

STUDYING THE MECHANISM OF PROTECTIVE ACTION OF INHIBITED PAINT COATING

N. A. Ismailova

Tashkent Institute of Chemical Technology

A. S. Sidikov

Tashkent Institute of Chemical Technology

N. E. Shamadinova

Tashkent Institute of Chemical Technology

M. Sh. Atamuratova

Tashkent Institute of Chemical Technology

ABSTRACT:

The article studies the diffusion of nitrobenzene as an inhibitor through the enamel coating EP-750, the calculation of the diffusion rate constant and diffusion coefficient is given in the article.

Keywords: organic compounds, nitrobenzene, captax, chemical compounds, hydrochloric acid, sulfurous acid, corrosion inhibitor, metal protection, protective effect, corrosion rate, electrode potential, membrane, diffusion, amines, Gibbs energy.

INTRODUCTION:

One of the most important tasks in studying the mechanism of protective action of inhibitors on the coating is to study the kinetics of the diffusion and chemical distribution of molecules in a heterogeneous system. The possibilities of using chemical and diffusion kinetics have greatly expanded in recent years due to advances in computer technology.

The diffusion of electrolytes in paint coatings can be represented as the diffusion of free water molecules, electrolyte, hydrated molecules and ions, as well as dissolved oxygen molecules [1].

In connection with the above, we have studied the diffusion of nitrobenzene as an inhibitor through the EP-750 enamel paint coating [2].

The diffusion of the used corrosion inhibitor (nitrobenzene) through the film was studied in a cell where the film thickness was ≈ 50 mm with an area of 0.196 cm². The membrane (film) was formed by applying EP-750 enamel on porous glass in two layers. The upper part of the cell was filled with a saturated captax solution, the lower part with distilled water with a volume of 150 ml. The amount of nitrobenzene that passed through the membrane was determined by the method described in [2].

The quantitative determination of amines is based mainly on their basicity, as well as on the mobility of hydrogen atoms bound to nitrogen. They can be titrated in an aqueous solution of hydrochloric acid in the presence of indicators [3].

The sample in the amount of 4 ml was dissolved in 20 ml of water and titrated by methyl orange 0.1 n hydrochloric acid. The amount of nitrobenzene in the sample was determined by the formula:

$$a = \frac{E \cdot V_1 \cdot N}{1000 \cdot V_2}$$

where: V_1 - amount of HCl consumed, ml;
 N - HCl normality; V_2 - sample volume, ml; a - the amount of nitrobenzene in the sample, g; E - equivalent weight of nitrobenzene, g.

According to the first law of the FIC, the diffusion rate $\frac{\alpha m}{\alpha t}$ is proportional to the cross-sectional area S and the concentration gradient $\frac{\alpha C}{\alpha x}$ [2]:

$$\frac{\alpha m}{\alpha t} = -D \cdot S \cdot \frac{\alpha C}{\alpha x} \quad (1)$$

where: m - nitrobenzene mass, time t passed through the film into the water layer, g;
 D - proportionality coefficient, i.e. diffusion coefficient, m^2/s ; S - film surface, m^2 ; $\frac{\alpha C}{\alpha x}$ - concentration gradient; t - time, day.

Equation (1) is reduced to the following form:

$$\frac{\alpha C}{\alpha t} = \frac{D \cdot S}{\delta \cdot V} \cdot (C_0 - C) \quad (2)$$

where: D - film thickness, m ; V - solvent volume, ml; C_0 - the initial concentration of nitrobenzene in the cell, mol/l.

Denote $\frac{D \cdot S}{\delta \cdot V}$ by K , then equation (2) has the form

$$\frac{\alpha C}{\alpha t} = K \cdot (C_0 - C) \quad (3)$$

Integrating equation (3), we obtain an equation for calculating the diffusion rate constant:

$$K = \frac{1}{t} \ln \frac{C_0}{C_0 - C}$$

and the diffusion coefficient

$$D = \frac{K \cdot \delta \cdot V}{S}$$

The diffusion rate constant and diffusion coefficients calculated in this way are shown in Table 1.

Table 1 Results of nitrobenzene diffusion through EP-750 enamel film at room temperature

№ п.п.	Duration of tests, day.	The amount of nitrobenzene passed through the film, gr	The concentration of nitrobenzene in the lower part of the membrane		$K \cdot 10^{-7}, c^{-1}$	$D \cdot 10^{-7}, cm^2 \cdot c^{-1}$
			mass. %	mol/l		
1	5	-	-	-	-	-
2	10	-	-	-	-	-
3	15	0,34	0,22	0,024	1,59	4,18
4	20	0,45	0,29	0,032	1,98	4,23
5	25	0,59	0,39	0,043	2,29	4,31
6	30	0,74	0,5	0,053	2,53	4,38
7	35	0,89	0,595	0,064	2,83	4,49
8	40	1,00	0,67	0,072	3,07	4,55
9	45	1,18	0,79	0,085	3,21	4,68
10	50	1,28	0,85	0,092	3,49	4,93
11	55	1,53	1,01	0,109	4,89	5,01
12	60	1,56	1,04	0,110	4,91	5,12
13	65	1,56	1,04	0,110	4,91	5,12

It can be seen that a noticeable concentration of nitrobenzene on the reverse side of the EP-750 enamel membrane is detected after 10 days.

In the future, there is a linear increase in the concentration of nitrobenzene over time due to diffusion (Fig.1). After 60 days, equilibrium occurs in the diffusion process.

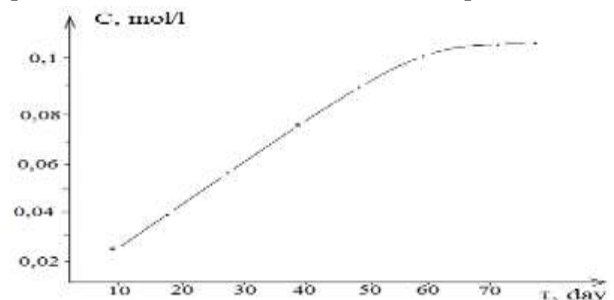


Fig.1. The change in the concentration of nitrobenzene over time due to diffusion

Based on the diffusion coefficient , we determine the distribution coefficient by the formula:

$$K_{\text{distr}} = \frac{C_2}{C_1}$$

where: C_1 - the concentration of nitrobenzene in the upper part of the membrane, mol/l; C_2 - the concentration of nitrobenzene in the lower part of the membrane, mol/l.

$$K_p = \frac{0,11}{3,4} = 0,0323$$

Having determined the distribution coefficient, we can calculate the Gibbs energy by the formula:

$$\Delta G = -RT \ln K_p = -RT \ln \frac{0,011}{0,34}$$

$$\Delta G = -2,3 \cdot 8,314 \cdot 298 \cdot \frac{0,11}{3,4} = -170,6 \text{ J}$$

The negative value of the Gibbs energy allows us to conclude about the direction of the process, i.e. the inhibitor molecules diffuse spontaneously through the coating film and, evenly distributed on the metal surface, form an oxide film, preventing further penetration of molecules of aggressive components to the metal surface, protect it from corrosion [4].

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