Hydrogen evolution is one of the oldest targets of electrochemical research. The first fundamental laws of electrochemistry were established on the basis of investigations of this object. Despite the significant progress made in identifying features of the kinetics and mechanism of this process, interest in this area is preserved. This is due to various reasons. First, hydrogen is an important utility for numerous applications in multiple industries including its use as a promising source of energy in the future. Though hydrogen plants are designed to serve heavy duties, portable hydrogen generators also have demand. As an example, we mention that they are promising in the automotive industry, because electrochemically generated H2 gas can help burn diesel fuel more efficiently. Hydrogen evolution often attends the electrodeposition of metals as a side reaction, which should be taken into account when the main process is studied. Most often the onset of the hydrogen evolution is followed by a progressive rise of the voltammogram. However, current maxima are observed when the plating solutions contain such ligands as hydroxy acids, which can generate hydrated protons (H3O+) establishing the conditions for the CE mechanism (chemical + electrochemical step). Then, hydronium ions are formed additionally with hydrated protons:

\[
\text{H}_2\text{O} + \text{A}^- \rightarrow \text{H}_3\text{O}^+ + \text{A}^-.
\]

To simplify the records, hereinafter the charges of anions are omitted.

Involved in the Hydrogen Evolution as Proton Donors

Voltammetric Characterization of the Lability of Weak Acids

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Linear sweep voltammetry data, obtained for hydrogen evolution on a copper electrode were used to estimate the lability of weak monoprotic acids as proton donors. Analysis of differential equations involving diffusion and kinetic terms shows that the total mass transport of proton donors and acceptors does not depend on the kinetics of chemical steps. Their surface concentrations as functions of the electrode potential can be easily obtained by convolution of experimental voltammograms and used in further analysis. The results show that acetic and glycolic acids are sufficiently labile, whereas the dissociation of the carboxylic group in gluconic acid is kinetically inhibited. The zwitterions formed in glycine solutions cannot be regarded as labile proton donors due to the inertness of the protonated amino group. Transforms necessary for constructing linear Tafel plots are discussed.

The present article deals with this problem of estimation of system lability. Further, taking into account the results obtained, adequate methods of analysis of experimental data are considered with a view to determining the kinetic parameters of the charge transfer step. LSV data on hydrogen evolution in solutions of simple monoprotic acids are used for this purpose.

Theoretical Notes

Let us suppose that the hydrogen evolution proceeds in the solution of a weak acid HA. Its stepwise dissociation can be represented in a general way as follows:

\[
\text{H}_\text{M}_{j-1}\text{A}^- \rightleftharpoons \text{H}^+ + \text{H}_\text{M}_j\text{A}^{-j-1}.
\]

The index j means the serial number of a proton released from the acid molecule; it takes integer values from 1 to M. The rates of recombination (w_j) and dissociation (w_{j-1}) of species participating in the reversible process 1 are characterized by the corresponding rate constants (k_j and k_{j-1}, respectively):

\[
w_j = k_j [\text{H}^+][\text{H}_\text{M}_j\text{A}].
\]

To simplify the records, hereinafter the charges of anions are omitted. When the hydrogen evolution proceeds, all these species take part in mass transfer, as well as OH− ions, which interact simultaneously with hydrated protons:

\[
\text{H}^+ + \text{OH}^- \rightleftharpoons \text{H}_2\text{O}.
\]

The rates of the forward and reverse processes are, respectively:

\[
w_w = k_w [\text{H}^+][\text{OH}^-],
\]

\[
w_{w-j} = k_{w-j} [\text{H}_\text{M}_{j-1}\text{A}].
\]

In the presence of supporting electrolyte, when migration effects can be neglected, differential equations for planar diffusion of H+ ions

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and proton-containing species take the form:

\[
\frac{\partial[H^+]}{\partial t} = D \frac{\partial^2[H^+]}{\partial x^2} + \sum_{j=1}^{n} (w_{-j} - w_j) + w_{-w} - w_w, \quad [7]
\]

\[
\frac{\partial[H_{M,j}A]}{\partial t} = D \frac{\partial^2[H_{M,j}A]}{\partial x^2} + w_{-j} - w_j - (w_{-j+1} - w_{j+1}) \quad [8]
\]

In the above records, the kinetic terms \((w_j\text{ or } w_{-j})\) are equal to zero at \(j < 1\) and \(j > N\). The mass transfer equation should also be written for \(OH^−\) ions

\[
\frac{\partial[OH^-]}{\partial t} = D \frac{\partial^2[OH^-]}{\partial x^2} + w_{-w} - w_w, \quad [9]
\]

When kinetic characteristics of chemical stages are known, the evaluation of their role does not present fundamental difficulties. One can, for example, use a set of the above differential equations, which, supplemented by proper initial and boundary conditions, make it possible to determine the surface concentrations of all species, including those that take part in the charge transfer step. The latter concentrations should be inserted into the kinetic equation formulated in accordance with the assumption mechanism of the electrochemical process. Eventually, it is possible to simulate voltammograms, which can be compared with the corresponding experimental data and/or used in fitting procedures.

Note that there is no need for a preliminary assessment of the system lability in this case. However, if this feature is of special interest, simulated concentration profiles can be used to reveal the region of the diffusion layer in which deviations from the equilibrium distribution are observed. In this regard, we refer the reader to our article, which details the use of concentration profiles as lability indicators.

Certain key ideas, which contribute to the understanding of the processes under discussion, could be also obtained from the results of such simulations. Though most general approaches cover a wide range of options, they do not contain desirable details. In this connection, it seemed to us expedient to make calculations using the differential equations with the limited set of diffusion and kinetic characteristics and considering only those that are most typical of the systems discussed here. The data were obtained without limitations in reaction order at \(c_{01} = 0.01 \text{ M}, c_{x1} = 0.02 \text{ M}\) and different kinetics of chemical step. The values of other parameters (stability constant \(k_1\), diffusion coefficient \(D\), exchange current density \(i_0\) and cathodic charge transfer coefficient \(\alpha_w\)) were maintained constant. Since the formation of water is extremely rapid, it was assumed that the concentration of \(OH^-\) ions is determined by the ionic product of water.

The cathodic current decreases with decreasing pre-reaction rate as well and the peak potential \(E_p\) is shifted toward smaller cathodic overvoltages, i.e. to more positive potentials (Figure 1). In accordance with the data published earlier, two limiting cases are realized that correspond to relatively high or rather low rates of chemical steps (lines 1 and 2 in Figure 2). In both cases, the dependences of current peaks \(i_p\) vs. \(\sqrt{v}\) are linear and obey the relationship

\[
i_p = 0.282nF \sqrt{\frac{\pi F}{RT}} \alpha_w D c \quad [10]
\]

that was derived for a simple irreversible redox process. It is not difficult to verify that in the first case (labile systems), the total concentration \(c_{01}\) should be substituted for \(c\) (line 1) and in the second limiting case (inert systems) the equilibrium bulk concentration of the electrochemically active particle should be used, i.e. \(c = [H^+]\) (line 2). The behavior of peak potentials \(E_p\) is shown in Figure 3. Again, in the case of sufficiently rapid \((k_1 > 100 \text{ s}^{-1})\) or very slow \((k_1 < 0.1 \text{ s}^{-1})\) chemical step the slopes of linear \(E_p - \log v\) dependences are in agreement with the theoretical relation derived for simple redox

---

**Figure 1.** Examples of LS voltammograms simulated for \(H^+\) reduction in the model system at different rate constants \(k_1\) (indicated at the curves) and corresponding values of \(k_1 = K_1 k_{-1}\). Constant parameters are also listed.

**Figure 2.** Dependences of peak currents vs. \(\sqrt{v}\) obtained at different kinetics of the preceding chemical step. The data are located between two straight lines corresponding to perfectly labile (line 1) and particularly inert (line 2) systems.

**Figure 3.** Dependences of peak potentials vs. \(\log v\) obtained at different kinetics of the preceding chemical step. \(E_p\) values were reckoned from the equilibrium value \(E_{eq}\). Limiting cases corresponding to labile and inert systems are represented by lines 1 and 2 respectively.
process\textsuperscript{10}
\[ \partial E_p \partial \ln v = - \frac{RT}{2a_i F}. \]  

Equation 13 supplemented by the proper initial and boundary conditions\textsuperscript{3} has an analytical solution  
\[ \Delta c_{\text{H}}(t) = c_{\text{b},\text{H}} - c_{\text{b},\text{H}}(t) = \frac{1}{nF\sqrt{2D}} \int_0^t \frac{i(t - u)}{\sqrt{u}} \psi(u) du, \]  

where subscripts b and s denote bulk and surface concentrations respectively, the variable t in the time-dependent current density (i(t) is replaced by the auxiliary variable (t - u). The function \( \psi(u) \) takes into account the existence of 5-thick diffusion layer; in the case of semi-infinite diffusion, \( \psi(u) = 1. \)

We would like to draw attention to a number of important features concerning the above relationships. First, the same Equations 12 and 13 are also obtained for more complex systems containing mixtures of acids. In this case, Equations 14 and 15 must be transformed in accordance with the composition of the solutions used. Further, the derivation of Equation 18 is not associated with any preliminary assumption about the nature of the electrochemically active species; it can be used at different mechanisms of the process. Finally, since Eq. 18 contains no kinetic characteristics of chemical steps, it is suitable for estimating the total surface concentration both in labile and inert systems.

### Experimental

Solutions were prepared using deionized water, sodium acetate, sodium gluconate, aminoacetic acid (glycine) (all Sigma-Aldrich, 99% pure) and hydroxyacetic (glycolic) acid (Reakhim, Russia). 0.3 M sodium perchlorate (Fluka, > 98%) was used as a supporting electrolyte. Specified values of pH were adjusted by addition of HClO\textsubscript{4} or NaOH. Solutions were deaerated before experiments with an argon stream for over 0.5 h. Measurements were carried out using platinum and copper electrodes. To prepare the working electrodes, a 1 cm\textsuperscript{2} platinum disc was coated with 5–7 \( \mu \)m thick copper in a solution containing (g dm\textsuperscript{-3}): CuSO\textsubscript{4} \( \cdot \)5H\textsubscript{2}O – 250, H\textsubscript{2}SO\textsubscript{4} – 50. A polycrystalline layer with well-exhibited crystallographic edges and faces was formed. Detailed characteristics of surface morphology are given elsewhere.\textsuperscript{34}

LSV measurements were performed using a potentiostat/galvanostat REF 600 from Gamry Instruments. Voltammograms were recorded at a potential sweep rate \( \nu \) ranging from 0.01 to 0.2 V s\textsuperscript{-1}. In all cases, cathodic scans were applied, starting with the open-circuit potential. The electrode potential was measured in reference to the Ag | AgCl | KCl(sat) electrode and was converted to the standard hydrogen scale. All experiments were performed at 20°C.

### Results and Discussion

Four simple monoprotic carboxylic acids were selected for research. Acetic acid CH\textsubscript{3}COOH solutions are the most studied object that can be used for experimental verification of the regularities of theoretical models. Two derivatives – hydroxyacetic (glycolic) acid HO-CH\textsubscript{2}-COOH and aminoacetic acid (glycine) H\textsubscript{2}N-CH\textsubscript{2}-COOH - are slightly stronger due to the electron-withdrawing power of the terminal groups. Unlike the previous ones, glumatic acid (CH\textsubscript{2}-(CH-OH)\textsubscript{5}-COOH has a substantially longer hydrocarbon chain. Its deprotonated OH groups are capable of forming strong coordination bonds only in alkaline media. Therefore, in weakly acidic solutions, glutamic acid, like the rest, is considered to be monoprotic.

The set of parameters used in the present investigation is listed in Table I. Equilibrium characteristics (the values of \( K_i = 1c_i \text{K}_i \)) are widely represented in various databases and can be simply selected as most appropriate to the composition and ionic strength of the solutions used. Diffusion characteristics\textsuperscript{19–21} given mainly for 25°C,
as well as rate constants available in literature are also reported. Since the main experimental material discussed below refers to 0.04 M acid solutions at pH 3, we also present total concentrations of proton donors (see Table I) obtained from well-known material balance equations with the activity coefficient of hydronium ions equal to 0.7. Some features concerning glycoline solutions are discussed below. Voltamograms display well-defined, even current peaks whose shape is actually the same for both platinum and copper electrodes despite the fact that these metals differently absorb hydrogen with the only difference that the voltamograms for Pt are markedly (about 0.5 V) shifted to more positive potentials. This phenomenon indicates that the shape of voltamograms is specified, in a fundamental way, by the processes taking place in the near-electrode (diffusion) layer, but not at the interphase. Bearing this in mind, we provide further data obtained for copper electrode.

Typical curves are presented in Figure 4. The height of current peaks is different for each acid and decreases in the same order as the total concentration of proton donors $c_{H}$ (see Table I). At the same time, $i_{p}$ varies linearly with $\sqrt{v}$ (inset in Figure 4).

As already noted, before proceeding to the quantitative analysis of the experimental curves, it is necessary to estimate the degree of system lability. This is most easily done, if diffusion and kinetic characteristics of the system are known. The acetate system is in a favorable position in this respect. Comparison of kinetic parameters (Table I) with the data of Figure 2 makes it possible to judge a sufficiently high lability of this system under LSV conditions. Then Equation 10 with $c = c_{H}$ should hold true. Since $i_{p}$ values depend on $v$, we eliminated this effect through the analysis of slopes of the $i_{p} - \sqrt{v}$ dependences obtained for the solutions with different pH and $c_{A}$. These data plotted vs. $c_{H}$ fit the line with the slope equal to $618 \text{ A s}^{0.5} \text{ V}^{-0.5} \text{ cm mol}^{-1}$ (see Figure 7 in our article). Then, a completely reasonable value of $\alpha_{D}D = 4 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ follows from Equation 10.

Since the kinetic constants for glycolic acid system were not available to us, we had to use only voltammetric data. Certain conclusions can be obtained from the analysis of surface concentrations obtained by convolution of experimental voltamograms according to Equation 18. It is evident that the $\Delta c_{H}$ cannot exceed the bulk value of $c_{H}$. This limiting case can be realized in labile systems. Since the decrease in [H$^{+}$], is promptly compensated by rapid dissociation of HA molecules, this results in simultaneous fall of both [H$^{+}$], and [HA]. As a result, the concentrations of all particles containing mobile H$^{+}$ ions tend to zero in the region of limiting current or at the respective regions of non-steady current transients. Then, the maximum value of $\Delta c_{H}$, determined by 18, approaches the total concentration of protons and their donors in the bulk of solution:

$$\Delta c_{H}(t)_{\max} = c_{H,b}.$$  \hspace{1cm} (19)

Hence, the fulfillment of condition 19 is an indisputable sign indicating a labile character of the system under the conditions applied. Another limiting case is possible in highly inert systems, where dissociation of the electrochemically inactive HA is considered to be very slow. Therefore, its surface concentration will vary slightly with $i$ and all changes in $\Delta c_{H}$ will be caused by a decrease in the concentration of hydronium ions. Then, the condition 19 changes to

$$\Delta c_{H}(t)_{\max} = [\text{H}^{+}]_{b}.$$  \hspace{1cm} (20)

In view of the foregoing, lability estimates, based on the analysis of the $\Delta c_{H}$ values, are possible.

Table I. Characteristics of weak monoprotic acids (0.04 M solutions at pH 3.0).

| Acid   | $\log K_{1}$ | $D$/cm$^2$ s$^{-1}$ | $k_{1}$/M$^{-1}$ s$^{-1}$ | $k_{-1}$/s$^{-1}$ | $c_{H}$/mM |
|--------|--------------|----------------------|--------------------------|------------------|-------------|
| acetic | 4.6          | $(1.0-1.2) \times 10^{-5}$ | $4.5 \times 10^{10}$ | $7.8 \times 10^{3}$ | 40.7        |
| glycolic | 3.2       | $9.8 \times 10^{-6}$ | $2 \times 10^{11}$ | $7.0 \times 10^{4}$ | 29.2        |
| glycine | 2.4         | $9.4 \times 10^{-6}$ | $1.2 \times 10^{11}$ | $3.4 \times 10^{6}$ | 27.5        |
| gluconic | 3.7       | $6.75 \times 10^{-6}$ | $1.0 \times 10^{6}$ | $2.5 \times 10^{2}$ | 36.5        |

Figure 4. LS voltammograms obtained for 0.04 M solutions of indicated acids. Selection for pH 3 and $v = 0.1$ V s$^{-1}$. Variations of the respective peak currents with $\sqrt{v}$ are shown in the inset.

Figure 5. Example of LS voltammograms transformed according to Eq. 18 at different potential sweep rates as indicated. The bulk concentration of proton donors is shown by the dotted line.

The case of labile system is demonstrated in Figure 5. At sufficiently high cathodic polarizations ($E < -1$ V), the convoluted experimental voltammograms reach the plateau, where $\Delta c_{H}$ approaches the bulk concentration of proton donors (see Table I). A further increase in this quantity, observed at $E < -1.2$ V, arises from the discharge of water molecules. Similar results are also typical of acetate system.

The lability of systems opens up a relatively simple way of further analysis of the experimental data. When chemical interactions are sufficiently fast, the deviations from the equilibria in the diffusion layer can be considered to be insignificant. Then the interconnections between species concentrations can be expressed in terms of the corresponding equilibrium constants. Further, the surface distribution can be determined on the basis of common mass balance equations taking into account that a certain profile of $c_{H}$ is established in the diffusion layer, whereas the gradient of $c_{A}$ is absent due to the electrochemical inertness of anion-containing species. In other words, the $c_{A}$ quantity is constant throughout the system. The above procedures are required for determining kinetic parameters of the charge transfer process.

According to the simplest mechanism, which has been taken as a basis for the studies of the kinetics of dissociation of some monoprotic carboxylic acids, the charge transfer $\text{H}^{+} + \text{e} \rightarrow \text{HA}$, can be considered as the rate-determining step. In this case, at sufficiently

\[\text{H}^{+} + \text{e} \rightarrow \text{HA} \]
Figure 6. Normalized Tafel plots obtained for 0.04 M glycolic acid solutions at pH 3 and different potential sweep rates. Kinetic parameters following from NTP analysis are also presented.

large cathodic overvoltages, \( \eta_c \), the kinetic equation takes the form:

\[
\ln i_{\text{norm}} = \ln i_0 + \frac{\alpha_F}{RT} \eta_c.
\]

where

\[
i_{\text{norm}} = \frac{[\text{H}^+]}{[\text{H}^+]_0}.
\]

These expressions describe the so-called normalized Tafel plots (NTP). Experimental voltammetric data can be transformed into linear NTPs when the current density is normalized with respect to the potential-dependent surface concentration \([\text{H}^+]_0\). This procedure has been widely applied in various investigations including electroreduction of metal complexes\(^1\) and hydrogen evolution.\(^2\)\(^3\)\(^4\)\(^5\) NTPs close to linear were obtained for the acetate system even in such cases when voltammograms contained double current peaks.\(^5\)

Below (Figure 6), we present the NTP obtained for a sufficiently labile system containing glycolic acid. The data obtained at different potential sweep rates can be approximated by one general line. Its slope and intercept yield kinetic parameters listed in the figure. Note that the solutions were not saturated with hydrogen and the open-circuit potentials were more positive than the equilibrium potential \(E_q = -0.058\) pH. Since the overvoltage was determined with respect to the theoretical \(E_q\) value, the exchange current density, obtained from the NTP intercept, is treated as effective.

Kinetic parameters of hydrogen evolution depend on various factors: the composition and acidity of the solution, the nature of the metal, the method of its preparation before measurements, the adopted mechanism of the process, the procedures used in processing and interpreting the experimental data, etc. A critical review of the literature data obtained for hydrogen evolution on Cu electrodes has shown\(^24\) that reliable values of \(i_0\) obtained at pH 0.0–1.0 fall within the range from \(10^{-7.5}\) to \(10^{-6}\) A cm\(^{-2}\). Thus, a comparatively low value of \(i_0\) (~60 nA cm\(^{-2}\)) was obtained for the Cu|HCl system under high-purity conditions.\(^25\) This quantity was found to be tenfold higher for hydrogen evolution on polished copper in slightly acid H\(_2\)BO\(_3\) solutions saturated with hydrogen.\(^26\) It was assumed in this case that the Volmer reaction is the rate-determining step. The \(i_0\) quantities of several µA cm\(^{-2}\) follow from the NTPs obtained for copper coatings in solutions of carboxylic acids containing 0.5 M K\(_2\)SO\(_4\) as a supporting electrolyte.\(^27\) Such solutions contain HSO\(_4^\) ions acting as additional proton donors. As can be seen from the above, the exchange current densities in perchlorate media are rather low. On the basis of the foregoing, we can conclude that there are no fundamental contradictions between the kinetic data obtained by us and published previously.

Voltammograms with well-defined current peaks are also typical of gluconate solutions. Transform of the experimental voltammograms according to Eq. 18 produces the \(\Delta c_{\text{H}^+} - t\) dependences that are also similar to those obtained for acetic or glycolate solutions (see Figure 5). However, the height of plateau on this curve coincides with the bulk concentration of proton donors \(c_{\text{H}^+}\) (Table I) when the apparent \(D = 3.4 \times 10^{-6}\) cm\(^2\) s\(^{-1}\). In contrast to the above systems, the \(D\) obtained is twice lower than \(D = 6.75 \times 10^{-6}\) cm\(^2\) s\(^{-1}\) determined for gluconic acid and glucose by reasonable methods.\(^28\)\(^29\)\(^30\) Even more low \(D = 1.5 \times 10^{-6}\) cm\(^2\) s\(^{-1}\) was obtained in a similar manner for gluconate solutions containing sulfate as a supporting electrolyte.\(^31\) It follows from Eq. 18 at \(D = 6.75 \times 10^{-6}\) cm\(^2\) s\(^{-1}\), that the surface concentration of proton donors \(c_{\text{H}^+}\) is ~0.3 \(c_{\text{H}^+}\) and does not approach zero. The result obtained seems to arise from the limited dissociation rate of gluconic acid, which becomes the controlling factor at high enough overvoltages. This conclusion is in line with the kinetic data given in Table I. The dissociation/recombination rates for gluconic acid are significantly (by ~4 orders) lower as compared with those for the acetic system.

It was of interest to revise the voltammetric data in order to detect other indications of limited lability of the system. It turned out that the linear dependencies of \(i_0\) vs. \(\sqrt{v}\) and \(E_q\) vs. \(\log v\) can be also constructed for the gluconate system. Moreover, NTPs, obtained ignoring kinetic limitations, can be approximated by a single general line at different potential sweep rates over a wide potential range.\(^3\) Finally, it was also of interest to compare shapes of current peaks obtained for the acetate and gluconate systems. It turned out\(^7\) that the peak regions of voltammograms, each normalized with respect to its individual \(i_0\), can be displaced along the potential axis so, that they would actually coincide. Consequently, the shape of the voltammogram also contains no signs for assessing the presence of slow chemical steps.

Before proceeding to the analysis of the data obtained for the glycine system, it is necessary to discuss some of its distinctive features which are not characteristic of previous research objects. Glycine (H\(_2\)A) in aqueous solutions promotes formation of a zwitterion \(\text{H}_2\text{N}−\text{CH}_2−\text{COO}^−\), which together with its protonated form \(\text{H}_3\text{N}−\text{CH}_2−\text{COOH}\) (H\(_2\)A\(^+\)) dominates in acid media. Both species are capable of splitting off one and two protons, respectively. On this basis, the total concentration of proton donors and acceptors might be expressed as follows:

\[
c_{\text{H}^+} = [\text{H}^+] + [\text{HA}] + [2\text{H}_2\text{A}^+] − [\text{OH}^−].
\]

As a result of a preliminary study of this system,\(^4\) the question arose, whether all the species in Eq. 23 are labile. One can suggest by analogy with two previous systems that the carboxyl group dissociates relatively fast. Assuming further that the proton attached to the amino group is insufficiently mobile, the zwitterion LH should be excluded from consideration and the \(\text{H}_2\text{L}^+_2\) species should be treated as the particle containing only one mobile proton, which is split off from the carboxyl group. As a result, we get for labile components that

\[
c_{\text{H}^+} = [\text{H}^+] + [\text{H}_2\text{L}^+] − [\text{OH}^−].
\]

Equations 23 and 24 give rather differing results, e.g. 51.4 and 11.4 mM for 0.04 M glycine solution at pH 3 (see Table I).

We conducted additional experiments extending the range of the solution compositions. The results accumulated in the mentioned studies are summarized in Figure 7. The \(c_{\text{H}^+}\) quantities obtained for different solutions by Eq. 24 are displayed by dotted lines. Plateaus of \(c_{\text{H}^+}−E\) dependences agree with these values when \(D = (8.4±0.4)\times10^{-6}\) cm\(^2\) s\(^{-1}\) is used. This value is close to \(D = 9.4\times10^{-6}\) cm\(^2\) s\(^{-1}\), which has been estimated earlier.\(^3\) The generalized experimental data confirm the conclusion\(^4\) that protonated \(\text{H}_2\text{N}−\text{CH}_2−\text{COOH}\) species can be treated as labile proton donors, whereas zwitterions \(\text{H}_3\text{N}−\text{CH}_2−\text{COO}^−\) do not fall into this category.

Proceeding from the latter assumption, we constructed NTPs using the method described above. It is evident from the presented example (inset in Figure 7) that the linear graph is not obtained. The reasons for such a result have yet to be clarified. It seems possible that the mechanism of the process in this system can exhibit a number of distinctions; therefore further research is needed to elucidate it.
Figure 7. Variations in surface $c_H$ obtained at different pH and glycine concentrations as indicated. Dotted lines show the respective bulk concentrations of labile proton donors determined by Eq. 24. An example of normalized Tafel plot is shown in the inset.

Concluding Remarks

Methods for estimating the lability of weak acids, which are involved as proton donors in the electrochemical hydrogen evolution, have been considered. Simulations by differential equations including diffusion and kinetic terms show that, under the conditions of common linear sweep voltammetry, those acids whose dissociation rate constant $k_{-1}$ exceeds $10^3$–$10^4$ s$^{-1}$ might be classified as labile. In the absence of kinetic data of chemical stages, the system lability can be estimated using the data of the surface concentrations of proton donors and acceptors, which can be obtained by convolution of experimental voltammograms. It has been found that acetic or glycolic acid systems show labile behavior, while the dissociation of gluconic acid has certain kinetic limitations. Protonated glycine exhibits dual behavior: a fast split of the proton from the carboxyl group and a slow dissociation of the protonated amino group.

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