CORROSION SCIENCE AND ENGINEERING

BENZOIC ACIDS AS CORROSION INHIBITORS FOR PURE IRON IN SULPHURIC ACID

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Corrosion of iron in 0.1N sulphuric acid and inhibition by benzoic, salicylic, orthonitrobenzoic and anthranilic acids were studied by weight loss and small amplitude cyclic voltammetric methods. Detailed description on adsorption isotherms is presented.

Key words: Corrosion inhibition, benzoic acid, cyclic voltammetry, adsorption isotherm

INTRODUCTION

Mineral acids have been used to pickle steel components before polishing. Most commonly used are hydrochloric and sulphuric acids in the concentration range of 1.0N to 5.0N upto 353K. The aromatic organic compounds were used in the study of inhibition of iron in acid solutions. Aniline and its derivatives were found to inhibit iron in sulphuric acid solution by adsorption mechanism. Ring substituted anilines obey linear free energy relationship for iron in acid solutions. [1]. Toluidines adsorb on iron parallel to the electrode surface [2]. The electrochemical behaviour of benzoic acid and substituted benzoic acids for iron in sulphuric acid has been studied by measuring the corrosion potentials and open circuit capacitance [3]. It was observed that the increase in electron density at the adsorption site increased the inhibition efficiency. In 1.0N sulphuric acid solutions, for a high purity zone-refined iron, amino benzoic acid inhibited more than hydroxy benzoic acids, anilines and phenols. It was observed that in the case of phenol and meta and para hydroxy acids the oxidation of -OH group on iron occurs during corrosion. The study of inhibition by benzoic acids in 1.0N sulphuric acid solution to understand the nature of adsorption is presented in this paper.

EXPERIMENTAL

Analar grade chemicals and pure iron (99.95% Fe, 0.0056% Mn, 0.001% Si and 0.025% C) have been used in the present studies.

For weight loss experiments iron specimens (75 x 25 cm) in triplicate were weighed and suspended by using glass hooks without touching each other in 400 ml beakers kept in a thermostat ($\pm$ 0.1K). After the specified period of immersion, specimens were

TABLE-1: Percentage inhibition efficiency for pure iron in 1.0N sulphuric acid containing different amounts of inhibitor

Inhibitor concentration	303K				323K				363K			
	A	**B**	**C**	**D**	**A**	**B**	**C**	**D**	**A**	**B**	**C**	**D**
0.005 M/BA	41	25	36	30	29	22	11	16	15	12	24	9
SA	41	39	39	39	18	17	16	15	25	3	23	7
ONBA	7	6	5	6	17	42	31	52	77	70	67	68
AA	74	71	74	70	80	80	75	74	85	82	77	77
0.01M/BA	38	24	40	33	30	23	14	15	12	15	16	3
SA	48	39	40	40	22	15	20	26	4	18	17	3
ONBA	9	9	4	5	-	18	30	46	46	55	56	59
AA	66	60	59	56	71	76	60	70	81	73	70	70
0.02M/BA	60	40	36	47	35	34	16	15	13	20	16	3
SA	49	39	50	41	40	20	23	12	26	32	28	12
ONBA	15	12	14	6	-	26	21	46	40	50	56	60
AA	52	53	45	44	69	65	58	62	83	74	69	70

A-30 minutes; B-60 minutes; C-90 minutes; D-120 minutes

removed, washed in running tap water and then in distilled water, dried and weighed. The variation in weight changes for three specimens was within the range of $\pm$ 5%.

A three electrode cell with platinum as an auxiliary electrode and saturated calomel as reference electrode was used for electrochemical studies. The small amplitude cyclic voltammetric studies were carried out using 'CORROVIT' in conjunction with x-y-t recorder.

RESULTS

Inhibition efficiency

The percentage inhibition efficiency obtained at different temperatures and concentrations is given in Table I. In the case of benzoic and salicylic acids the efficiency generally decreases with increase in temperature while in the case of orthonitrobenzoic and anthranilic acids, the efficiency increases with temperature. Anthranilic acid shows the highest efficiency in the range 70-80% at a temperature of 353K. Maximum efficiency is generally obtained within 30 minutes. In fact, there is a marginal decrease in efficiency with increase in immersion time. Concentration changes also have only marginal influence. In the case of orthonitrobenzoic and anthranilic acids efficiency tends to decrease with increase in concentration.

The corrosion rates obtained with and without inhibitors in 1.0N H_2SO_4 containing 0.02M inhibitor concentration were used to calculate the activation energy for corrosion processes. Table II presents activation energy calculated using 30 and 60 minutes (immersion time) values. It may be seen that orthonitrobenzoic acid decreases the energy of activation while benzoic acid, salicylic acid and anthranilic acid increase the energy of activation.

Isotherms

Various isotherms have been tried and the adsorption of benzoic acid, orthonitrobenzoic acid and salicylic acid is found to obey Langmuir isotherm (Fig.1).

$$\frac{\theta}{1-\theta}= AC \exp\left(\frac{-\Delta G}{RT} \text{ ads}\right) \qquad \ldots (1)$$
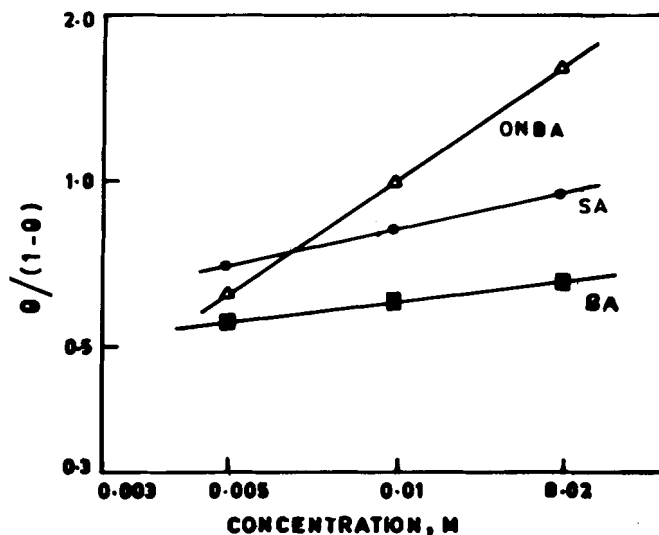

Fig. 1: $Log\left(\frac{\theta}{1-\theta}\right)$vs log C plot for benzoic, orthonitrobenzoic and salicylic acids at 303K

At higher temperatures, this isotherm however is found to be not applicable. As adsorption is a primary process, to offer inhibition it may be thought that the inhibitor molecules are well adsorbed over the metal following Langmuir isotherm. Increase of temperature affected the rate of adsorption and desorption and if the rate of corrosion is faster than the rate of adsorption, there may be a decrease in inhibition with temperature. This explains why benzoic acid and salicylic acid offer low inhibition at higher temperatures. In the case of anthranilic acid, commonly used isotherms were found to be not applicable. The adsorbed unprotonated aminobenzoic acid lies flat on the corroding iron. This organic may displace some solvent molecules and the

TABLE-II: Energy of activation $\Delta G^{\pm}$ for corrosion of pure iron in 1.0N sulphuric acid containing 0.02 M concentrations of inhibitors

System	$\Delta G^{\pm}$ calculated from 30 minutes data K.cal. mole⁻¹	$\Delta G^{\pm}$ calculated from 60 minutes data K.cal. mole⁻¹	$\Delta G^{\pm}$ Average value K.cal. mole⁻¹
1.0 N Sulphuric acid	14.81	16.71	15.76
1.0 N Sulphuric acid + 0.02M orthonitro benzoic acid	12.56	14.66	13.61
1.0 N Sulphuric acid + 0.02M benzoic acid	18.00	26.53	22.27
1.0 N Sulphuric acid + 0.02M salicylic acid	28.41	26.68	27.54
1.0 N Sulphuric acid + 0.02M anthranilic acid	30.10	29.73	29.92

thermodynamics of it depends upon the relative size(x) of the inhibitor and solvent molecule. Other isotherms are

$$\frac{\Theta}{x(1-\theta)^x} = \frac{C_{org}}{55.4} \exp{-\Delta G_{ads}/RT}$$
... (2)

and

$$\frac{\theta}{(1-\theta)^x}\left[\frac{\theta + x(1-\theta)}{x^x}\right] = \frac{C_{org}}{55.4} \exp{-\Delta G_{ads}/RT}$$
... (3)

where C_{org} is the concentration of inhibitor in the bulk of the solution [4,5]. A plot of L.H.S. of the above equations against concentration gives a straight line passing through origin for the most probable x value. Figs. 2 and 3 give the best straight line for x = 3. The free energy of adsorption obtained from Figs. 4 and 5 are -5.95 and -1.19 k cal. mole⁻¹ for isotherms (2) and (3) respectively.

Fig.4: Free energy of adsorption plot for anthranilic acid using Flory-Huggins isotherm
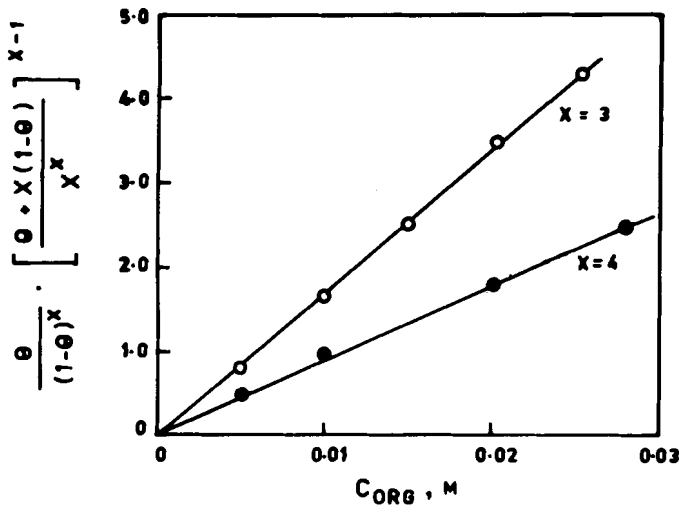

Fig.2: Bockris-Swinkles adsorption isotherm for adsorption of anthranilic acid on iron from 1.0N H₂SO₄ at different x values
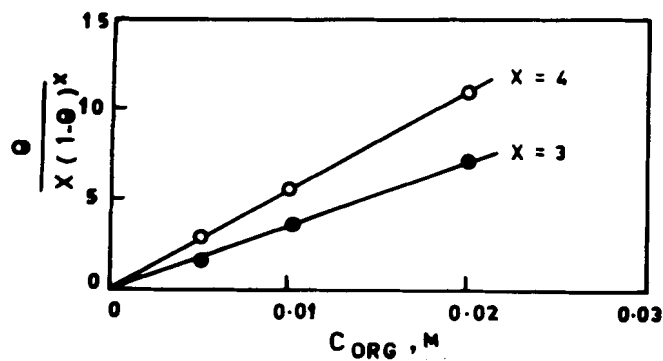

Fig.3: Flory-Huggins adsorption isotherm for adsorption of anthranilic acid on iron from 1.0 N H₂SO₄ at different x values
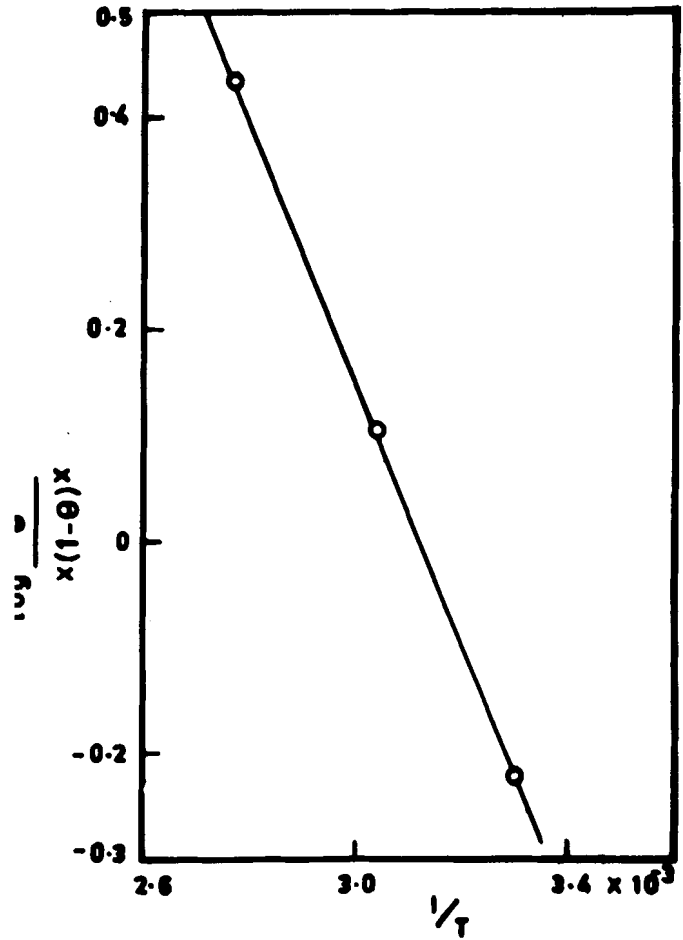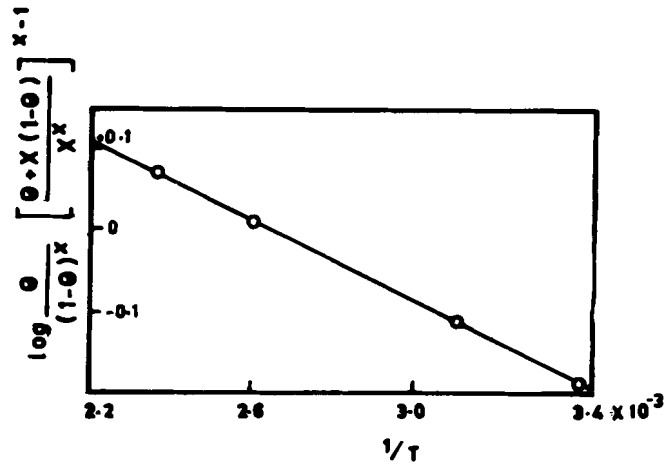

Fig. 5: Free energy of adsorption plot for anthranilic acid using Bockris- Swinkle isotherm

TABLE-III: Corrosion potentials and percentage inhibition for pure iron at different concentrations of inhibitors in 1.0 N sulphuric acid solution at 303K

Concen-tration mole/litre	Benzoic acid			Orthonitro benzoic acid			Salicylic acid			Anthranilic acid		
	E_{corr} vs SCE mV	Steady state potential mV	% Inhi-bition	E_{corr} vs SCE mV	Steady state potential mV	% Inhi-bition	E_{corr} vs SCE mV	Steady state potential mV	% Inhi-bition	E_{corr} vs SCE mV	Steady state potential mV	% Inhi-bition
0.005	-500	-530	41.00	-460	-510	7.00	-490	-510	41.70	-480	-490	74.20
0.01	-530	-550	37.70	-275	-200	8.80	-490	-510	48.40	-470	-475	66.20
0.02	-470	-530	60.00	-260	-350	15.40	-480	-510	48.80	-460	-510	52.00

E_{corr} for pure iron in 1.0 N sulphuric acid = -530 mV vs SCE
E_{corr} values are taken as soon as the specimen is immersed
% inhibition values correspond to 30 minutes values

Potential-time behaviour

The variation in open circuit potential was followed up to one hour and in all cases (with and without inhibitors), steady values were obtained at the end of 25 minutes. Table III presents the corrosion potentials along with percentage of inhibition for different concentrations of inhibitors. When compared with the values obtained in uninhibited sulphuric acid solution, the open circuit potential for all the inhibitors remain in the positive direction. The shift in the positive direction indicates the interference of these inhibitors with the anodic partial process. There is no quantitative relation between percentage inhibition efficiency and shift in potential in the positive direction. Orthonitrobenzoic acid exhibits very high positive potentials compared with other inhibitors but it has low efficiency.

Small amplitude cyclic voltammetry (SACV)

In the small amplitude cyclic voltammetry, a triangular potential function is imposed across the metal/solution interface [6]. In general, E-i curves exhibit hysteresis between the forward and reverse sweep with exponential type decay. At the start of both the sweep directions, the degree of hysteresis is sensitive to sweep rate (v) and only at the lowest sweep rate, it is considered to be negligible. The gradient i_h vs v plot at v = 0, is

$$\left(\frac{di_h}{dv}\right)_{v \longrightarrow 0} = \frac{2 R_p^2 C_{dl}}{(R_p + R_s)^2} \quad\quad \ldots (4)$$

When $R_p \gg R_s$,

$$\left(\frac{di_h}{dv}\right)_{v \longrightarrow 0} = 2 C_{dl} \text{ and}$$

$$\left(\frac{d\eta}{di}\right)_{v \longrightarrow 0} = R_p$$

The electrode was polarized in the anodic direction up to 12.5 mV and in the cathodic direction up to -12.5 mV at different scan rates. It is seen from Table IV that polarization resistance values for orthonitrobenzoic acid are slightly less than in 1.0N uninhibited acid suggesting that orthonitrobenzoic acid is not an inhibitor. The R_p values for other acids suggest that the order of inhibition is anthranilic acid > salicylic acid > benzoic acid. Table V presents a comparison of C_{dl} obtained from SACV method with earlier galvanostatic pulse method. In the case of salicylic and anthranilic acids, very high capacitance values are observed. Benzoic acids do not have any influence on capacitance values.

DISCUSSION

Any organic compound may perform the following functions at a corroding electrode: (a) Chemisorbing on the surface (b) Forming a more or less stable complex with a corrosion intermediate and effectively removing the intermediate from the dissolution sequence (c) Formation of a complex with a final oxidative propensity. The electron distribution (electron density) throughout the molecule will have some effect in the above three functions. A molecule with a great tendency for adsorption may have a small tendency for the formation of a surface complex. A molecule with a great affinity for lattice ion but a negligible tendency for long lived adsorption will function as an accelerator to corrosion. The scheme may be as follows:

Dissolution

(1) $Fe + OH^- \rightleftharpoons FeOH_{ads} + e$

(2) $FeOH_{ads} \rightleftharpoons FeOH^+ + e$

(3) $FeOH^+ \longrightarrow Fe^{2+} + OH^-$

This is similar to what is proposed earlier [1-3].

TABLE-IV: $R_p = \left(\dfrac{dn}{di}\right)_{\mathcal{U} \to 0}$ in ohms obtained from SACV method for pure iron in 1.0 N sulphuric acid containing different concentrations of inhibitors at 303K

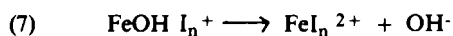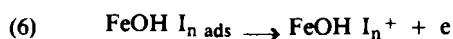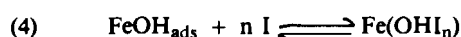| Concentration of inhibitor Mole/litre	Orthonitrobenzoic acid	Benzoic acid	Salicylic acid	Anthranilic acid
0.005	2.8	10.0	10.0	20.0
0.01	3.0	10.0	10.0	20.0
0.02	3.0	16.6	13.3	20.0

$R_p = \left(\dfrac{dn}{di}\right)_{\mathcal{U} \to 0}$ for pure iron in 1.0 N sulphuric acid = 3.8 ohms

TABLE-V: A comparison of C_{dl} (capacitance of double layer) obtained from SACV method with the earlier galvanostatic pulse method [1, 2]

Solution	C_{dl} $\mu F.cm^{-2}$
1.0 N Sulphuric acid	36.1 (36.0)*
1.0 Sulphuric acid + 0.02 M benzoic acid	36.4 (35.0)*
1.0 N Sulphuric acid + 0.02 M orthonitrobenzoic acid	35.0
1.0 N Sulphuric acid + 0.02 M salicylic acid	157.5
1.0 N Sulphuric acid + 0.02 M anthranilic acid	145.8

* Earlier work

Surface chelation

(4) $FeOH_{ads} + n \, I \rightleftharpoons Fe(OHI_n)$

(5) $FeOH \, I_n \longrightarrow FeOH \, I_{n \, ads}$

(6) $FeOH \, I_{n \, ads} \longrightarrow FeOH \, I_n^+ + e$

(7) $FeOH \, I_n^+ \longrightarrow FeI_n^{2+} + OH^-$

The inhibitor may interact or displace the solvent molecule or specifically adsorbed ion.

(8) $I + S \longrightarrow I_{ads} + S$
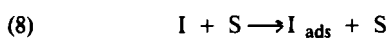
If step(4) is the dominant mechanism for the production of chelate, then the formation of chelate would be enhanced by increased coverage of adsorbed inhibitor. More coverage of FeOH leads to the formation of $FeOH^+$ also, then the chelation (step 4) must be faster than step (2), or the adsorbed inhibitor concentration is to be more. If chelation forms by step (1) and the equilibria are shifted to the right relative to each other and the stoichiometry of (2) i.e. whether $n > 1$ will determine whether the inhibition will increase or decrease or remain constant.

The cathodic reaction associated with the corrosion of iron in acid solution is the hydrogen evolution reaction. [7].

Benzoic acid (BA)

Inhibition or adsorption is determined by the electron distribution in the anchoring group of the adsorbate. In the case of benzoic acid, one may think of benzene ring as anchoring group.

Salicylic acid (SA)

The hydroxy group substituted in the ring improves delocalisation of electrons in the aromatic ring. Increasing inhibition with concentration suggests that chelation may take place with $(FeOH)_{ads}$ (step 4). The observed adsorption pseudo capacitance 157.5 $\mu F.cm^{-2}$ compared with uninhibited values suggests the roughening of the surface taking place during corrosion and the true area of the surface increases with time.

Orthonitrobenzoic acid (ONBA)

The presence of nitrogroup reduces the electron density in the aromatic ring and hence the tendency for adsorption. At room temperature, the inhibition offered at all concentrations are negligible. At higher temperatures and at all concentrations, an inhibition efficiency $\simeq 50\%$ and the formation of a black film on the surface suggest inhibition by a nonporous product which is not observed at 303K. The reduction of orthonitrobenzoic acid to aminobenzoic acid is expected at concentrations above 0.01M. A shift in corrosion potential to -200mV and -350mV compared with -460mV (uninhibited acid) suggests that this compound gets reduced on iron. At higher temperatures, the reduction product (hydroxo or amino) adheres to the surface and brings about enhanced inhibition.

Anthranilic acid (AA)

The presence of amino group stabilises the electron density in the benzene ring. It is seen from the weight loss data that increase of concentration decreases the efficiency, while temperature increases the efficiency. The energy of activation for corrosion is found to be high in the presence of anthranilic acid. It displaces three water molecules as evidenced by isotherms considered. The smaller negative values of free energy of adsorption suggest weak Van der Waal types of forces. The adsorption may be due to the six membered benzene ring and nitrogen atom of the amino group. The adsorption of ring substituted anilines on mercury was found to be parallel to the electrode surface [8] and was attached to the surface by π bonds of the aromatic ring. Therefore the electron density at nitrogen was directly coupled to the density at the aromatic ring. In this case, adsorption is due to the interaction of π electrons as evident by increasing inhibitor efficiency compared with benzoic acid. The greater inhibition is achieved only by the adsorption occurring parallel to the electrode surface. The tendency to adsorb is greater than the formation of surface complex (Step 8). The inhibition efficiency remaining constant with time (within 5%) suggests that adsorption is favoured. If chelation is favoured (i.e. step 5) inhibition efficiency would increase with time of immersion. An inhibition efficiency of 60 to 80% suggests that the coverage by $(FeOH)_{ads}$ is low. Due to better inhibition, surface roughening cannot occur. Hence a high value of adsorption pseudo capacitance of 145.8 $\mu F.cm^{-2}$ needs to be understood in terms of protonated amine or a proton. The presence of protonated amine or proton may affect the dielectric constant of the medium. The inhibition efficiency is due to unprotonated aminobenzoic acid. There exists a dynamic equilibrium between unprotonated and protonated amino acids. The presence of $(FeOH)_{ads}$ affects the area available for proton discharge in the cathodic reaction.

CONCLUSION

Benzoic acids offer inhibition of corrosion of pure iron in H_2SO_4 solutions by adsorption on the metal/solution interface. The anchoring group during adsorption is the 6-membered aromatic ring by π electron which is evidenced by poor inhibition. Amino or hydroxyl groups favour delocalisation and offer more inhibition. While benzoic, o-nitrobenzoic and salicylic acids obey Langmuir isotherm, anthranilic acid behaves differently. Ortho-nitrobenzoic acid has got a great tendency for ferrous ions in the lattice and negligible tendency for long time adsorption. This favours dissolution. Concentration dependence on the inhibition suggests salicylic acid chelates with adsorbed intermediates. Anthranilic acid was found to adsorb displacing three water molecules and adsorb parallel to the surface. The lone pair of electrons lie in the same plane as π electrons in the aromatic ring. The greater delocalisation of π electrons suggests - NH_2 group to be present as protonated aminobenzoic acid and even if protonated they fragment to give proton and unprotonated aminobenzoic acids.

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