SELECTIVE INHIBITION AND SELF-INHIBITION
OF ELECTRODE REACTIONS BY ORGANIC COMPOUNDS

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The oxidation of Br^- and I^- on Pt electrodes in $HClO_4$ was found to be selectively inhibited by phenol. The rate of oxygen evolution is essentially unaltered under the same experimental conditions. The species causing inhibition is not the neutral phenol molecule but the phenoxy radical formed from it in an anodic charge-transfer adsorption process. The initial potential for inhibition was related to the concentration of phenol in solution and to the pH. The adsorption of the phenoxy radical is controlled by the combined effects of charge transfer and competition with adsorbed water molecules. The inhibition effects of various derivatives of phenol, as well as that of isomers of naphthol, di- and trihydroxy benzene were studied. Self-inhibition effects were observed in systems in which the half wave potentials are less anodic than the initial inhibition potential. The pH dependence of these potentials is discussed.

All heterogeneous reactions, including electrode reactions, are sensitive to small amounts of impurities or additives which inhibit or poison the reaction. The poison or inhibitor is adsorbed on the surface and thus interferes with the desired reaction. It is often found that the reaction rate decreases in larger proportion than does the decrease of available free surface. In gas phase kinetics this may be due to the fact that reaction can only occur on "active sites" on the surface, which constitute a small fraction of the total surface, and adsorption of the poison occurs on these very sites. In electrode reactions the rate may be further influenced by the change of surface potential due to adsorption of the inhibitor.

Three types of species may be adsorbed on the surface of an electrode: ions, neutral molecules and radicals formed by charge transfer. The adsorption of ions and neutral molecules has been studied most widely for mercury[1-5], but work on some solid metals has been reported[6-10]. Adsorption isotherms for ions and neutral molecules were derived[11-14] and in particular the potential dependence of adsorption has been discussed[15,16]. The adsorption of radicals formed by charge transfer has been studied mostly on noble metals[17-20]. Adsorption isotherms which depend primarily

on the nature of the surface were discussed[21-25]. In a recent publication[26] the adsorption of phenoxy radicals on the surface of a platinum electrode was reported. The isotherm applicable in this case is a combined isotherm including the potential dependence of adsorption of neutral molecules and that due to charge transfer, as will be seen below.

Simple derivatives of phenol, *e.g.* cresol and naphthol behave qualitatively in the same way as phenol[27]. The behaviour of di- and trihydroxybenzenes[28] is complicated by the ease of oxidation of these compounds (except resorcinol and phloroglucinol, in which the OH groups are in the *meta* position to each other and a corresponding quinone cannot be formed). The kinetics of the quinone–hydroquinone system has been studied[29-37], since it serves as a useful reversible hydrogen electrode in acid and neutral media. The oxidation of other hydroxybenzenes has been studied, mostly from the analytical point of view[38-44]. In several recent reviews on electro-organic reactions[45-47] the oxidation of phenols, dihydroxybenzenes and various derivatives of these compounds were discussed, and further references quoted. In a recent study[28], self-inhibition effects have been observed in the oxidation of these compounds as will be discussed below.

EXPERIMENTAL

Details of experimental procedures were reported elsewhere[26]. All steady-state current–potential measurements were taken potentiostatically. Reagents used were all AR grade. Phenol and its derivatives were redistilled or recrystallised and stored under refrigeration.

RESULTS AND DISCUSSION

Experimental

The inhibition of bromine and iodine evolution by various concentrations of phenol in 1M-HClO$_4$ is shown in Fig. 1 and 2, respectively. Similar results were obtained for the three isomers of cresol and for α- and β-naphthol[27]. It is clearly seen in all these cases that inhibition does not start until a well-defined potential E_i is reached, which depends on both pH and concentration of the inhibitor. Beyond the potential E_i inhibition sets in sharply over a very narrow potential range, implying the existence of strong lateral attraction interactions, as will be discussed below.

The adsorption of neutral organic molecules on platinum was also studied[48-50]. It was established experimentally that maximum adsorption occurs at c. $E_{max} = 0.3$ V s.c.e. and the degree of coverage decreases nearly symmetrically on either side of this maximum, approaching zero beyond -0.1 V on the negative side and beyond 0.7 V on the positive side. Thus, the initial inhibition potential E_i falls outside the range of adsorption of neutral phenol molecules. Hence inhibition cannot be caused by phenol itself. It is the phenoxy radical, formed by charge transfer,

which is adsorbed on the surface causing inhibition.

$$[\varPhi OH]_{soln} \quad \rightleftharpoons \quad [\varPhi O\cdot]_{ads} + H^+ + e \qquad (1)$$
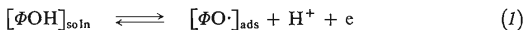
This mechanism of inhibition is substantiated by the fact that anisol, in which the hydrogen atom has been replaced by a methyl group, was found to cause no inhibition. Obviously, this compound cannot easily form the phenoxy radical and it is hence not adsorbed in the potential range in question. In a further experiment, an excess of Br_2 was added to a solution containing $HClO_4$, Br^- and phenol, where the potential was held in the inhibition region. All the phenol in solution was precipitated immediatly as tribromophenol but the inhibited current did not increase, showing that the adsorbed layer remained intact. This observation supports the assumption that the adsorbed species is not the neutral phenol molecule but the strongly bound phenoxy radical. The same mechanism of adsorption and inhibition probably applies for the three isomers of cresol and the two naphthols tested[27].

THE CHANGE OF E_i WITH CONCENTRATION AND pH

The initial inhibition potential E_i is defined as the potential at which inhibition just starts. It can be seen from Fig. 2 that this potential is very well-defined for each
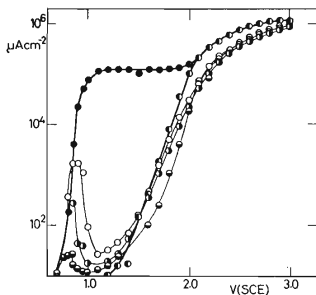

FIG. 1

Inhibition of Br_2 Evolution on Pt by Various Concentrations of Phenol

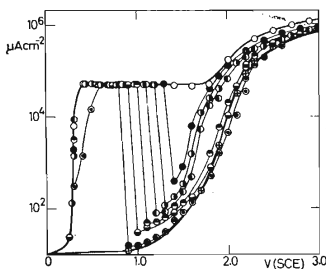● 0M, ○ 0·001M, ◑ 0·01M, ◓ 0·1M, ◐ pure $HClO_4$.

FIG. 2

Inhibition of I_2 Evolution on Pt by Various Concentrations of Phenol

○ 0M, ● 0·001M, ◑ 0·005M, ◐ 0·01M, ◓ 0·05M, ◒ 0·1M, ⊙ 0·5M, ⊕ $HClO_4$, 0·1M phenol.

phenol concentration, due to the sudden decrease of current density beyond this potential. The dependence of E_i on concentration of the inhibitor is shown in Fig. 3 for phenol and for m-cresol. Fig. 4 shows the dependence of E_i for phenol on pH in acid and neutral solutions (up to pH 9).

For the interpretation of these results two effects must be considered. On the one hand, the adsorbed species is a relatively large organic molecule replacing several molecules of water from the surface. The extent of its adsorption should depend on potential according to the equations describing the potential dependence of organic adsorption[15−16]. On the other hand, the phenoxy radical adsorbed on the surface is formed by charge-transfer (cf. equation (1)) and the extent of its absorption should depend on potential according to the equations developed for the adsorption of intermediates formed in charge-transfer processes[21−25]. A further assumption is made, namely that E_i corresponds always to some critical value of the surface coverage Θ_i independent of concentration and pH.

The model of competition with water developed by Bockris and coworkers[15]. yields for the potential dependence of adsorption of neutral molecules the isotherm*

$$\frac{\Theta}{1-\Theta} = Kc \exp - \left[nZ \left(\frac{\mu X - Z\varepsilon m}{kT} \right) \right] \tag{2}$$
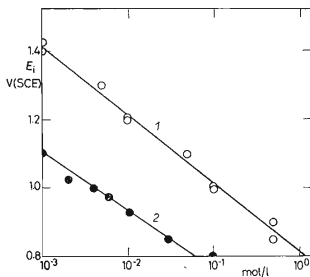

FIG. 3

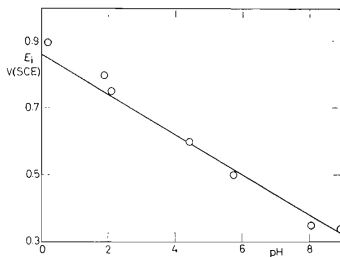Dependence of the Initial Inhibition Potential E_i of Phenol 1 and m-Cresol 2 on Concentration

FIG. 4

Dependence of the Initial Inhibition Potential E_i of Phenol on pH

* An earlier model proposed by Frumkin[16] in 1926 accounts for the potential dependence of electrosorption of neutral molecules in terms of the change of energy of the double layer. The validity of the model of Bockris and coworkers has been questioned recently[51], but it was shown[52] that the competition with water accounts for most of the potential dependence of adsorption. while the change of energy of the double layer may contribute 10—20% at most to this variation.

In this model it is assumed that water is adsorbed on the surface in one of two positions. The quantity Z is related to the number of water molecules per cm^2 in the two possible positions by:

$$Z = \frac{N_\uparrow - N_\downarrow}{N_\uparrow + N_\downarrow} . \tag{3}$$

On the other hand, Z is related to the field strength X as:

$$Z = \tan h \left(\frac{\mu X - Z\varepsilon m}{kT} \right), \tag{4}$$

where μ is the moment dipole of a water molecule, ε is the energy of interaction between two adjacent water molecules and m is a coordination number.

When adsorption of a neutral molecule is concerned, the constant K in equation (2) is independent of potential. In the case of adsorption of a radical formed by charge-transfer according to (1) the dependence of K on potential and on pH is given by

$$K = K' c_{H^+}^{-1} \exp \left(EF/RT \right). \tag{5}$$

Combining equations (2) and (5) and taking the high-field approximation $(\mu X \gg \gg Z\varepsilon m)$ one has

$$\frac{\Theta}{1 - \Theta} = K' c_\Phi c_{H^+}^{-1} \exp \left(EF/RT \right) \exp - \left[n\mu X/kT \right], \tag{6}$$

where c_Φ is the concentration of inhibitor. Equation (6) can be rearranged by writing the field strength in terms of the potential

$$\frac{n\mu X}{kT} = \frac{n\mu}{\delta} \left(\frac{E - E_{max}}{kT} \right) = \frac{n\mu}{e_0 \delta} \frac{e_0 N}{N} \left(\frac{E - E_{max}}{kT} \right) = \frac{n\mu}{e_0 \delta} \frac{F(E - E_{max})}{RT}, \tag{7}$$

where δ is the thickness of the compact part of the double layer, equal in this case to the diameter of water molecules. Combining equations (6) and (7) one has

$$\frac{\Theta}{1 - \Theta} = K' c_\Phi c_{H^+}^{-1} \exp \left(EF/RT \right) \left(1 - \frac{n\mu}{e_0 \delta} \right) + \frac{n\mu}{e_0 \delta} \frac{E_{max} F}{RT} . \tag{8}$$

Since E_{max} is essentially independent of the concentration of phenol (or other inhibitor) one has from equation (8)

$$\left(\frac{\partial E_i}{\partial \log c_\Phi}\right)_{pH} = \left(\frac{\partial E}{\partial \log c_\Phi}\right)_{pH,\theta} = -(2 \cdot 3RT/F)\left(1 - n\mu/e_0\delta\right)^{-1}. \qquad (9)$$

The observed slope of E_i vs. $\log c_\Phi$ is $-0 \cdot 20$ V, and $-0 \cdot 18$ V for phenol and m-cresol, respectively (cf. Fig. 3). Using the numerical values of μ, e_0 and δ in equation (9) one has $(\mu/e_0\delta) = 0 \cdot 14$ and hence n comes out to be $5 \cdot 0$ and $4 \cdot 8$ for phenol and m-cresol, respectively. In an independent study of the electrosorption of benzene on Pt [49] a value of $n = 9 \pm 2$ was calculated. The lower value for the phenoxy radical here shows that adsorption occurs through the oxygen atom with the aromatic ring at an angle to the surface. The difference between the results for phenol and m-cresol is not significant, showing that the added methyl group is situated far from the surface and does not interfere with adsorbed water molecules.

The dependence of E_i on pH can be obtained from equation (8) as

$$\left(\frac{\partial E_i}{\partial \log c_{H^+}}\right)_{c_\Phi} = \left(\frac{\partial E_i}{\partial \log c_{H^+}}\right)_{c_\Phi,\theta} = \left[\frac{2 \cdot 3RT}{F} - \frac{n\mu}{e_0\delta}\left(\frac{\partial E_{max}}{\partial \log c_{H^+}}\right)_{c_\Phi}\right]\left(1 - \frac{n\mu}{e_0\delta}\right)^{-1}. \quad (10)$$

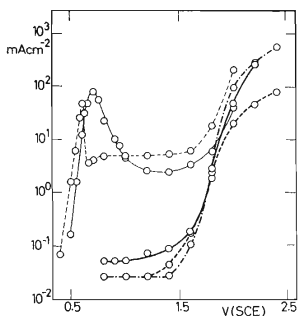It was shown experimentally[49] that for the electrosorption of benzene on platinum

Fig. 5

Current–Potential Curves for the Oxidation of Three Isomers of Dihydroxy Benzene in 1M-HClO₄

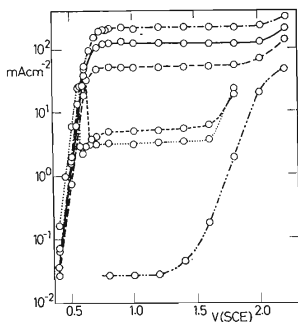Upper group of lines: ———— catechol, — — — hydroquinone; lower group of lines: ———— phenol, — — — b.g., –·–· resorcinol,

Fig. 6

Effect of Concentration on the Oxidation and Self Inhibition of Hydroquinone in 1M-HClO₄

–··– b.g., ······ 0·40M, – – – 0·20M, ·–·–· 0·10M, ———— 0·05M, — — 0·02M.

$(\partial E_{max}/\partial \log c_{H^+})_{c_\Phi} = 2 \cdot 3RT/F$. Substituting this relation in equation (10) yields $(\partial E_i/\partial \log c_{H^+})_{c_\Phi} = 2 \cdot 3RT/F$ in agreement with experiment (*cf.* Fig. 4). It should be noted that this relationship holds only up to a pH value well below the $pK = 9 \cdot 9$ for phenol. The expected behaviour at higher pH will be discussed below.

Oxidation and Self-Inhibition of Isomers of Di- and Tri-hydroxybenzene

Effect of structure. Current–potential curves for oxidation of the three isomers of dihydroxybenzene are shown in Fig. 5. Two of these compounds, hydroquinone and catechol, can be easily oxidised to the corresponding quinones, while the *meta*-isomer, resorcinol, is difficult to oxidise. It is noted that under the experimental conditions chosen, a limiting current behaviour is not observed. Instead, the current first rises with potential and then decreases sharply, in a manner reminiscent of the current–potential curves for oxidation of Br^- in the presence of phenol, shown in Fig. 1. The phenomenon observed here appears to be one of self inhibition.

Taking hydroquinone as an example, the following two reactions may take place:

$$ \quad + \; 2H^+ \; + \; 2e \qquad (A) $$

$$ \quad + \; H^+ \; + \; e \qquad (B) $$
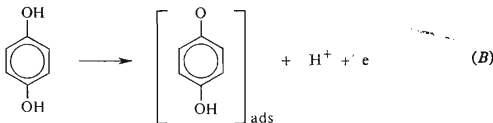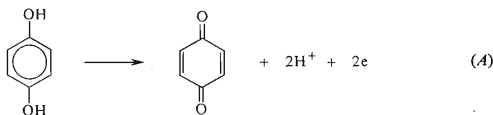
Reaction (A) becomes significant at potentials close to $E_{1/2}$ while reaction (B) is predominant at or above the initial inhibition potential E_i. For the *ortho* and *para* isomers $E_{1/2} < E_i$ and hence oxidation takes place, followed by self inhibition at potentials above E_i (*cf.* Fig. 5). For the *meta* isomer (as well as for phenol) it appears that $E_{1/2} > E_i$, so that the surface becomes first covered with the adsorbed radical and when the potential $E_{1/2}$ is reached oxidation does not occur, due to self inhibition. A similar distinction in behaviour has been observed between the two isomers of tri-

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*   Exactly where the reaction becomes significant, *i.e.* measurable, depends on its reversibility. For a highly reversible case this would occur quite close to $E_{1/2}$ but in the case of an irreversible reaction the observed $E_{1/2}$ may be shifted from its thermodynamically significant value and oxidation may then start substantially below $E_{1/2}$. In the present paper we have used $E_{1/2}$ as a relative measure of the potential at which oxidation starts.

hydroxybenzene which have OH groups in the *ortho* or *para* position, on the one hand, and the symmetrical isomer in which all three hydroxyl groups are in the *meta* position to each other, on the other. It is not necessary to assume here that the initial potential for inhibition or self inhibition E_i should be identical for all the isomers of hydroxybenzene tested. It is reasonable to assume, however, that the potential at which the adsorbed radical is formed (*cf.* equation (*B*)) would depen on the position of the other OH groups much less than the half wave potential for the oxidation reaction (*cf.* equation (*A*)) which is increased by nearly half a volt for the *meta* isomers which cannot form corresponding quinones.

The phenomenon of self-inhibition throws some light on the mechanism of oxidation of these compounds. Referring to equations (*A*) and (*B*) it becomes clear that self-inhibition will only occur if the adsorbed radical formed in reaction (*B*) is so strongly bound to the surface that it cannot be readily oxidised further to the corresponding quinone. Reversing the same argument, since self inhibition *does* occur, it must be concluded that the oxidation process (equation (*A*)) does not proceed through an intermediate adsorbed radical. It was shown by Hale and Parsons[29] that the energy of activation for the transfer of the two electrons from hydroquinone is nearly the same and the electrons are transferred one at a time. Thus the radical is formed as an intermediate in solution and a second charge transfer occurs before adsorption could take place. This mechanism could be varified by studies on a rotating ring-disc electrode, provided that the lifetime of the radical formed on the disc by the first charge transfer is long enough for it to be detected on the ring.

Effect of Concentration and Potential

The effect of concentration on oxidation and self inhibition is shown in Fig. 6 for the case of hydroquinone in 1M-HClO$_4$. It is seen clearly that, up to a concentration of 0·10M simple behaviour is encountered, and a limiting current is reached. The value of this limiting current is nearly equal to that measured for bromine and iodine evolution in solutions of the same equivalent concentration. The critical concentration beyond which self inhibition occurs depends to some extent on experimental conditions, but the transition in every case is very sharp[28]. Thus, in Fig. 6 it is seen that in 0·1N solution no inhibition occurs, while in 0·2N solution the inhibited current is about two orders of magnitude lower than the diffusion limited current. A similar sharp change in oxidation current with potential can be seen if one compares the values the current in the vicinity of 0·60 V s.c.e. for 0·1N and 0·20N solutions in Fig. 6. Up to 0·60 V s.c.e. the points for the two concentrations practically coincide. At 0·62 V the ratio of currents is 2·3 and at 0·66 V the ratio already exceeds 30. If the current is proportional to the fraction of the surface which is free $(1 - \Theta)$ and one assumes $\Theta \simeq 0$ for 0·10N solution then for 0·20N solution of hydroquinone Θ changes from zero at 0·60 V to 0·50 at 0·62 V and to 0·97 at 0·66 V.

The rate of change of Θ with chemical or electrochemical potential of adsorbate in solutions depends on the type of isotherm applicable to the system. The behaviour observed here is characteristic of an isotherm involving a large lateral attraction energy[53,54]. It was shown that in such a case Θ passes suddenly from a very low value to nearly unity as a result of a small change of concentration or potential. The data presented above imply a change of Θ from 0·03 to 0·097 roughly, due to an increase of 60 mV in potential, or a change of concentration by a factor of two. If the Langmuir isotherm were applicable, the same change in Θ would be brought about by an increase of potential of 0·18 Volt, or by three orders of magnitude change in concentration.

Dependence of E_i and $E_{1/2}$ on pH

The current–potential curves for the oxidation of the three isomers of dihydroxy benzene at pH = 12 are shown in Fig. 7. Comparison with Fig. 5 shows a striking difference only for resorcinol, which can be oxidised in alkaline solution at about the same rate as the other two isomers, although at a higher potential. This point is further emphasised in Fig. 8 which shows the oxidation behaviour of phenol, resorcinol and phloroglucinol in 1N-NaOH. It must be concluded on the basis of these findings that $E_{1/2}$ and E_i for the last three compounds change with pH in different ways, so that at low pH $E_{1/2} > E_i$ while at high pH $E_{1/2} < E_i$.
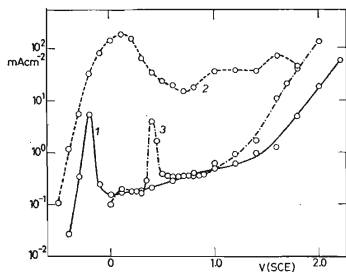

FIG. 7

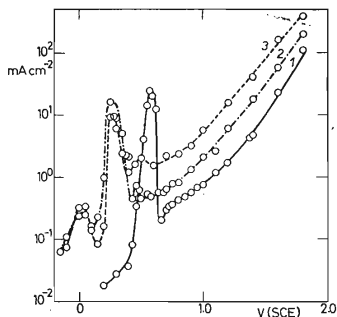Current–Potential Curves for the Oxidation of Catechol 1, Hydroquinone 2, and Resorcinol 3 at pH 12

FIG. 8

Current–Potential Curves for the Oxidation of Phenol 1, Resorcinol 2 and Phloroglucinol 3 in 1M-NaOH

Up to pH 9, we found experimentally, in agreement with theory, a slope of $(\partial E_i/\partial pH)_{c_\Phi} = -2\cdot3RTF$ (cf. Fig. 4 and equation (10)). The acid dissociation constant for phenol is pK 9·9. Thus at pH $\geqslant$ 11·0 the molecule is mostly ionized and the absorption equilibrium may be described by the equation

$$[\Phi O^-]_{soln} \quad \rightleftharpoons \quad [\Phi O\cdot]_{ads} + e \qquad (11)$$

instead of by equation (1). Where this equation is applicable, the initial inhibition-potential will be independent of pH. The variation of E_i with pH is shown schematically in Fig. 9. Although the value of E_i may not be exactly the same for all compounds tested, the dependence on pH will be the same, with the break in the curve occurring at pH = pK for each compound.

It is not possible to decide how $E_{1/2}$ depends on pH unless the products of oxidation are known. For phenol a mixture of products was found[55–57]. If is assumed that the quinone is the main product, then the oxidation reaction in acid involves the transfer of four electrons and four protons and in alkaline medium it involves four electron and three protons. Thus the coefficient $(\partial E_{1/2}/\partial pH)_{c_\Phi}$ should change from 60 mV at low pH to 45 mV at high pH. The lines for $E_{1/2}$ for phenol and resorcinol in Fig. 9 were drawn on the basis of this assumption. It was found experimentally that phenol is not oxidised at pH = 12·7 but is already oxidised at pH = 13·1. Accordingly, the line for $E_{1/2}$ was drawn to cross the line for E_i at pH = 12·9. The line for re-
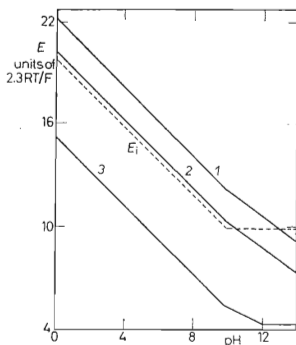

FIG. 9

Schematic Representation of the Variation of E_i and $E_{1/2}$ for Phenol *1*, Resorcinol *2*, and Catechol *3* with pH

sorcinol was placed below that for phenol by the difference in their reported half wave potentials. This line crosses the line for E_i at pH = 10·5. In agreement with this prediction it was found that no oxidation of resorcinol occurred at pH = 10 while at pH = 12 a well defined oxidation wave could be observed. The half wave potential for catechol lies well below E_i at all values of the pH. The slope $E_{1/2}$ vs. pH for the two-electron reaction changes from 60 mV in acid to 30 mV above pH = pK_1 = = 9·8 and to zero above pH = pK_2 = 12.

Fig. 9 is schematic in that a single value of E_i is used for all compounds, and the change in the observed value of $E_{1/2}$ due to kinetic factors, which may depend on pH, was not taken into account. It serves, nevertheless, to explain qualitatively the difference in behaviour between the easily oxidisable hydroxy benzene isomers and those which are difficult to oxidise, and provides an interpretation for the change of behaviour of the latter with pH.

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