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THE ELECTROCHEMICAL BEHAVIOUR OF SILVER-PYRIDINE-WATER TERNARY SYSTEM

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ABSTRACT

The ternary system silver-pyridine-water has been studied, the potential-pH equilibrium diagrams have been constructed and the theoretical domains of corrosion, passivation and immunity of the title metal in the presence and absence of pyridine have been discussed. The electrochemical conditions for the protection of silver in aqueous solution of pyridine have been recommended and the domains of pH in which silver pyridine complex is formed have been determined.

Finally, the effect of concentrations of both pyridine and silver ions on the complexation is also studied in aqueous solution, and it has been found that the zone of formation of silver pyridine coplex decreases as the ratio $[Ag^+]$ / $[Py]$ increases.

INTRODUCTION

The potential-pH equilibrium diagrams of Pourbaix[1,2] for the binary metal-water systems are valid only in the absence of substances with which metal can form soluble complexes or insoluble salts.

Systems of competition equilibria with exchange of electrons, protons, ions or molecules of complexing agent for the metal-ligand-water ternary systems have been studied recently[3,9].

THERMODYNAMIC DATA

In deriving such diagrams it is necessary to consider four different types of reactions that may occur:

1) *Chemical reactions* that involve neither H^+ ions nor electrons and can be expressed as

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$$\Sigma\, \upsilon\, [M] = 0$$

the equilibrium constant K of that reaction is given by

$$\log K = \frac{-\Sigma\upsilon\mu^\circ}{1363} \qquad \text{(I)}$$

in which υ represents stochiometric coefficients of species employed in the chemical reaction and μ° the standard chemical potentials of these species.

2) *Electrochemical reactions* that involve only electrons, these reactions will be potential dependent, and will be expressed as:

$$\Sigma\, \upsilon\, [M] + ne = 0$$

the equilibrium condition is

$$E = E^\circ + \frac{0.0591}{n}\, \Sigma\, \upsilon \log [M]$$

with

$$E^\circ = \frac{\Sigma\upsilon\mu^\circ}{-23060\ n} \qquad \text{(II)}$$

where E is the equilibrium potential, E° the standard potential, n number of electrons in the oxidation-reduction process and [M] the concentration of species M.

3) *Chemical reactions with water* that involve only H^+ ions, these reactions will be pH-dependent, and will be expressed as

$$A + c\, H_2O = B + m\, H^+$$

in which B is the alkaline form and A the acid form of the element in question, the condition for equilibrium will be of the form:

$$\log \frac{[B]}{[A]} = \log K + m\, pH \qquad \text{(III)}$$

4) *Electrochemical reactions with water* that involve both H^+ ions and electrons, these reactions will be dependent upon both potential and pH and will be expressed as:

$$A + c\, H_2O + ne = B + m\, H^+$$

in which A is the oxidized form and B the reduced form of the element in question, the condition for equilibrium will be of the form:

$$E = E^\circ - \frac{0.0591}{n} \log \frac{[A]}{[B]} \tag{IV}$$

Finally, if we put $[A] = [B]$ in equilibrium reactions of the type (III) or (IV) we obtain the following equations which express the conditions of pH and electrode potential for which the concentrations of these two forms are equal.

$$pH = \frac{1}{m} \log K \tag{V}$$

and $$E = E^\circ - \frac{0.591\ m}{n} pH \tag{VI}$$

equations (V) and (VI) are valid for the case when the forms A and B of the element in question are either both in the dissolved state or both in the gaseous state.

Since the hydrogen and oxygen evolution reactions are both pH-dependent and involve electrons, it has been drawn the lines:

$E = -0.0591$ pH ....(line a)

and $E = 1.223 - 0.0591$ pH ....(line b)

which express respectively the equilibria of both the reduction and oxidation of water at a hydrogen and oxygen pressrues of one atmosphere.

Standard chemical potentials μ° have been calculated at 25°C; for pyridinium ion HPy^+, using the standard free energy of formation of pyridine[10] and its protonation constant[11] $\log K = 5.18$; for pyridine complexes using the stability constants[12] $\log K_2 = 1.97$ and $\log K_2 = 2.38$ and for all other species using the data given in Reference (2). Chemical potentials are given in the folllowing table in Kcal / mol at 25°C.

Ag	0	Ag_2O	— 2.586	Py	—43.330
H^+	O	AgO	+ 2.600	HPy^+	—50.360
Ag^+	+18.430	AgO^-	— 5.490	$AgPy^+$	–27.585
H_2O	—56.690	AgO^+	+53.900	$AgPy_2^+$	—74.159
		Ag_2O_3	+20.800		
solid anhydrous oxide					

RESULTS AND DISCUSSION

From the chemical potential data, it is possible to calculate the basic equations including the possible reactions and equilibria as follows:

I. *Two Dissolved Substances:*

I. 1. Relative stability of the dissolved substances.

$Ag^+ + H_2O = AgO^- + 2\ H^+$

$$pH = 12.02 + 0.5 \log \frac{[AgO^-]}{[Ag^+]} \qquad (1)$$

$Ag^+ + H_2O = AgO^+ + 2\ H^+ + 2e$

$$E = 1.998 - 0.0591\ pH + 0.0295 \log \frac{[AgO^+]}{[Ag^+]} \qquad (2)$$

$AgO^- = AgO^+ + 2e$

$$E = 1.228 + 0.0295 \log \frac{[AgO^+]}{[AgO^-]} \qquad (3)$$

I.2. Limits of the domains of relative predominance of the dissolved substances.

Ag^+ / AgO^- $pH = 12.02$ (1')

Ag^+ / AgO^+ $E = 1.998 - 0.0591\ pH$ (2')

AgO^- / AgO^+ $E = 1.228$ (3')

II. *Two Solid Substances:*

Limits of the domains of relative stability of silver and its oxides.

$2\ Ag + H_2O = Ag_2O + 2\ H^+ + 2e$

$$E = 1.173 - 0.0591\ pH \qquad (4)$$

$Ag_2O + H_2O = 2\ AgO + 2\ H^+ + 2e$

$$E = 1.398 - 0.0591\ pH \qquad (5)$$

$2\ AgO + H_2O = Ag_2O_3 + 2\ H^+ + 2e$

$$E = 1.569 - 0.0591\ pH \qquad (6)$$

III. *One Solid Substance and One Dissolved Substance:*

Solubility of silver and its oxides.

$$2\ Ag^+ + H_2O = Ag_2O + 2\ H^+$$

$$pH = 6.330 - \log\ [Ag^+] \tag{7}$$

$$Ag_2O + H_2O = 2\ AgO^- + 2\ H^+$$

$$pH = 17.72 + \log\ [AgO^-] \tag{8}$$

$$Ag = Ag^+ + 3$$

$$E = 0.799 + 0.0591\ \log\ [Ag^+] \tag{9}$$

$$Ag + H_2O = AgO^- + 2\ H^+ + e$$

$$E = 2.22 - 0.1182\ pH + 0.0591\ \log\ [AgO^-] \tag{10}$$

$$Ag^+ + H_2O = AgO + 2\ H^+ + e$$

$$E = 1.772 - 0.1182\ pH - 0.0591\ \log\ [Ag^+] \tag{11}$$

$$AgO^- = AgO + e$$

$$E = 0.351 - 0.0591\ \log\ [AgO^-] \tag{12}$$

$$2\ Ag^+ + 3H_2O = Ag_2O_3 + 6H^+\ w\ 4e$$

$$E = 1.67 - 0.0886\ pH - 0.0295\ \log\ [Ag^+] \tag{13}$$

IV. *Equilibrium Between the Two Forms of Pyridine in the Presence of Hydrogen Ions:*

$$Py + H^+ = HPy^+$$

$$pH = 5.18 - \log\ \frac{[HPy^+]}{[Py]} \tag{14}$$

Limit of the domain of relative predominance of the two forms Py and HPy^+

$$Py\ /\ HPy^+ \qquad\qquad pH = 5.18 \tag{14'}$$

V. *Reactions of Silver Metal with Pyridine:*

$$Ag + 2\ HPy^+ = AgPy_2 + 2H^+ + e$$

$$E = 1.152 - 0.1182\ pH + 0.0591\ \log\ \frac{[AgPy_2]}{[HPy^+]^2} \tag{15}$$

$$Ag + 2\ Py = AgPy^+{}_2 + e$$

$$E = 0.541 + 0.0591\ \log\ \frac{[AgPy_2{}^+]}{[Py]^2} \tag{16}$$

VI. *Reactions of Silver Ion with Pyridine:*

$$Ag^+ + 2\,HPy^+ = AgPy^+_2 + 2H^+$$

$$pH = 2.983\ W \log\,[HPy^+] \qquad (17)$$

VII. *Decomposition of Pyrdine Complex with Water:*

$$2\,AgPy_2^+ + H_2O = 2H^+ + 4\,Py + Ag_2O$$

$$pH = 10.68 + \log \frac{[Py]^2}{[AgPy_2^+]} \qquad (18)$$

$$AgPy_2^+ + H_2O = AgO + 2H^+ + 2\,Py + c$$

$$E = 2.029\ W\ 0.1182\ pH + 0.0591 \log \frac{[Py]^2}{[AgPy_2^+]} \qquad (19)$$

$$2\,AgPy_2^+ + 3H_2O = Ag_2O_3 + 6H^+ + 4Py + 4e$$

$$E = 1.789\ W\ 0.0886\ pH + 0.0295 \log \frac{[Py]^2}{[AgPy_2^+]} \qquad (20)$$

$$2\,AgPy_2^+ + 3H_2O = Ag_2O_3 + 2H^+ + 4HPy^+ + 4e$$

$$E = 1.493 - 0.0295\ pH + 0.0295 \log \frac{[HPy^+]^2}{[AgPy_2^+]} \qquad (21)$$

RESULTS AND DISCUSSION

The present study is divided into two parts:

1) *Effect of pyridine on (E-pH) diagram of Ag-H_2O system:*

To study the effect of 0.1M aqueous solution of pyridine upon the behaviour of 0.01 M Ag^+ solution, diagram, of the Ag-Py-H_2O ternary system (Fig. 2) which represent the theoretical conditions of corrosion, immunity and passivation must be compared with that of Ag-H_2O binary system (Fig. 1) at the same Ag^+ concentration. Superimposing the two diagrams, it is possible to observe that:

— The presence of pyridine has no effect on the electrochemical behaviour of silver below pH 4 (line 17). This may be explained by the fact that below pH 4 pyridine is practically protonated. Above pH 4; and at potentials more positive than 0.54 volt, silver metal may be attacked by pyridine solution to form Ag

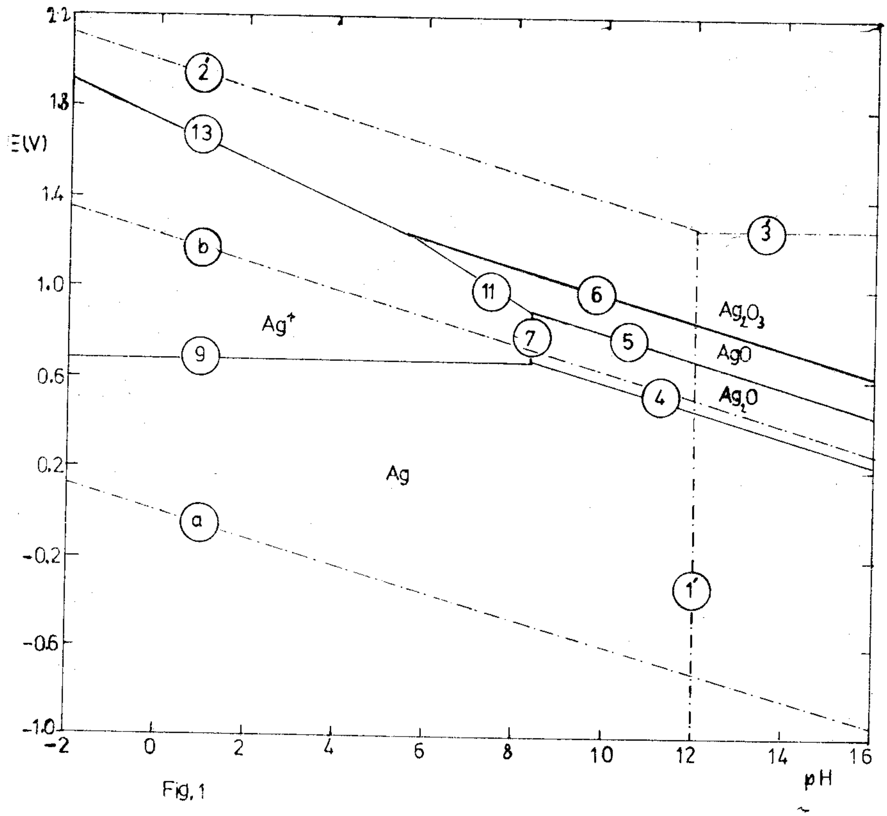


Fig 1. Pourbaix diagram for Ag-H2O binary system.

$Py_2{}^+$ complex. So, the reversibility of silver electrode with respect to (0.1 M) Ag^+ decreases from pH 7.3 (In the absence of complexing agent to pH 4 in the presence of 0.1 M pyridine).

— The nobility of silver decreases by the presence of pyridine; in the domain situated between pH 4.-10.9, zone included between the verticals 17 and 18 which indicate the zone of predomigance of the complex $AgPy_2{}^+$ in solution as a function of pH. It can also be seen from Fig. 2, that the silver complex is formed in the range of potentials 0.5 to 1.4 volt.

— The presence of pyridine, also diminishes the zone of passivation of silver through the formation of oxides. In the absence of pyridine passivation starts at pH 8.3 (at the conc. of Ag^+ used) but in the presence of pyridine, passivation starts at pH 10.9

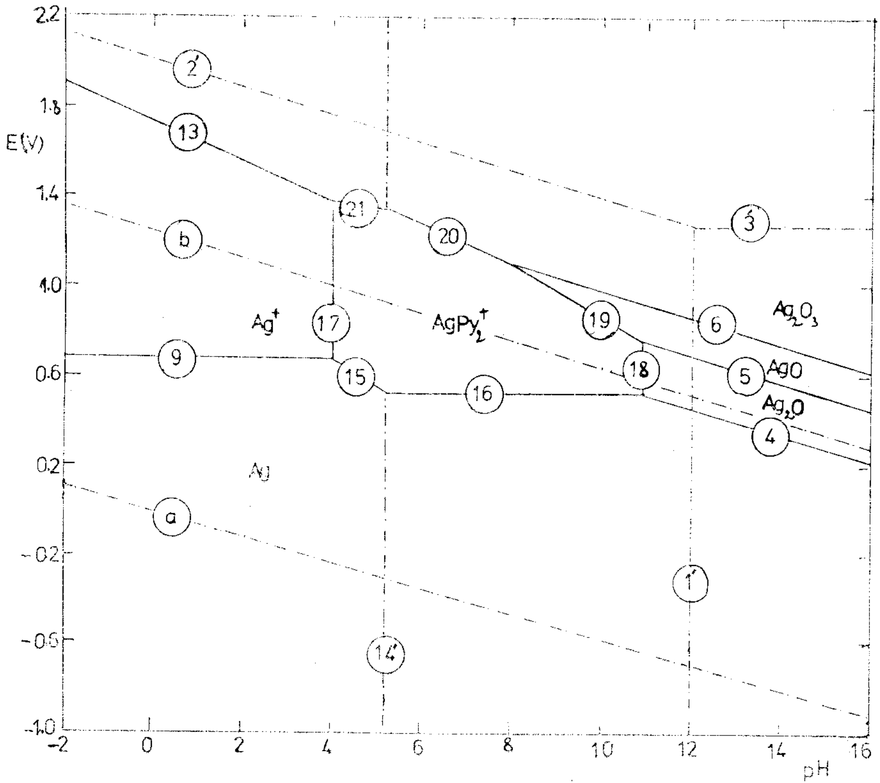


Fig.2

Fig. 2. Pourbaix diagram for Ag-Py-H_2O ternary system.

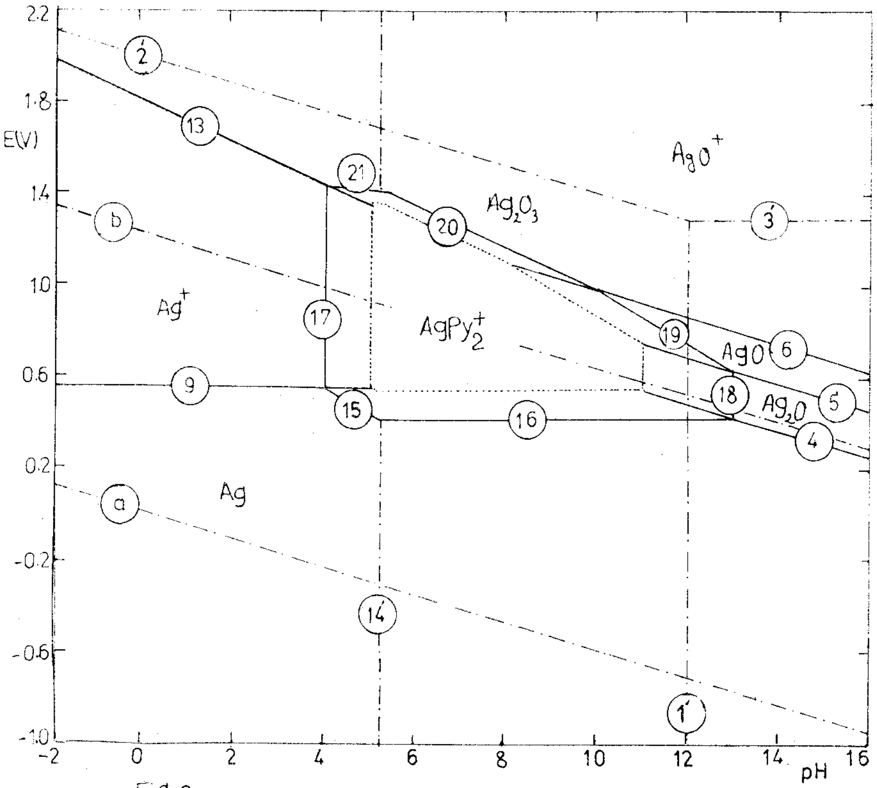
Diminishing the zone of passivation and growing the zone of corrosion of silver are attributed to the fact that silver oxide Ag_2O is impossible to exist in the presence of pyridine unless at pH values larger than 11.

— The zone of immunity of silver is also affected by the presence of pyridine. The potential of equilibrium of metallic silver is most affected at pH 5.2 as indicated by line 16, for which it is possible to write it again as: "in the pH range 5.2- 10.9, the potential E = 0.53 V".

— The protection of silver electrode (or silver metal) from aqueous solution of pyridine -according to the forementioned discussion- is carried out by using it below pH 4 and at potentials less than 0.54 volt.

2,a) *Effects of pyridine concentration:*

Fig. 3 represents the effect of (10^{-1} and 10^{-2} M) pyridine on the electrochemical behaviour of (10^{-2}M) silver, it can be seen from the diagram that:



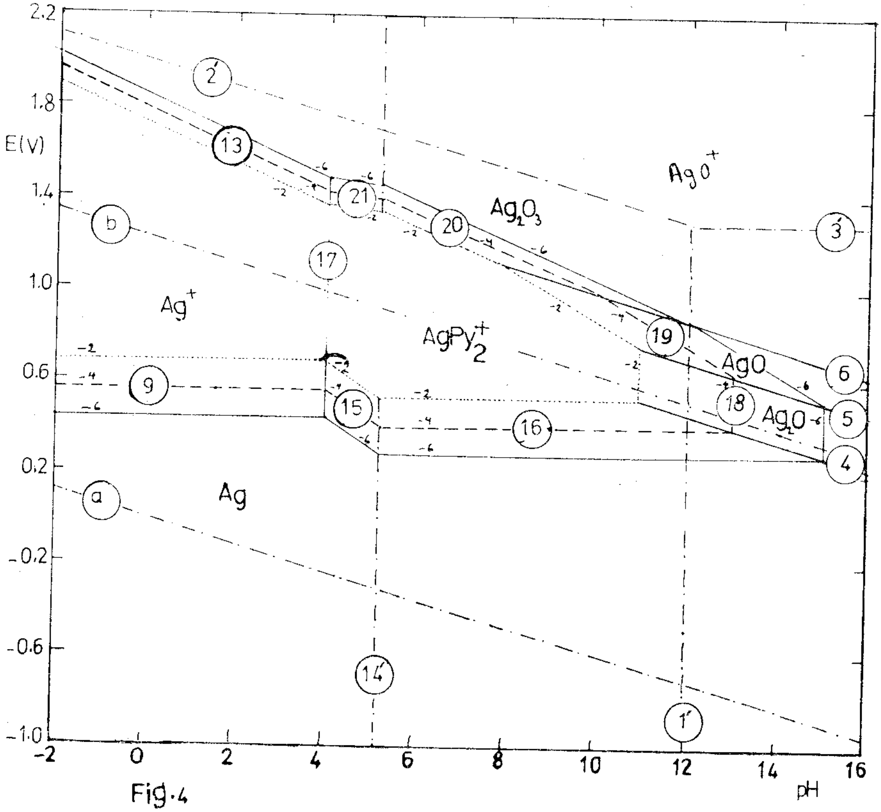
Fig·3

Fig. 3. Effect of change of pyridine conc. on Pourbaix diagram of Ag-Py-H_2O ternary system.

- As the concentration of pyridine increases, the zone of formation of $AgPy_2^+$ complex increases. The pH at which silver reacts with pyridine increases by one pH-unit, as the concentration of pyridine increases ten times (see equation 17).
- For 0.1 M pyridine solution, silver electrode is reversible below pH 4, but for lower pyridine conc. the reversibility increases.

2,b) *Effect. of Ag^+ concentration:*

Fig. 4 shows the effect of (0.1M) pyridine on (10^{-2}, 10^{-4} and 10^{-6}M) silver. From the diagram it is clear that, the zone of complex formation decreases with increasing Ag^+ concentration.



Fig·4

Fig. 4 Effect of pyridine solution on Pourbaix diagram of Ag-Py-H2O ternary system, for different Ag^+ conc.

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