

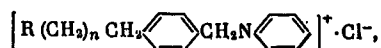
STRENGTHENING OF THE INHIBITING EFFECT OF KATAPIN ON CORROSION OF IRON IN SULFURIC ACID SOLUTIONS

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Katapin is now a popular anticorrosion agent for iron and steel articles [1-4], but little work has been done on its effect.

We studied three p-alkylbenzylpyridinium chlorides



where R is methyl-, ethyl-, and isopropyl, respectively. These Katapins were prepared from the pure individual products and were kindly provided by V. I. Komarov. Like tetraalkylammonium, Katapin cations were weakly adsorbed from sulfuric acid solutions on iron, the surface of which has a positive charge [5-9], but chloride ions reduce the latter as they are chemisorbed on iron [5]. On such a surface Katapin cations are adsorbed fairly readily and become effective inhibitors [3, 4] (Table 1).

TABLE 1. Coefficients of Retardation of Corrosion of Armco Iron at an Additive Concentration of 2.5 g/liter (time 200-300 h)

Solution composition	Methyl-Katapin	Ethyl-Katapin	Isopropyl-Katapin
1 N H ₂ SO ₄	110	440	35
+0.001 N Na ₂ S	400	700	550
+0.01 M SSA	215	500	110

TABLE 2. Retardation Coefficients γ

Solution composition	Additives			
	nil	0.001 N Na ₂ S	0.01 M SSA	0.0002 N KI
1 N H ₂ SO ₄ + methyl-Katapin 0.25 g/liter	19	290	130	210

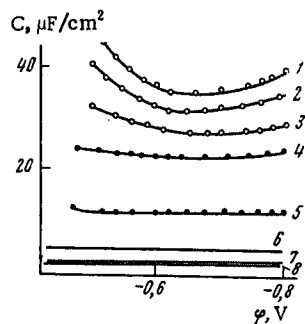


Fig. 1

Fig. 1. Differential capacitance C versus ϕ of an iron electrode in 1 N H₂SO₄ (1) and in the presence of isopropyl-Katapin (g/liter): 2) 0.01; 3) 0.1; 4) 0.25; 5) 0.5; 6) 1.0; 7) 2.5; 8) 5.0. Frequency 800 Hz.

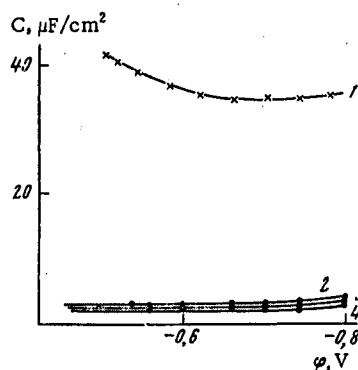


Fig. 2

Fig. 2. (C, ϕ) curves of an iron electrode in 1 N H₂SO₄ (1) + isopropyl-Katapin 2.5 g/liter (2) and with additions of 0.001 M sulfosalicylic acid (3), and 0.0001 N Na₂S (4). Frequency 800 Hz.

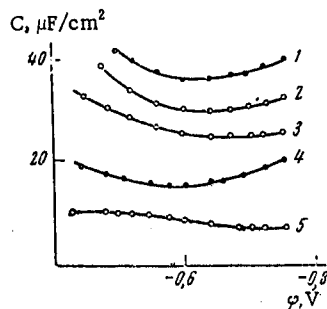


Fig.3. (C, φ) curves of an iron electrode in 1 N H_2SO_4 (1) isopropyl-Katapin 0.2 g/liter (2), and with additions of 0.008 M sulfosalicylic acid (3), 0.0008 N KI (4), and 0.001 N Na_2S (5).

TABLE 3. Retardation Coefficients γ

Solution composition	Additives			
	nil	10^{-4} N Na_2S	10^{-3} M SSA	10^{-5} N KI
1 N H_2SO_4 + methyl-Katapin 0.25 g/liter	20	180	120	70

The nature of the radical in Katapin affects the corrosion retardation coefficient. In all cases the addition of Na_2S or sulfosalicylic acid (SSA) greatly increases the inhibiting effect of Katapins owing to the appearance of a negative adsorption potential during their adsorption; in absence of inhibitors this promotes corrosion of iron (0.001 N Na_2S in 1 N H_2SO_4 gives $\gamma = 0.2$, and 0.001 M SSA $\gamma = 0.8$), but, in the presence of organic cations, promotes their adsorption and inhibiting effect [6, 7, 10].

The degree of adsorption of Katapin was studied by plotting the differential capacitance curves of the double electric layer C versus the potential φ on an electrode of pure zone-refined iron in 1 N H_2SO_4 with different isopropyl-Katapin contents* (Fig. 1). The curve of the degree of coverage of the iron surface by Katapin versus its concentration, calculated from these data, is the Temkin-Frumkin adsorption isotherm. The most marked reduction of the capacitance (and therefore the adsorption) is observed in the Katapin concentration range 0.1–0.25 g/liter (Fig. 1). In the case of methyl-Katapin concentrations below 0.005 g/liter, the capacitance hardly falls at all; with an increase to 1 g/liter or more, a certain increase is observed.

Addition of Na_2S , SSA, or KI to a solution of 1 N H_2SO_4 with 2.5 g/liter of isopropyl-Katapin leads to a very small additional reduction of the capacitance (Fig. 2), but greatly reduces the corrosion rate (Fig. 1). This is due to the fact that the limiting coverage of the iron surface is already reached at a Katapin concentration of 2.5 g/liter (see Fig. 1). The additives can be adsorbed only at the sites unoccupied by Katapin. Therefore the additional reduction of the capacitance due to the additives is very small, but the effect on the rate of the electrochemical reactions is very great (see Table 1).

Thus a marked reduction of the capacitance and marked retardation of corrosion can be obtained at a considerably lower Katapin concentration if we use Na_2S , SSA, KI, and certain other anions as the additive. Addition of 0.2–0.25 g/liter of Katapin with such an additive (Fig. 3) to a solution enables us to obtain virtually the same reduction of the capacitance and nearly the same corrosion retardation coefficient (Table 2) as for addition of 2.5 g/liter of Katapin without an additive. It is also possible to reduce the anion (HS^- , SSA, I^-) concentration greatly and obtain greater iron corrosion retardation coefficients in sulfuric acid than for a Katapin concentration 10–20 times greater but with no additive (Table 3).

* Isopropyl-Katapin is a deliquescent crystalline substance, methyl- and ethyl-Katapins are viscous liquids.

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