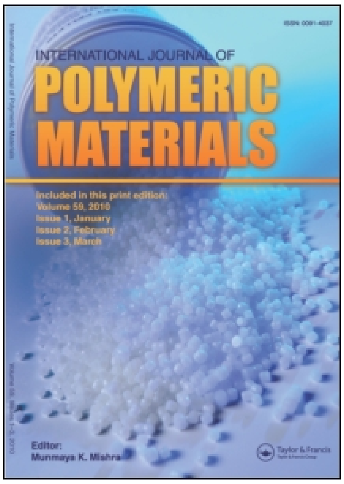

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Concerning the Diffusion Model of the Protective Action of Admixtures in Polymeric Coatings

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A theoretical analysis of the efficiency of protective admixtures introduced into polymeric coatings and inhibiting the diffusion of low-molecular aggressive substances has been attained by means of computational modelling. Certain cases of reversible and irreversible binding of the diffusant molecules by introducing the admixture are considered. A simple equation describing the inhibiting effect of admixture for the model of reversible binding is proposed. A technique for calculating the lifetime of the action of the protective coating by the use of special cases to solve the diffusion equation is presented for the model of irreversible binding.

KEY WORDS Diffusion, polymeric coatings, protective action, additives

INTRODUCTION

One of the methods to protect the products from the abusive action of corrosive media is to apply polymeric coatings on their surface. Since the polymeric coatings are destroyed by their contact with corrosive media, the lifetime of these coatings is finite, and as soon as the corrosive media reach the products, they start destroying the latter. For this reason, the investigation of ways and means of inhibiting the rate of permeability of corrosive media through the protective polymeric coatings is of interest.

The technique for introducing the admixtures, which bind the corrosive media into a polymer is not a new one. Thus, Reference 1 suggests an evaluation of the efficiency of the admixtures in absorbing oxygen and ozone and preventing the polymers from thermooxidative destruction. This technique was found to be effective only at low concentrations of aggressive molecules in the surrounding medium (a thousand th of a percent). In Reference 2, the diffusion of solutions of hydrochloric, hydrofluoric and nitric acids into pentaplast, polyacrylate and polypropylene was studied. Metals, metal oxides, metal hydroxides and salts of weak acids served as binding admixtures. The inhibiting effect was found to exist, the value of this effect being dependent on the acid concentration and the chemical nature of the components of the polymer-acid-admixture system.

RESULTS AND DISCUSSION

A theoretical analysis of the expected inhibiting effect of the admixtures exhibited in various binding mechanisms seems to be worth attention since the above mentioned publications do not contain any systematic study of this problem.

The simplest model of the inhibiting action of the protective admixture includes the sorption of the corrosive medium A by the polymer followed by the reaction between A and admixture B. The reaction between A and B may proceed reversibly

$$A + B \overset{K_{eq}}{\rightleftarrows} (AB) \tag{I}$$

or irreversibly

$$A + B \rightarrow (AB) \tag{II}$$

In both cases, the diffusion coefficient D_0 of the molecules of A which refers the polymer without the admixture will decrease due to reaction I and II immobilizing part of the diffusant molecule. The role of admixtures can be played by both substances specially introduced into the polymer and certain functional groups of macromolecules contained by the polymer (e.g., ~CONH~ and ~NH_2 in polyamide binding the H_2O and HCl molecules).

The assessment of the inhibiting effect of admixtures for the cases of reversible and irreversible binding proceeded on the basis of simplifying assumptions, namely; the rate of reactions I and II significantly exceeds that of the diffusion of A, admixture B in the polymer matrix is immobile, unilateral diffusion in the isotropic medium is considered, the polymer does not swell upon sorption, the polymer surface to be protected is impermeable for the molecules of A. The calculations made use of the values of $D_0 = 7 \cdot 10^{-13}$ m²/s and $B = 0.9$ mol/l approximately equal to the diffusion coefficient of water in polycaproamide and the concentration of its amide groups.*

I. Reversible Binding

It is obvious that for the most part the inhibiting effect of a diffusant depends on the relationship between the equilibrium concentrations of the diffusant and the admixture. Now we consider various cases of this relationship.

(a) $A_0 << B_0$. A formula for calculating the effective diffusion coefficient for component A is deduced in Reference 3:

$$D_{eff} = \frac{D_0}{1 + K_{eq}B_0} \tag{1}$$

The validity of Formula (1) can be confirmed by numerical (computational mod-

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* The values indicated here were chosen as tentative ones.

elling of the cases for different degrees of diffusant binding by changing the value of K_{eq}. Table I (the first five lines) represents the data confirming the validity of Formula (1). The fourth column of the table indicates the "experimental" diffusion coefficients. They were obtained as follows: the calculated sorption curve obtained in the numerical solution of the diffusion-kinetic equation with a computer was rectified in the coordinates of an analytical solution of only the diffusion equation at D = Const. (i.e., following the procedure which the experimenter would perform with a real (true) sorption curve disregarding the existence of reversible reaction I). As seen from the table, in the case of reversible binding of not less than 65% of the diffusant, the variation in the effective diffusion coefficient is predicted by Formula (1) with an accuracy of 5%; in the case of 90% binding the accuracy is 20%. The inhibiting effect of admixture in the situation when $A_0 << B_0$ is the effective diffusion coefficient at 90% binding is less than D_0 by an order of magnitude.

(b) $A_0 \simeq B_0$. At this relation of concentrations, Equation (1) is not satisfied even when only about 10% of the diffusant is bound because now D_{eff} substantially depends on the concentration of A. In fact, if we do not limit the relation of concentrations of A_0 and B_0, then from the system of equations

$$\begin{cases} \dfrac{\partial A}{\partial t} = D_0 \dfrac{\partial^2 A}{\partial x^2} + \dfrac{\partial B}{\partial t} \\ \dfrac{\partial B}{\partial t} = -\dfrac{\partial B^*}{\partial t} \\ B_0 = B + B^* \\ B^* = \dfrac{B_0}{1 + \dfrac{1}{K_{eq} B}} \end{cases} \qquad \text{(III)}$$

TABLE I

Dependence of D_{eff} on the relation of concentrations of A_0 and B_0 upon irreversible binding

A_0/B_0	Fraction of bound A, %	K_{eq}	$D_{eff} \cdot 10^{13}$ m^2/s Accord. to Formula (1)	$D_{eff} \cdot 10^{13}$ m^2/s "Experim."
—	0	0	0.71	0.71
0.1	11	12	0.63	0.62
	36	59	0.44	0.45
	64	183	0.25	0.26
	90	992	0.08	0.065
1.0	11	13.7	0.62	0.65
	64	418.5	0.14	0.32
	90	5062	0.014	0.1

where B^* is the concentration of the bound sites, we can derive the equation

$$\frac{\partial A}{\partial t} = \frac{D_0}{1 + \dfrac{K_{eq}B_0}{(1 + K_{eq}A)^2}} \cdot \frac{\partial^2 A}{\partial x^2} \tag{2}$$

Equation (2) shows that, in the general case, upon reversible binding the effective diffusion coefficient of the A molecules depends on their concentration and the calculation of this coefficient based on the data in the assumption that D = Const leads to incorrect results.

As seen from Table I (column 6), the inhibiting effect in the situation when $A_0 \simeq B_0$ is less than that in the case when $A_0 << B_0$ (the degrees of binding being equal). In practice, the inhibiting effect at $A_0 \simeq B_0$ can be calculated as follows: D_0 and D_{eff} are determined by the ordinary procedure on the basis of the experimental sorption curves obtained at $B_0 = 0$ (i.e., without admixture) and then at $A_0 << B_0$, K_{eq} is found according to Formula (1), then Equation (2) is solved numerically.

(c) $A_0 >> B_0$. This relation is of no practical values because the fraction of the immobilized diffusant is small at all degrees of binding, and the diffusion coefficient accounts for only a few percent.

II. Irreversible Binding

In the case of irreversible binding it is necessary to (1) calculate the time, t^* required for the diffusant to reach the impermeable wall; (2) described the kinetics of concentration variations in the free component of A at the polymer-wall interface; (3) calculate the effective concentration of the binding sites of B_0 in the polymeric coating. The latter point is important because the part of the admixture molecules which is introduced into the polymer in the course of reprocessing may appear in the polymer areas inaccessible for the diffusant and thus excluded from the binding process. Now we consider various relations between the concentration of A_0 and B_0.

(a) $A_0 \leq B_1$. In this case the polymer is impermeable for the molecules of A.

(b) $A_0 >> B_0$. This is of no practical value for the same reason as in the case of reversible binding.

(c) $A_0 > B_0$. In this relation of concentrations the diffusant of A will move in the polymer exhibiting a sharp front, the front concentration is constant and equal to that of B_0. The analytical solution of the problem concerning diffusion with a sharp front follows the solution given in References 4 and 5 (for times less than the time required for reaching the impermeable wall). The coordinate x of the sharp front moves according the the law:

$$X = \beta\sqrt{4D_0t} \tag{3}$$

The time t^* required for the diffusant front to reach the impermeable wall:

$$t^* = l^2/4D_0\beta^2 \tag{4}$$

The total quantity of the absorbed substance of A:

$$Q_A = B_0'\beta \cdot \exp(\beta^2)\sqrt{4D_0t} \tag{5}$$

where the parameter β is the square of the equation:

$$\frac{1}{\sqrt{\pi}} \cdot \frac{\exp(-\beta^2)}{\operatorname{erf}(\beta)} = \frac{B_0}{A_0 - B_0}\beta \tag{6}$$

If the values of D_0 and B_0 are known, then t^* is calculated by the sequential solution of Equations (6) and (4) or Equations (5) and (4). However, in the latter case we should have available the experimental curve of sorption and also take into account the fact that upon both reversible and irreversible binding the quantity of the absorbed substance is proportional to $\sqrt{t}$ up to the moment when the diffusant reaches the impermeable wall. For this reason, one may fail to distinguish between these two types of binding in the course of the sorption experiment. Below we propose a simpler procedure for solving this problem when t^*, D_0, and B_0 may be determined from the sorption curve and the kinetics of the free A component accumulation at the interface and the protected surface may be described.

Figure 1 presents the logarithmic anamorphosis of the calculated sorption curve for the times which are less or more than t^*. In the case of irreversible binding the anamorphosis exhibits a break (which is almost unnoticeable in the coordinates $Q_t/Q_\infty + t$). The analysis has shown that the break point correlates with the time t^*. Knowing the value of t'', the effective concentration of the binding sites of B_0 can be calculated from the sorption curve in the coordinates $Q_t/Q_\infty + t$.

Now we consider the calculation of D_0 from the sorption curve. At the moment when the sharp front of the diffusant reaches the impermeable wall, the concentrations of A inside the polymer will have the shape as shown in Figure 2 (in fact, the concentration of the free diffusant component does not have a linear shape though it approaches one; the greater the binding fraction, the more linear the shape). Thus it follows that after the moment of t^* diffusion proceeds without binding, at the constant diffusion coefficient D_0 and linear initial distribution of the diffusant along the diffusion coordinate.

To derive the equation describing the kinetics of sorption for the times exceeding t^* the results obtained in Reference 6 can be used. The authors of Reference 6 propose a solution of the problem about diffusion into a layer of thickness l with one impermeable wall and a certain initial distribution of diffusant $A = f(\bar{X})$ inside the layer. In our terms this solution will take the form:

$$A^{\text{free}}(x, t) = A_0^{\text{free}} + \frac{2}{l}\sum_{n=0}^{\infty} \exp\left[-\frac{D_0(2n+1)^2\pi^2 t}{4l^2}\right]$$
$$\cdot \cos\frac{(2n+1)\pi x}{2l}\left\{\frac{2l(-1)^{n+1}A_0^{\text{free}}}{(2n+1)\pi} + \int_0^l f(x')\cos\frac{(2n+1)\pi \cdot x}{2l}\,dx'\right\} \tag{7}$$

If we integrate (7) with respect to x taking into account that in our case $f(x')$

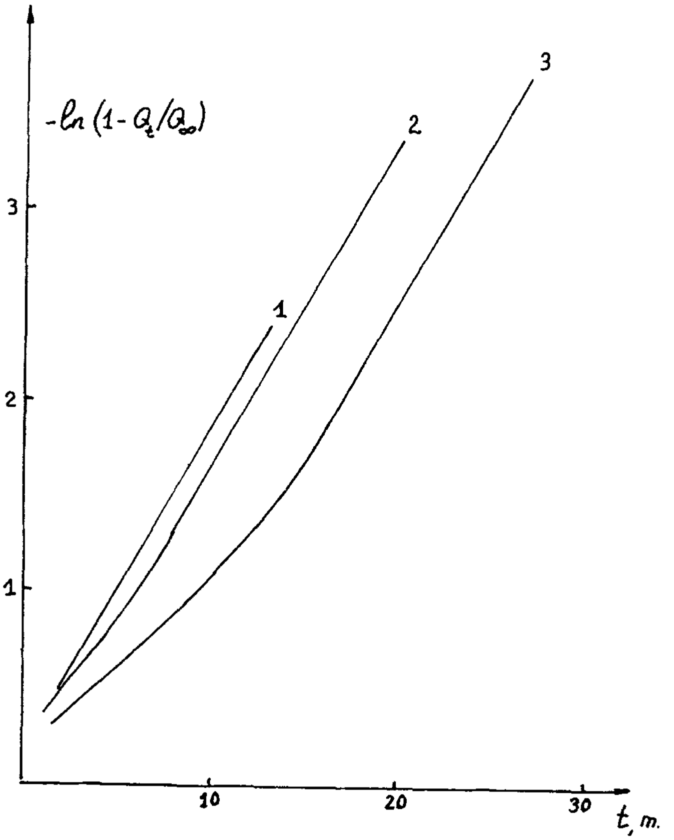

FIGURE 1 Logarithmic anamorphoses of the calculated sorption curves upon irreversible binding of the diffusant. $D_0 = 7\cdot10^{-13}$ m^2/s, 1-25 mkm. The fraction of binding A_0: 1—0.11; 2—0.36; 3—0.64.

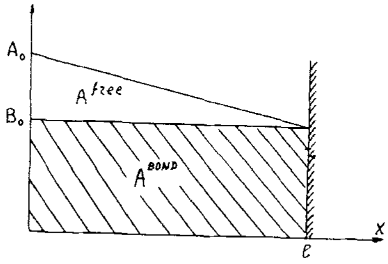

FIGURE 2 Diagram of the distribution of A concentration in the layer of 1 thickness for the moment of time t^*. The fraction of binding A_0—0.64.

$= A_0^{free}(1 - x/1)$ is limited in the total by the first term and shift the first calculation of time to point $t = t^*$, we obtain:

$$Q_t^{free} = Q_\infty^{free}\left[1 - \exp\left(-\frac{D_0\pi^2 t}{4l^2}\right)\right] \qquad (8)$$

where Q_t^{free} and Q_∞^{free} are the current and total quantity t^* of the absorbed substance after the moment t^*. In this case

$$Q_\infty^{\text{free}} \to Q_\infty^{\text{free}} - \tfrac{1}{2}A_0^{\text{free}} \cdot S \cdot 1 \tag{9}$$

where S is the sample area.

Equation (8) explains why all the logarithmic anamorphoses in Figure 1, irrespective of their degree of binding, represent straight lines with similar slopes after the moment t^*. Using Equation (8), D_0 can be calculated from the value of the slope. The diffusion coefficient, for example, was found graphically from Figure 1 and equals $7 \cdot 10^{-13}$ m²/s. It is the value which was used at the very beginning in numerical calculation of the sorption curve.

Taking $x = 1$, and using Equation (7), we can get the equation describing the variations in the concentration of the free component of A at the polymer-impermeable wall interface:

$$A^{\text{free}} = A_0^{\text{free}}\left(1 - \frac{8}{\pi^2} e - \frac{\pi^2 Dt}{4l^2}\right) \tag{10}$$

(it is natural that (10) is true provided the well-known condition for using only the first term in Equation (7) is satisfied.

III. Comparison of the Efficiency of the Inhibiting Action of Admixture upon Reversible and Irreversible Binding

The profiles of the concentrations upon reversible and irreversible binding differ both qualitatively and quantitatively. Figure 3 shows the calculated shapes of the concentration profile for the same time in the cases of the absence of binding ($B_0 = 0$) and the cases of reversible and irreversible bindings. The fraction of binding

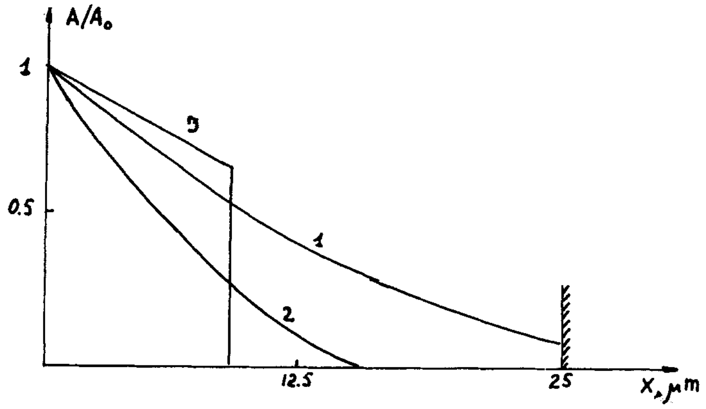

FIGURE 3 Calculated profiles of the concentrations of component A for a diffusion time of 2 min, the fraction of binding A_0—0.64, D_0—$7 \cdot 10^{-13}$ m²/s. 1—the absence of binding, 2—reversible binding, 3—irreversible binding.

(reversible or irreversible) being the same, the inhibiting effect of admixture is always higher in the case of irreversible binding.

It is a rather simple task to calculate or, at least, evaluate a decrease of the diffusion coefficient upon reversible binding. Figure 4 presents the graphs of the variations in D_{eff} depending on the binding degree for the cases when $A_0 << B_0$ and $A_0 \simeq B_0$ (the graphs were obtained according to the data of Table I). At $A_0 << B_0$, the variations of D_{eff} follow the simple equation:

$$D_{\mathrm{eff}} = (1 - \alpha)D_0 \tag{11}$$

At $A_0 \simeq B_0$, the inhibiting effect is always less than at $A_0 << B_0$, the dependence of D_{eff} on α is nonlinear, but the variation of D_{eff} can also be determined with some inaccuracy by the use of Equation (11).

In the case of irreversible binding it is difficult to derive an equation for D_{eff} since the latter depends on the fraction of diffusant binding in many ways. However, having the sorption curve for a polymer sample applied to the impermeable support we can calculate the values of D_0, B_0 and t^* which are of practical value.

The following data may be used to compare the efficiency of the inhibiting effect of admixtures when various mechanisms of binding are employed: at $D_0 = 7 \cdot 10^{-13}$ m^2/s and $\alpha = 0.64$, the thickness of coating 25 mkm, the calculation for the times required for the free diffusant component to reach the protected surface gives the ratio 0.5:2.5:14 (respectively, in the absence of binding, reversible binding and irreversible binding). In other words, in the case of irreversible binding the inhibiting effect of the admixture is equal to about 30, while in the case of reversible binding it is about 5.

The calculations given in this paper show that the introduction of diffusant-binding admixtures into the polymer inhibits the propogation of the corrosive medium towards the product surface by tens of times. This is the case of so-called pure diffusion inhibition. In real processes, e.g., in protecting the metals from corrosion, the effect of the introduction of admixtures can be calculated only by

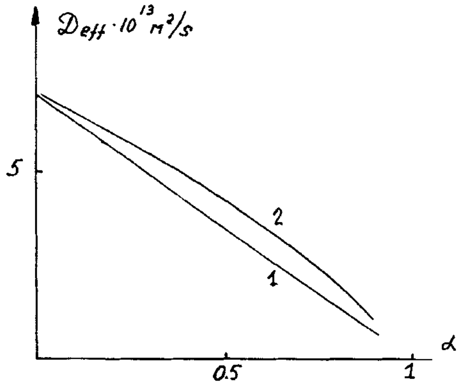

FIGURE 4 Dependence of D_{eff} on the fraction of binding upon reversible binding. 1—$A_0 << B_0$, 2—$A_0 \simeq B_0$.

solving the diffusion equation when the electrochemical reactions proceeding on the surface of the polymer-metal interface are taken into account.

CONCLUSION

(1) The theoretical analysis of the inhibition of the corrosive (aggressive) medium molecules diffusion by the sites of binding introduced into the polymer is presented. The cases of reversible and irreversible binding of the diffusant for various relations between the concentrations of the diffusant and the admixture are considered.

(2) In the case of irreversible binding, the inhibiting effect can be determined according to the formula:

$$D_{\mathrm{eff}} = (1 - \alpha)D_0,$$

where α is fraction of the diffusant binding.

(3) In the case of irreversible binding of the diffusant, a method for calculating the effective diffusion coefficient of the sorbate, the time required for the aggressive medium to reach the surface of the product, and the kinetics of the accumulation of the aggressive medium on this surface are described.

(4) The inhibiting effect of the admixture binding the diffusant through the irreversible mechanism exceeds that of the reversible one by an order of magnitude.

References

1. Yu. A. Shlyapnikov, S. G. Kiryushkin and A. P. Maryin, *Antiokislitelnaya stabilizatsiaya polimerov* (*Antioxidizing Stabilization of Polymers*), Moscow, 1986, pp. 121–124, Russian.
2. A. L. Shterenzon, I. B. Gemusova and Yu. A. Mulin, *Tezisy Vsesoyuzncgo seminara* "Diffusionnye protsessy v protivokorrozionnykh polumernykh pokrytiyakh" (All-Union Seminar on "Diffusion Processes in Anticorrosive Polymeric Coatings," Abstracts.); Moscow, 1988, p. 31–35, Russian.
3. G. E. Zaikov, A. L. Iordanskii and V. S. Markin, *Diffusiaya elektrolitov v polimerakh*; (*Diffusion of Electrolytes in Polymers*); Moscow, 1984, p. 121, Russian.
4. J. Crank, *The Mathematics of Diffusion*, Oxford, Clarendon Press, 1975, p. 286.
5. G. Carslow and D. Eger, *Teploprovodnost tverdykh tel*, (*Thermoconductance of Solids*), Moscow, 1964, p. 105, Russian.