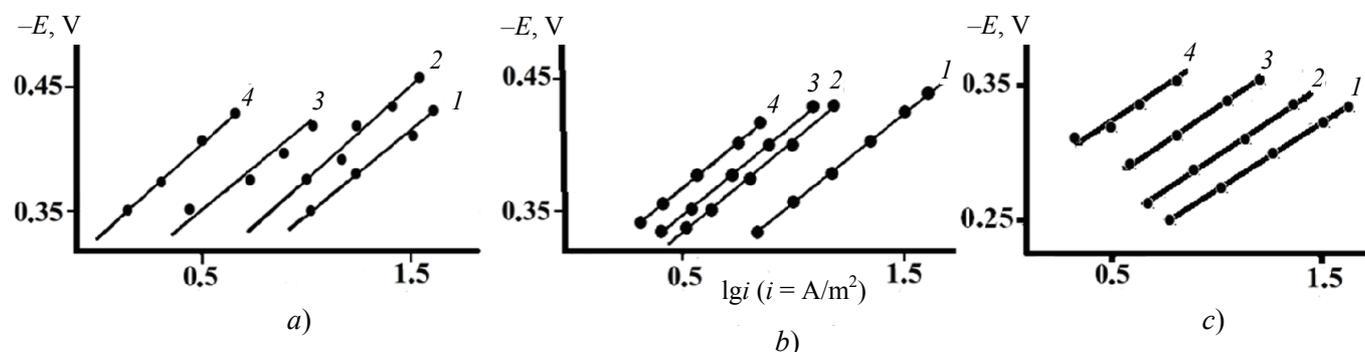
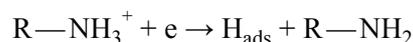


Fig. 1. E , $\lg i$ dependence on iron in x M HCl + $(1-x)$ M LiCl solutions: *a* – background solution; presence of 0.5 mM: *b* – phenylbiguanidine; *c* – *m*-nitrophenylbiguanidine; x , mole/l: 1 – 0.05; 2 – 0.10; 3 – 0.50; 4 – 0.99

Results and Discussion

The values of fractional electric charges (δ) on atoms in the molecules of phenylbiguanidine (**PBG**) and *m*-nitrophenylbiguanidine (***m*-NPBG**) have been estimated by the semi-empirical quantum-mechanical method. These data are important for interpretation of the possibility of the HER rate-determining step nature change in case of their adsorption on iron surface. The values of charges on nitrogen atoms in the molecules of PBG and *m*-NPBG are slightly higher than in the biguanidine molecule, but less than in guanidine one, data for which have been estimated before [7]. It is impossible to achieve the charge equalization at protonation due to delocalization of electron density in the molecules of PBG and *m*-NPBG, therefore we postulate that they do not substantially differ in their basicity and with respect to guanidine (GU) [16]. GU and its studied derivatives are entirely protonated in acid media because they are the strong bases. pK_a of their protonated form is equal to 11–13.6 [16].

In the additional experiments it was shown that the HER rate order with respect to PBG and *m*-NPBG is near or equal to 0. Therefore, the reaction of the type



can be neglected.

The dependence of the HER kinetics on iron disk electrode rotation rate was estimated at the fixed value of cathodic polarization $\Delta E_c = E_{cor} - E_c$, where E_{cor} is corrosion potential of iron, E_c is potential under cathodic current. ΔE_c value was equal to 0.05 and 0.10 V. In all the cases the HER kinetics does not depend on disk electrode rotation rate. Thus, it confirms that the experiments were made in the absence of diffusion limitations.

Figure 1 illustrates the HER rate dependence on electrode potential and hydrogen ion concentration

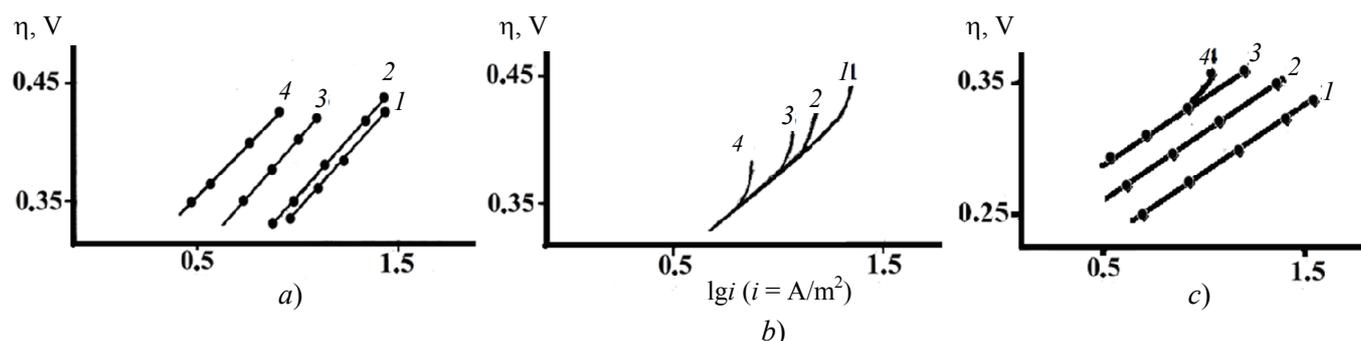


Fig. 2. η , $\log i$ dependence on iron in x M HCl + $(1-x)$ M LiCl solutions:
a – background solution; presence of 0.5 mM: *b* – phenylbiguanidine; *c* – m-nitrophenylbiguanidine;
x, mole/l: 1– 0.05; 2 – 0.10; 3 – 0.50; 4 – 0.99

(with constant ionic strength) in conditions of cathodic polarization. Measurements were made in the background solutions (*a*) and in the presence of 0.5 mM of PBG (*b*) and m-NPBG (*c*). The comparative position of polarization curves (Fig. 1) shows that the $d\log i_c/d\log c_{H^+}$ value changes at the injection of already minimum concentration (0.5 mM) of guanidine derivatives.

Even stronger influence of these factors was observed when the dependence of the HER rate on hydrogen overpotential was estimated (Fig. 2). For example, in the presence of PBG the connection between i_c and η was absent (Fig. 2, *b*). To estimate the HER rate-determining step the following kinetic

parameters were used: $dE/d\log i_c$, $dE/d\log c_{H^+}$, $(d\log i_c/d\log c_{H^+})_E$, $d\eta/d\log i_c$, $d\eta/d\log c_{H^+}$ and $(\partial\log i_c/\partial\log c_{H^+})_\eta$. The corresponding values are given in Table. To analyze the data of the Table we have used the results of the theoretical analysis of the HER kinetics made in [17, 18].

Then in conditions of slow surface diffusion of H_{ads} the following kinetic parameters were observed: $d\eta/d\log i_c$ and $(d\log i_c/d\log c_{H^+})_\eta$ were equal to 0.079V and 0.25 respectively. The $(d\log i_c/d\log c_{H^+})_E$ value was equal to 0.75. The $d\eta/d\log c_{H^+}$ value was not estimated in [17, 18].

**Kinetic parameters of HER on iron in acidic chloride aqueous solutions
with constant ionic strength equal to 1 in the presence of guanidine derivatives.
Numerator – experiment, denominator – theoretical value**

c_{SAS} , mM	$-dE/d\log i_c$, V/decade	$dE/d\log c_{H^+}$, V/decade	$(d\log i_c/d\log c_{H^+})_E$	$d\eta_H/d\log i_c$, V/decade	$-d\eta_H/d\log c_{H^+}$, V/decade	$(d\log i_c/d\log c_{H^+})_\eta$
phenylbiguanidine						
0	0.110/0.116	0.085/0.116	0.85/1.0	0.110/0.116	0.060/0.058	0.55/0.50
0.5	0.115/0.029*	0.055/0.058	0.50/0.50	0.115/0.030*	0/0	0/0
1.0	0.125/0.029*	0.075/0.058	0.50/0.50	0.125/0.030*	0/0	0/0
5.0	0.125/0.140	0.090/-**	0.60/0.75	0.125/0.079	0.035/-**	0.15/0.25
10.0	0.130/0.140	0.065/-**	0.75/0.75	0.130/0.079	0.035/-**	0.25/0.25
m-nitrophenylbiguanidine						
0.1	0.115/0.029*	0.055/0.058	0.50/0.50	0.115/0.030 ^a	0/0	0/0
0.3	0.115/0.029*	0.055/0.058	0.50/0.50	0.115/0.030 ^a	0/0	0/0
0.5	0.100/0.140	0.070/-**	0.75/0.75	0.100/0.079	0.070/-**	0.25/0.25
1.0	0.125/0.140	0.075/-**	0.75/0.75	0.125/0.079	0.040/-**	0.25/0.25
5.0	0.100/0.116	0.100/0.116	0.85/1.00	0.100/0.116	0.060/0.058	0.50/0.50
10.0	0.100/0.116	0.100/0.116	0.85/1.00	0.100/0.116	0.060/0.058	0.50/0.50

* With no account taken of energy surface heterogeneity

** Theoretical value is unknown.

Additionally, in the rds conditions (3), the Tafel slope coefficient of the cathodic polarization curves should be equal to $2.303RT/2F$, i. e. 0.029 V at $T = 295$ K. However, this value is practically never received, which in accordance with [8] is explained by energy heterogeneity of active centers leading to the dependence

$$\eta = \text{const} + (RT/2\beta F)\log i_c$$

with $\beta < 1$ (i_c is the outer cathodic current density).

According to the Table data and the experimental values obtained in [7], the HER proceeds on iron in the background solutions according to (1), (3) consequent steps with discharge rate-determining step. In the presence of PBG (0.5 mM) the Tafel reaction becomes rds (Table) and the Volmer reaction is quasi-equilibrium.

Kinetic parameters of the HER do not practically change with twofold increase in c_{PBG} (Table 1) and the recombination reaction remains rds. The PBG concentration growth up to 5 mM leads to some ambiguous situation: the rates of chemical recombination and surface diffusion of H_{ads} become commensurable at quasi equilibrium discharge reaction. Such a situation is proved by the following facts:

- some increase of $dE/d\log c_{\text{H}^+}$ kinetic parameter (Table);

- approximation of $-d\eta/d\log c_{\text{H}^+}$ value to 0.035, some increase of $(d\log i_c/d\log c_{\text{H}^+})_{\eta}$.

Further twofold increase in c_{PBG} leads to rds of surface diffusion (SD) (Table). The Volmer and Tafel reactions become quasi-equilibrium ones.

Adding m-NPBG confirmed the observed situation. The study of m-NPBG concentration influence on the possibility of the HER rds nature change on iron is of special interest. If PBG has the adsorption centers connected with the presence of 5 nitrogen atoms with δ values from -0.253 to -0.316 e in the molecule capable of having donor-acceptor interaction with surface iron atoms, then there is a possibility of additional sorption of m-NPBG molecule due to NO_2 group. For m-NPBG two additional adsorption centers are based on oxygen of nitro-group with $\delta = -0.330$ e and its nitrogen atom with δ equal to $+0.478$ e. This effect can lead to both repulsion of adsorbate particles and positive attractive effect or their mutual neutralization.

In the presence of 0.1 and 0.3 mM of m-NPBG the Tafel reaction becomes rds. The further growth in $c_{\text{m-NPBG}}$ up to 0.5 and 1.0 mM leads to the SD rds, but at $c_{\text{m-NPBG}} = 5$ mM the kinetic parameters correspond quite closely to the slow discharge theory requirements. Perhaps, it is connected with the

adsorbate mono layer formation. This idea is proved by measuring the double layer capacitance that allows estimating the connection between surface coverage θ and $c_{\text{m-NPBG}}$ in the solution. If $c_{\text{m-NPBG}} = 0.2$ mM, $\Theta \approx 0.98$, the further minimum double layer capacitance can be received with the increase of SAS concentration. Consequently, the maximum surface coverage occurs. The surface coverage was calculated according to the formula [19]:

$$\Theta = (C_0 - C)/(C_0 - C_\infty), \quad (8)$$

where C_0 is the double layer capacitance in the background solution, C is the same in the solution containing SAS, C_∞ is the double layer capacitance corresponding to the adsorbed SAS monolayer formation. It is noteworthy that active centers on iron surface are energetically heterogeneous [20], and the dependence $\Delta G_{\text{ads}} = f(\Theta)$ is valid. They are able to adsorb hydrogen atoms and SAS molecules. On the whole, the expression $\Theta_\Sigma = \Theta_{\text{H}} + \Theta_{\text{SAS}}$ is correct, where Θ_i is the active centres portion, occupied by i -adsorbate particles (i is H or SAS). Then Θ_{SAS} growth decreases Θ_{H} . Correspondingly, the Tafel reaction rate decreases. The further Θ_{SAS} growth retards the surface diffusion of H_{ads} necessary for H_2 formation according to (3). Therefore SD becomes rds. When the adsorbate monolayer is formed, the Volmer reaction takes place on the particles of this monolayer and becomes the rds once again. This possibility was considered in [10, 21].

Summary and Conclusion

Thus, the successive change of the rds nature of the HER in the SAS presence is observed on iron quite often and can be used to manage this process. In the simplest case, it is achieved by changing the solvent nature when the discharge rds is replaced by the Tafel rds. In particular, it is observed on iron at the injection of 10 %wt. H_2O into the ethylene glycol solution of HCl [13]. But much greater changes are observed at the injection of SAS, in particular PBG and m-NPBG, in the solution. In this case the successive change of the HER rds takes place according to the consequence: discharge \rightarrow chemical recombination \rightarrow surface diffusion \rightarrow repeated discharge.

The observed phenomenon permits to control the rds nature of HER on iron. This is important for the following processes:

- creation of conditions for metal hydrogenation decrease;
- stimulation of hydrogen accumulation by solid phase;

- study of HER kinetic regularities in conditions of rds particular nature;
- study of the influence of the rds nature on kinetics and mechanism of secondary processes initiated by HER, for example, solid phase hydrogen diffusion into metal.

References

1. Chialvo M.R.G. & Chialvo A.C. (1998). *Electrochim. Acta*, 44, 841-845.
2. Chialvo & Chialvo A.C. (2000). *J. Electrochem. Soc.*, 147, 1619-1622.
3. Gabrielli C., Grand P.P., Lasia A. & Perrot H. (2004). *J. Electrochem. Soc.*, 151, 1925-1936.
4. Lukaszewski M., Kedra T. & Czerwinski A. (2010). *J. Electroanal. Chem.*, 638, 123-130.
5. Daoping T. et al. (2010). *J. Electroanal. Chem.*, 644, 144-149.
6. Vigdorovich V.I., Tsygankova L.E. & Balybi, D.V. (2011). *J. Electroanal. Chem.*, 653, 1-6.
7. Vigdorovich V.I., Tsygankova L.E., Balybin D.V. & Kichigin V.I. (2013). *J. Electroanal. Chem.*, 689, 117-123.
8. Frumkin A.N., Bagotsky B.S., Iofa Z.A. & Kabanov B.N. (1952). *Kinetika elektrodnoogo protsessa* [Kinetics of Electrode Process]. M.: Moscow State University. (Rus)
9. Frumkin, A.N. (1987). *Izbrannyye raboty: Vodородnoe perenapryazhenie* [Selected Works: Hydrogen Overvoltage]. M.: Nauka. (Rus)
10. Tsygankova L.E., Vigdorovich V.I. & Vigdorovich M.V. (2006). In P.N. Jiang (Ed). *Electroanalytical Chemistry Research Developments* (pp. 135-182). New York: Nova Science Publishers.
11. Kuznetsov V.V., Haldeev G.V. & Kichigin V.I. (1993). *Navodorozhivanie metallov v elektrolitah* [Hydrogenation of metals in electrolytes]. M.: Mashinostroenie. (Rus)
12. Devanathan M.A. & Stachurski V. (1964). *J. Electrochem. Soc.*, 111, 619-623.
13. Vigdorovich V.I., Tsygankova L.E. & Kopylova E.Yu. (2003). *Elektrohimija* [Electrochemistry], 39, 832-839. (Rus)
14. Vigdorovich V.I. & Matveeva M.V. (2006). *Elektrohimija* [Electrochemistry], 42, 1480-1487. (Rus)
15. Aleskovskiy V.B. & Yatsimirskiy K.B. (Eds). (1971). *Fizikohimicheskie metody analiza* [Physicochemical methods of analysis]. Leningrad: Himija. (Rus)
16. Albert A. & Sergeant E.P. (1962). *Ionization Constants of Acids and Bases*. New York: John Wiley.
17. Vvedenskii A.V. (2011). *Corrosion: materials, protection*, 12, 23-29
18. Vvedenskii A.V., Kozaderov, O.A. & Gutorov I.A. (2010). *Surf. Interf. Anal.*, 42, 629-635.
19. Damaskin B.B., Petrii O.A. & Batrakov V.V. (1968). *Adsorbtsia organicheskikh soedineniy na elektrodah* [Adsorption of organic compounds on electrodes]. M.: Nauka. (Rus)
20. Temkin M.I. (1941). *J. Phys. Chem.*, 15, 96-307.
21. Krishtalik L.I. & Kuzmenko B.B. (1973). *Elektrohimija* [Electrochemistry], 9, 664-666. (Rus)