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Diffusion of highly corrosive media (HCM) into protective polymer coating materials

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Abstract

An important element of modern design of chemical technological devices operating under exposure to highly corrosive media (HCM) are polymer protective anti-corrosion coatings. Basic protective mechanism for these coatings is a barrier mechanism. It is based on ensuring a low solubility of the corrosive medium in the polymer and on a low diffusion transfer of the most corrosive components through the coating. So, the study and control of mass transfer, in particular studies of diffusion, constitute the most important task in the design of coating systems for highly corrosive media. A comparative analysis of the laws of sorption and diffusion of water and solutions of salts and acids by the most widely used classes of anti-corrosive polymers, *i.e.*, hydrophobic thermoplastics and moderately hydrophilic cross-linked thermoplastics, is made. Data on the concentration profiles of distribution of diffusing acids, regularities of the acids penetration depth and the values of sorption are analyzed. Models of diffusion of highly corrosive media into polymers with binding the medium on chemically reactive polymer groups are considered. It is shown that the binding model can be used to describe the diffusion of acids solutions in a wide range of concentrations and temperatures. A mathematical model of the diffusion of chemically reactive corrosive media into multi-layer composite polymer coatings is suggested and tested experimentally. It is shown that by using a combination of layers of different polymer materials, one can significantly reduce the permeability of the polymer coating, which allows the penetration depth to be reduced tenfold and time "before breakdown" to be extended hundred-fold or more. It is also important that combining layers of a hydrophobic material and a material capable of binding the medium in one coating allows one to simultaneously solve the problem of eliminating the penetration of the most corrosive volatile components at the initial stage of coating operation. The experience of using coatings in various fields of industry is considered.

Keywords: *electrolytes, aqueous solution, corrosion inhibitors, sweet and sour corrosion, acid pickling processes.*

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Introduction

According to the data of the World Corrosion Organization (WCO), the total annual direct economic damage due to corrosion exceeds $1.8 trn [1]. Especially large losses are observed in operations related to application of technological highly corrosive media (HCM).

Anticorrosion polymer coatings constitute an important element in the design of technological equipment in modern engineering and chemical technology [2–6].

Due to the variety in corrosive media and types and conditions of equipment operation, diverse anticorrosion polymer coatings are used in industry, but as regards the mechanism of their protective effect, they can be divided into coatings of predominantly barrier, adhesion–inhibiting, and protective action.

As it is well known for HCM, unlike in atmospheric corrosion, the adhesion–inhibiting mechanism alone does not provide long-term protection and the barrier mechanism is most important.

The simplest method of enhancing barrier properties is to increase the thickness, but such a straightforward solution to the problem leads to various complications.

Historically, the application of protective polymer coatings started by the development of laminated rubber coatings [7]. Despite the good protective properties of rubber coatings and other laminated polymer linings [8, 9], their application remains extremely technologically unfeasible and they are now being replaced by coatings based on reactive resins [10]. There are also certain limitations for coatings based on reactive resins that are mainly related to the growing risks of increasing the thickness.

This fault is not inherent in multilayer composite coatings applied by modern methods and having a structure that provides good protective properties. In particular, the greatest protective barrier effect is observed for composite systems of chemically stable coatings [11, 12] including layers of both hydrophobic thermoplastics and hydrophilic reactive resins. It allows one to significantly decrease the coating thicknesses to 0.8–2 mm without the use of reinforcing armoring and in the absence of construction joints that are difficult to isolate.

The barrier mechanism of the protective action of polymer coatings is based on ensuring a low solubility of the corrosive medium in the polymer and slow diffusion transport of the most corrosive components through the coating. It is for HCM that study and control of mass transport and therefore diffusion studies are most important tasks in designing coating systems.

This work considers the theoretical bases and experimental data on HCM sorption and diffusion into polymers; formulates the theoretical models of decreasing their diffusion transport in multilayer composite coatings, and also describes the experience in the use of coatings for HCM in various branches of industry.

1. Sorption of highly corrosive media by polymers

Diffusion transport of HCM is observed in the case of true dissolution of molecules of the permeating medium in the coating polymer matrix.

A specific feature of HCM sorption by protective materials is that it generally occurs from aqueous solutions and is accompanied by sorption of not only the electrolyte but also water. Strong interaction of electrolytes with water causes association of water molecules and electrolyte molecules in the polymer matrix. In the case of active sorption of water in a polymer, electrolytic dissociation of the acid or salt molecules to anions and cations can be observed. The presence of ionogenic groups in polymer macromolecules leads to different values of sorption of cations and anions contained in the electrolyte.

It is these regularities that determine the mechanism, quantitative and time parameters of the process of the electrolyte solution sorption by a polymer.

1.1. Water sorption

The simplest equation describing the solubility of single-component media, including water, in polymers is given by the Henry equation: $C = k_D \cdot P$, where C is the sorbate concentration in the polymer, k_D is the sorption constant, and P is the partial pressure of the sorbate vapor.

From the thermodynamic point of view, the Henry law is a consequence of solution ideality; in terms of structure, such solutions are characterized by a statistically disordered arrangement of sorbate molecules in the polymer.

It has been shown experimentally that the Henry law is observed in the case of water vapor sorption (at low relative pressures) and sorption of corrosive dry gases by hydrophobic polymers.

Table 1. Sorption constants of some corrosive media by polymers (PVC – polyvinylchloride, LDPE – low density polyethylene, ED-20 – hardened epoxy resin).

Polymer	**Sorbate / Temperature, °C**	**k_D, kg/(kg·Pa)**	**Reference**
PVC	HNO_3 (conc.) / 20	$5.0 \cdot 10^{-6}$	[13]
LDPE	HCl (gas) / 20	$1.3 \cdot 10^{-7}$	
ED-20	HCl (gas) / 30	$8.2 \cdot 10^{-6}$	[14]
ED-20	NH_3 (gas) / 30	$6.2 \cdot 10^{-8}$	
ED-20	Water / 30	$1.1 \cdot 10^{-7}$	

In general, ideal sorption related only to the entropy factor in the systems under consideration is rather an exception.

In fact, as shown in [15], deviation of a solution from ideality due to the presence of a strong intermolecular interaction between molecules of the same type can cause disturbance of the solution homogeneity and formation of water clusters in the solution. An excess of the average number $G_{11} \cdot \varphi_1 / V_1$ of molecules in a cluster as compared to the mean sorbate concentration φ_1 in the polymer can be determined by the following expression:

$$\frac{G_{11} \cdot \varphi_1}{\bar{V}_1} = -\varphi_2 \cdot \left[1 - \frac{1}{\varphi_1} \cdot \frac{1}{\dfrac{d \ln a_1}{d\varphi_1}} \right] - \varphi_1 \tag{1}$$

As one can see from the above equation, the cluster size is determined by the concentration dependence of activity, namely, $d\ln a_1 / d\varphi_1$. As shown in [16, p. 11], the mean number of water molecules in a cluster in fluoroplastics is 1.4 to 2.5.

In other words, even in the absence of any specific energy interaction between a polymer and a sorbate, formation of sorbate clusters is possible in the precritical region (at approach to the binodal or in case of solution saturation), *i.e.*, regions characterized by an excess of a solvent, in addition to the sorbate statistically distributed in the polymer.

Immobilization in clusters results in a noticeable decrease in the mobility of water molecules, which explains a decrease in the effective diffusion coefficient of water with an increase in its overall concentration in the polymer [17].

In addition to the above clusterization mechanism in the precritical region, in the systems where the interaction energy between the cluster-forming particles significantly exceeds the interaction energy of these particles with the polymer, water associates of fundamentally different nature can also appear in the polymer due to the presence of soluble admixtures.

According to Thomas and Southern [18], in this case water sorption can be described on the basis of the osmotic theory:

$$c_\mathrm{s}^{(1)} RT = c_\mathrm{s} / c_\mathrm{w} (\rho_\mathrm{w} RT) - \frac{E}{6} \left[5 - 4 \left(\frac{c_\mathrm{w}}{c_\mathrm{s}} + 1 \right)^{-1/3} \left(\frac{c_\mathrm{w}}{c_\mathrm{s}} + 1 \right)^{-4/3} \right] \tag{2}$$

where c_s and c_w are the concentrations of soluble admixtures and water in microdrops within the polymer; $c_\mathrm{s}^{(1)}$ is the external solution concentration; and E is Young's modulus of the polymer matrix.

The effect that is of interest for estimating the effect of water sorption regularities in a polymer on the water mobility and diffusion transport through the anticorrosion coating [19–28] is the phenomenon of water existence in "bound" and "free" states with different mobility in polymers. For example, for hydrophilic systems [29] containing amino groups of different nature ($-N(CH_3)^+Cl^-$, $-CONH_2$) with an overall water content of 14–24 moles of water per mole of polar groups, the "free" mobile water fraction is 10–47%.

For hydrophobic polymers, *e.g.*, polyethylene, association of water molecules and formation of through cluster channels is possible even at low water activity, at $P/P_\mathrm{s} \sim 0.1$ [23,30,31]. It has been shown for polyethyleneterephthalate as an example that as the polymer is humidified, the number and size of clusters increase; eventually, a system of micropores appears [32] and a complex of capillary phenomena is observed [33].

Thus, generalization of the concept of water sorption by polymers [34–44] leads to the conclusion that both localized water sorption on the binding sites and clusterization of water molecules are observed in hydrophilic (*e.g*., polyamide/water) and hydrophobic (*e.g*., polyethylene/water) polymers in addition to the matrix filling by “free” water molecules.

Such clusterization [45–55] can occur on ionogenic groups of polymers, on process-related impurities such as NaCl in epoxides, or on functional groups formed under exposure to penetrating acids and other chemically reactive compounds.

This is the fundamental reason enabling a difference in the composition of the external and internal (in the polymer bulk) electrolyte [56–66].

1.2. Sorption of neutral salts

1.2.1. Sorption of dry salts

In a dry state, salts of inorganic acids are practically insoluble in polymers, but the effect of penetration of a dry inorganic salt, namely solid electrolyte, plutonium Pu(IV) nitrate, into polymers was described in [67].

The values of diffusion coefficients of the dry plutonium salt for polyethylene, polyethyleneterephthalate, fluoroplastic, polyvinylchloride, and polystyrene calculated by A. Shterenzon [68] on the basis of the data from [35] are $3.3–14.0 \cdot 10^{-13}$ cm^2/s and correlate satisfactorily with the data [69] for nitric acid solutions with a high (85%) Pu(IV) content.

For these solutions, noticeable Pu(IV) sorption is observed only in the presence of a salting-out salt, sodium nitrate. Here, the sorption value in the 1–5 μm thick surface layer of a polyvinyl chloride plasticate reaches 10–100 mg/cm^2.

As compared to the gaseous diffusant, sulfur dioxide SO_2 [70], in the case of penetration into hydrophobic polymers, sorption activity of the dry plutonium nitrate salt is approximately 5 to 8 orders of magnitude lower [26].

Thus, sorption and diffusion can principally occur from dry volatile salts into polymers and even into hydrophobic matrices. However, the sorption values and diffusion coefficients are negligible. This fundamentally correlates with the data on the diffusion transport of other anhydrous electrolytes into hydrophobic polymers, namely, gaseous HCl, HF and concentrated sulfuric acid at elevated temperatures [26].

1.2.2. Sorption of salts from aqueous solutions by polymers

In dissolved state, inorganic acid salts are weakly soluble in polymers in case of sorption from aqueous solutions.

In relation to inert electrolytes such as salts of inorganic acids, *e.g*., NaCl, K_2SO_4, and $Ca_3(PO_4)_2$, polymers can be subdivided into hydrophobic ones, polymers with no ion exchange properties, as well as cation exchange and anion exchange hydrophilic polymers.

Extremely low ion concentrations in the polymer matrix are observed for inert hydrophobic polymers in contact with neutral salt solutions [23, 26].

According to IR spectroscopy data, carboxy, ketone groups (1720 cm^{-1}) and oxygen-containing groups (1707 cm^{-1}) recorded in hydrocarbon polymers impart them certain cation exchange properties. However, determination of the full exchange capacity of hydroxo complexes for such ions as $[BeOH]^+$, $Ca[CaOH]^+$, $[CoOH]^+$, $Cu[CuOH]^+$, $[MgOH]^+$, $[NiOH]^+$, $[PbOH]^+$, $[VO(OH)]^+$, $[AlOH]_2^+$, $[CrOH]_2^+$, $[FeOH]_2^+$, and $Zn[ZnOH]^+$ showed that it is extremely low, namely, 0.010 mmol-eq/g for polypropylene and 0.025 mmol-eq/g for polyethylene terephthalate [33].

At the same time, the mechanism of enhanced and selective ion sorption may not be ruled out even for inert polymers in the course of thermooxidative degradation owing to the formation of oxygen-containing groups of different types in such polymers.

For example, weakly oxidized polyethylene can sorb the Ca cation owing to the presence of $3 \cdot 10^{-4}$ meq/cm^3 of carboxy groups [54]. Moreover, it is reported [23, 54, 71] that polyethylene is permeable to for Cl^- anions, while no penetration of Na^+ cations is observed because it is below the sensitivity level. This is explained by the charge existing on the pore walls that hinders the cation motion.

Only strong oxidation of polyethylene with sulfur dioxide [70], where the accumulation of carbonyl groups converts the hydrophobic polymer into a polycarboxylic acid, allows imparting pronounced ion exchange properties to the matrix and enhances the sorption of salt and water solutions to 20%.

Thus, one can state that the low polarity of macromolecules of inert hydrophobic polymers causes a low solubility of not only water but also salt electrolytes in them, as their molecules are present in the polymer matrix in associated state [23, 30, 31].

1.2.3. Sorption of salts by moderately hydrophilic reactive resins

As regards corrosion protection, of greatest interest are coatings based on synthetic resins that are cross-linked due to chemical reactions with various solidifiers. Such protective coatings include functional groups of different nature capable of interaction with the diffusing anions. However, as the amount of reactive groups is much lower than that in conventional ion exchange resins, the coatings weakly swell in water and ion sorption is limited.

Anticorrosive moderately hydrophilic materials with a small number of polar groups weakly swell in water and in solutions of neutral salts. The equilibrium weight gain is 2 to 10% [42].

The presence of selective penetration where Cl^- anions penetrate into the epoxy resin ahead of K^+ cations was shown for Q345 cross-linked epoxy resin [72] exposed to 5 wt.% KCl using a scanning electron microscope equipped with an energy-dispersive spectrometer.

In addition to neutral salts such as chlorides and phosphates, sorption of partially substituted acid phosphates of such amphoteric metals as Zn and Al was studied [73]. These salts are characterized by much higher sorption (28–38 %) than neutral alkali or alkali earth phosphates (3–5%) with all degrees of substitution. It was concluded that the equilibrium internal diffusant solution in the polymer is significantly, by 1–2 orders of magnitude, depleted of Al, Zn, Na, and K cations in comparison with the outside solution from which the diffusion occurs.

1.2.4. Conclusion regarding salts

Thus, one can conclude that sorption of inert electrolytes, salts, by hydrophobic polymer macromolecules, owing to their low polarity, is observed at the quantification limit, or else after at least some weak ion exchange properties are imparted to polymer matrices. Meanwhile, hydrophilic polymers, particularly, amine-solidified epoxy resins (as the most frequent base for anticorrosion coatings) are characterized by the presence of selective sorption of cations and anions. In this case, anion sorption can be 1–2 orders of magnitude higher than cation sorption.

The results discussed above allow one to assume that the phenomenon of anion sorption selectivity is also possible for such chemically reactive electrolytes as acids.

1.3. Sorption of chemically active electrolytes. Acids

In the case of sorption of acid solutions by polymer coatings, specific interaction is observed in the ternary polymer–electrolyte–water system that results in thermodynamic nonideality of the solution within the polymer.

Let us at first consider a simpler variant: sorption in hydrophobic polymers.

For hydrophobic polymers with a chemically inert chain, the sorption of dry volatile electrolytes, as well as nonvolatile ones at elevated temperatures, does not differ from the sorption of chemically inert polar gases and follows the Henry law ($C = k_D \cdot P$, Table 1).

However, even for inert polymers (PE), the sorption of HCl in the presence of water is much higher [65] than from a dry gas phase due to the formation of $HCl \cdot nH_2O$ hydrates with $n = 3.7–6.3$.

For hydrophilic polymers noticeably swelling in corrosive media, such as a linear ternary butadiene–styrene copolymer with a moderate amount of the pyridine nitrogen–containing component, the composition of the internal phosphoric acid solution practically coincides in the entire concentration range with the composition of the outside corrosive medium [74]. The swelling pressure in such ternary systems is relatively low and amounts to 1–48 MJ/m^3 for phosphoric acid concentrations within 0.3–3.0 mol/l.

On the other hand, for cross-linked polymers, ionites with a large number of ionogenic groups [75], the swelling pressure at similar volume swelling is considerably, by 1–2 orders of magnitude, higher. Similar studies of ionites with an imidazoline nitrogen–containing component were also carried out both for phosphate and other anions, both inorganic (F^-, Cl^-, Br^-, NO_3, SO_4^{2-}, $Mo_7O_{24}^{6-}$) and organic (malate, citrate, malonate, tartrate, lactate, and oxalate) [76].

It was found for the sorption of dilute solutions of inorganic acids in non-crosslinked nitrogen-containing polyamides [77–81] that the internal solution is more concentrated than the outside solution. Also, the concentration of the internal solution is stabilized with an increase in the concentration of the outside solution.

It was shown for moderately hydrophilic cross-linked nitrogen-containing epoxy resins [82] that the acid content in the internal solution is proportional to the amount of the amine solidifier. Only some amine groups are characterized by sorption activity. The sorption value is 0.2 moles of an acid per 1 mole of amino groups. Sorption saturation is observed. The overall amount of the sorbed medium is proportional to the amount of the sorbed acid.

Moreover, amine-solidified epoxy resins feature the selective sorption of acid anions, where the acid/water ratio changes upon penetration of the outside acid solution into the epoxy matrix.

It was shown [83–85] that the phosphonic acid/water ratio in the internal solution is higher than in the outside one, *i.e.*, the internal solution is enriched in comparison to the outside one, $C_{\text{in}}/C_{\text{out}} = 1.2–30.7$.

As regards the partial vapor pressure p_s of the acid, electrolytes can be tentatively subdivided into volatile, such as HF, HCl, HNO_3, and nonvolatile, *e.g.*, H_2SO_4, H_3PO_4 that can however manifest enhanced partial pressure at elevated temperatures and pass into the volatile class.

The experimental results presented for hydrophilic and hydrophobic polymers allow one to suggest a sorption model with a chemical reaction where chemosorption or donor–acceptor interaction of the acid with reduced or residual ionogenic groups, particularly amino groups, results in immobilization of acid molecules on the binding sites and hydration of the salt groups formed.

2. HCM diffusion into materials of anticorrosion coatings based on reactive resins

2.1. Phenomenological regularities of HCM diffusion

Vast experimental data on HCM diffusion into polymer materials and reactive resin-based coatings has been accumulated to date [86]. This allows one to point out some important features of acid penetration into solidified reactive resins, namely, that such penetration is accompanied by the appearance of a diffusion boundary both for anhydrous acids and aqueous acid solutions. The motion of this boundary follows the formal Fick kinetics ($X– t^{0.5}$). Stepwise abrupt profiles of the chemical active diffusant distribution are registered. A relationship between the sorption value and diffusion front permeation depth is observed in cross-linked reactive resins containing residual ternary and sometimes secondary amine groups and also reduced hydroxy groups.

2.2. Profiles and boundary of acid penetration into reactive resins

2.2.1. Diffusion

The diffusion of electrolytes from aqueous solutions into a polymer occurs differently than that of dry gases. This is due to faster penetration of water into the polymer from aqueous solutions and its ability to form associates with more slowly diffusing acid or salt molecules in the polymer bulk. Electrolytic dissociation can favor the diffusant binding by ionogenic groups of the polymer matrix, cause changes in the diffusion activity of ions with different charges and bring about a concentration dependence of the diffusion coefficient and polymer coating permeability.

2.2.2. Water diffusion

A specific feature of polymer coatings of any thickness, both based on hydrophobic or hydrophilic polymers and on composite multilayer systems, is their permeability to diffusing water. Moreover, water diffusion is faster in almost all types of aqueous solutions of electrolytes than the electrolyte diffusion [42].

The regularities of water diffusion in polymers are estimated using diffusion coefficients, their concentration and temperature dependences, specific features of sorption and diffusion in Fickian and non-Fickian systems [87].

In the literature, there are several types of dependences of the water diffusion coefficient on the water content in a polymer and on temperature: rising and falling plots, S-type and extremal $D \sim p/p_s$ curves are observed.

The character of the dependence depends on the temperature range in which the polymer exists, *i.e.*, above or below the glass transition point, and on whether the polymer undergoes devitrification with an increase in relative humidity ψ. Here, different regularities in the glass transition point shift are observed for water "bound" by polar radicals and water “freely” involved in the thermal motion together with the segments of macromolecules [87].

D remains constant in the entire relative humidity range for hydrophobic polyolefins [18, 22, 18], polyethyleneterephthalate [32, 41], and hydrophilic solidified epoxy and phenol resins [38] that are important in corrosion protection. However, a decrease in *D* with an increase in ψ is also observed for hydrophobic polyethylene [39] and hydrophilic solidified epoxy resins plastified with diphenyls and phthalates [40], which is more typical of hydrophobic polymers [87] and occurs in the case of clusterization of water molecules in the range of $\psi < 0.3$. For hydrophilic polymers, this type of the $D \sim \psi$ dependence is observed at $\psi > 0.3$. The generalizing analysis of many works [89] shows that the more polar groups a polymer contains, the lower the *D* value of water; the lowest *D* of water is observed in polyvinyl alcohol [87]. However, an increase in *D* by 2–3 orders of magnitude is observed [26] in polar and glassy polymers of cellulose–water or polyamide–water types with an increase in the water concentration by 10% in the range of $\psi < 0.2$–0.3.

To describe the concentration dependences of the water diffusion coefficient in polymers, a number of approaches were analyzed [42, 87], including the dissociative diffusion model, the general relationships of the thermodynamic and molecular–kinetic diffusion theory, and the method of group contributions. As analysis of model concepts shows, one can assume D = const with 10% error for hydrophobic polymers, where $\psi < 1$ wt.% at $p/p_s = 1$. For hydrophilic polymers, where $\psi > 1$ wt.% at $p/p_s = 1$, the complexity of D calculation is caused by the necessity of accounting for the "free" water fraction against the overall sorbed water amount. This requires determining the constants of "bound" water cluster formation and "bound"/"free" water equilibrium constant, as well as the "free" water content by independent methods. Besides, it is necessary to estimate in post-experiments the change in the polymer crystallinity degree and polymer glass transition point; determine the amount of plastifiers, modifiers, and polymer hydrolysis products desorbed from the polymer matrix; estimate the amount of polar carbonyl, ester, and hydroxy groups in polymer chains in the course of hydrolytic thermal ageing of macromolecules and cross-linked networks.

For hydrophilic coatings, a differently directed effect of the polymer base modifications on the protective properties of the coatings can be observed. It was found [56] that an increase in the side aliphatic chain in epoxyamidoamines caused a decrease in water sorption with a simultaneous increase in water diffusion in the polymer chain.

It is important to point out in the analysis of water diffusion processes in polymers that the free volume theory allows one to describe the dependence of the diffusion coefficient of the electrolyte in polymers on the bulk fraction of water in the polymer. Here, *e.g.*, the permeability of cellulose acetate changes from 10^{-10} g/(cm·h·mmHg) at a water bulk fraction of about 0.08 to 10^{-4}g/(cm·h·mmHg) at a water bulk fraction of about 0.56 [42, 46].

Thus, one can conclude that, in addition to independent diffusion, water plays a fundamental role in the transport of electrolytes, acids, and their salts in anticorrosion polymer materials.

2.2.3. Diffusion of neutral salts

In hydrophobic polymers, the diffusion of nonvolatile electrolytes, salts, estimated from their permeability through the coating film is below the sensitivity of conventional techniques due to the extremely low salt solubility in polyolefines, *e.g.*, of KCl in polypropylene [23].

The high electric resistance of hydrophobic films contacting salt solutions [19, 20, 23, 90] does not allow one to estimate the self-diffusion of cations and anions in a hydrophobic polymer, either. It is assumed that due to low polarity of hydrophobic polymers, nonvolatile electrolytes exist in these polymers in the form of non-dissociated molecules with no hydrate shells [48, 91].

The hydrophilic polymers containing cation exchange groups in films of Nafion-117, a copolymer of perfluorosulfonic acid and PTFE (in acidic form (H^+)) show an increase in the self-diffusion coefficient of ions in the series: Sr^{2+}, Ba^{2+}, Cs^+, Ca^{2+}, Zn^{2+}, K^+, Na^+, Ag^+, while the D values are $0.2–1.6 \cdot 10^{-6}$ cm^2/s [47].

Hydrophilic polymers containing anion exchange groups, such as epoxy resins solidified by amines and polyamide, are the oldest objects of studies in the anticorrosion branch of physical chemistry [14, 40, 50, 58, 72, 73, 77, 78, 80, 81, 84, 85, 92, 93, 94, 95, 96, 97, 98, 99, 100, 101]. Various forms of diffusion transport, both "transport in pores" and "pure diffusion permeability", were studied in polymer matrices containing polar groups.

According to the free volume theory [45, 56, 102], the diffusion of an electrolyte is due to the volume fraction of water in a hydrophilic polymer. Assuming that the free volume in a swollen polymer is proportional to the volume fraction of water in the polymer [64], it was shown in a series of experiments [45] that D of the NaCl electrolyte in a polar polymer changes from 10^{-10} cm^2/s at a water volume fraction of about 0.08 to 10^{-5} cm^2/s in pure water.

In epoxy and epoxypolyamide coatings, the diffusion transport of NaCl and KCl solutions estimated from permeability [49, 50, 51, 52] is below 10^{-8} to 10^{-12} g/(cm·h·mmHg), which allows one to state that the diffusion permeability of these coatings is at the level of permeability of hydrophobic polymers to nonvolatile electrolytes. Nevertheless, if hydrophilicity is enhanced by increasing the polyamide component content threefold, the electric resistance of epoxypolyamide coatings in the NaCl solution decreases by 9 orders of magnitude, which points to enhanced salt dissociation in the largely increased water amount in the polymer [53].

When salt solutions permeate an epoxy polymer, efficient corrosion inhibitors containing HPO_4^{2-} anions slow down the mobility of water with an increase in concentration from 0.1 μM to 0.6 M [63]. Salt anions compete with water molecules in fast binding with reactive groups (OH, NH) and in the subsequent slower water accumulation in the polymer matrix micropores.

Thus, one can conclude that anions that are of importance for corrosion protection manifest diffusion activity in hydrophilic polymers at water concentrations 10% in the polymer [42], while the diffusion regularities of salt electrolytes at concentrations below 0.5% are similar to those in hydrophobic polymers.

2.2.4. Acid diffusion

Solutions of mineral and organic acids and their mixtures with salts and gases are corrosive media most frequently used in chemical industry.

In terms of their partial vapor pressure, acids can be separated into nonvolatile (sulfuric acid H_2SO_4 and phosphoric acid H_3PO_4) and volatile acids (HF, HCl, organic acids) [26, 86, 103].

The diffusion flow in the case of steady-state transport of dehydrated corrosive gases through membranes of hydrophobic polymers [91, 104, 105] is proportional to the pressure, while permeability coefficient P is independent of partial vapor pressure p_s or concentration: $J = P \cdot p_s$.

It should be pointed out that the permeability coefficients P of nonvolatile acids are 2–4 orders of magnitude lower than those of volatile ones, and penetration of nonvolatile electrolytes can only be detected at elevated temperatures [103,106].

The flow of an electrolyte is also proportional to its partial vapor pressure for aqueous solutions of electrolytes in the case of steady state transport through hydrophobic polymers [104].

Here, however, a concentration dependence of the diffusion coefficient is observed (Figure 1) [107] due to the thermodynamic nonideality of the internal electrolyte solution in the polymer as a result of strong specific interaction of the components of the polymer–electrolyte–water system.

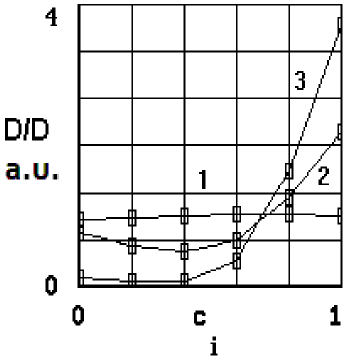

Figure 1. Dependence of the relative diffusion coefficient of HCl on the relative HCl concentration in the polymer in case of diffusion of hydrochloric acid through membranes of polyethylene LDPE (1), modified fluoroplastics PTFE F-4MB (2), and lavsan polyester (3). The temperature is 50°C; the concentration of HCl is 35.5%.

2.2.4.1. HCM distribution profiles

The diffusion regularities of aqueous electrolyte solutions in moderately hydrophilic reactive resins with reactive groups have characteristic features that also affect the diffusion profiles. In such systems [12], three concentration groups of acid distribution diffusion profiles are observed:

- smooth Fick profiles are characteristic of dilute solutions of volatile and nonvolatile inorganic acids;
- at average concentrations of mineral acids (5–30%) and for organic acids in amine–cross-linked epoxy reactive resins, abrupt stepwise profiles are observed (Figures 2, 3), while sharp diffusion fronts and strong concentration gradients are observed in reactive resins solidified with anhydrides [93];
- at high concentrations of oxidative acids, stepped profiles are combined with indications of polymer surface degradation.

An important point of detailed studies [94, 95] is that the authors confirmed the presence of a concentration gradient in the surface zone in the case of broken profiles. Later studies of various authors confirmed the above regularities of the acid distribution profiles upon diffusion [96, 97, 98, 99, 100, 101, 108,109].

The above regularities were also confirmed [84] for multifunctional phosphonic acids (hydroxyethylidenediphosphonic acid (HEDPA), nitrilotrismethylphosphonic acid (NTPA)), as well as organic salts of amines and heteropolyacids (phosphomolybdic acid (PMA) and phosphotungstic acid (PTA)) (Figure 4).

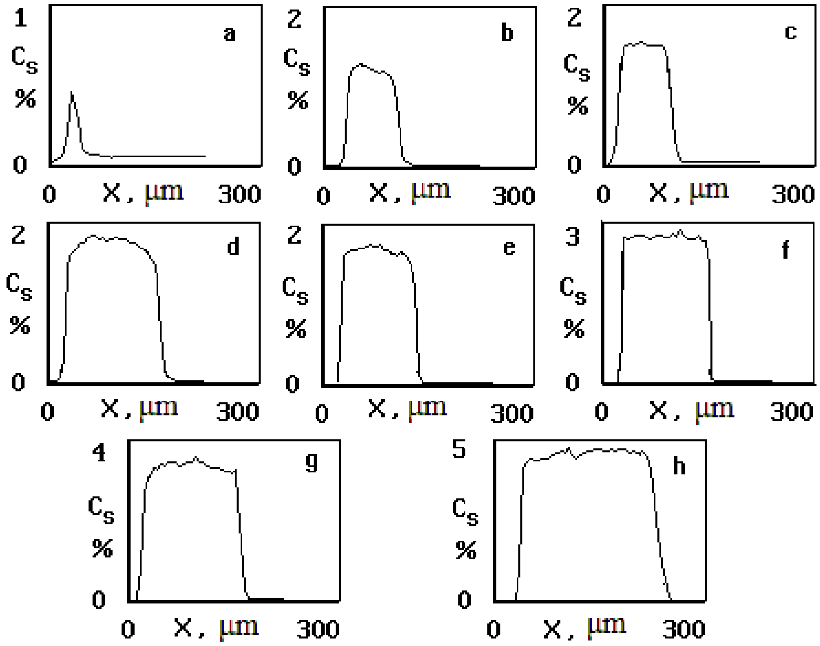

Figure 2. Diffusion profiles of sulfur concentration C_S % in an epoxy reactive resin obtained by local X-ray spectral analysis for the diffusion of 30% H_2SO_4 at 90°C for 384 h. The content of the aliphatic amine solidifier per 100 mass pt. of ED-20 epoxy resin is (a) 4; (b) 6; (c) 8; (d) 10; (e) 12; (f) 16; (g) 18; (h) 20 mass pt.

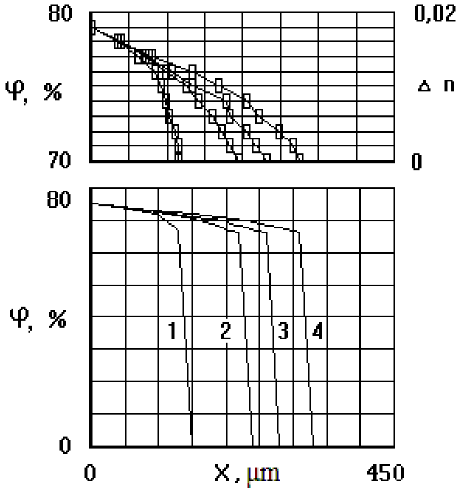

Figure 3. Diffusion profiles of formic acid at 70°C in an epoxy formulation of ED-20 epoxy resin/metaphenylenediamine MPDA amine solidifier (100 mass pt./14.5 mass pt.) for exposure times of (1) 40; (2) 102; (3) 131; (4) 165 min.

Being organoelement compounds, phosphonic acids are very interesting objects for studying the diffusion transport in coating materials. Their feature is that, like many compounds with organic substituents, they can have a plastifying effect toward glassy polymers.

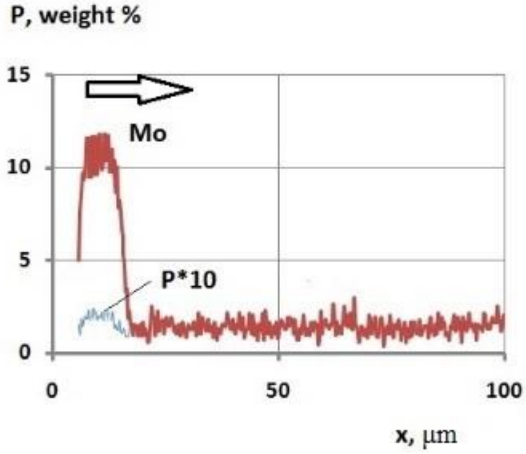

Figure 4. Diffusion profiles of phosphorus P and molybdenum Mo for a saturated PMA+dimethylbenzylamine solution that penetrated for 557 days at 50°C into an epoxy formulation [84].

Two-step diffusion profiles were obtained [73, 83, 85] for epoxy systems containing various concentrations of phosphonates studied using local X-ray spectral analysis [110] (Figures 5–7; the arrows indicate the direction of diffusion).

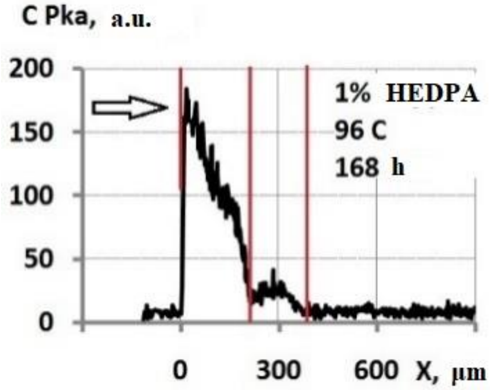

Figure 5. Diffusion profile of phosphorus P for 1% HEDPA that penetrated for 168 h into an epoxy formulation at 96ºC.

An indirect confirmation of a more complex profile with a low "primary" step was obtained from the results (Figure 8) of microprobe luminescent analysis of the sample face cut in the direction of diffusion [94, 95].

The results of luminescent analysis for all combinations of optical filters indicate that chemical changes occur in the acid penetration zone of the polymer matrix.

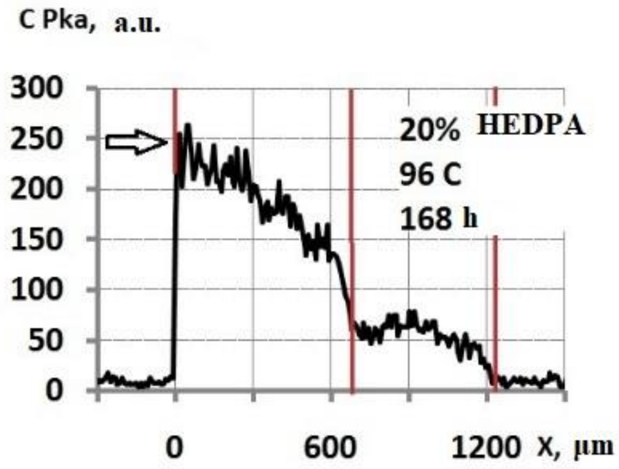

Figure 6. Diffusion profile of phosphorus P for 20% HEDPA that penetrated for 168 h into an epoxy formulation at 96ºC.

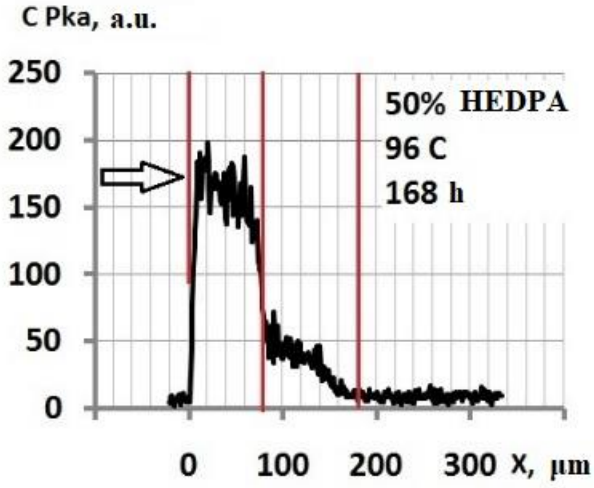

Figure 7. Diffusion profile of phosphorus P for 50% HEDPA that penetrated for 168 h into an epoxy formulation at 96ºC.

One can see that the profiles of organoelement acid distribution in the diffusion zone manifest two acid penetration zones, namely:

- the first and "primary" one; internal as regards the diffusion coordinates, with a low diffusant concentration, with a less pronounced profile break;
- the second one; outside as regards the diffusion coordinate, with the maximum concentration at the sample boundary, with an abrupt stepwise concentration decrease.

The second outside zone with a higher concentration with an abrupt decrease in permeation is characteristic of the previously studied HCl and H_2SO_4 mineral acids.

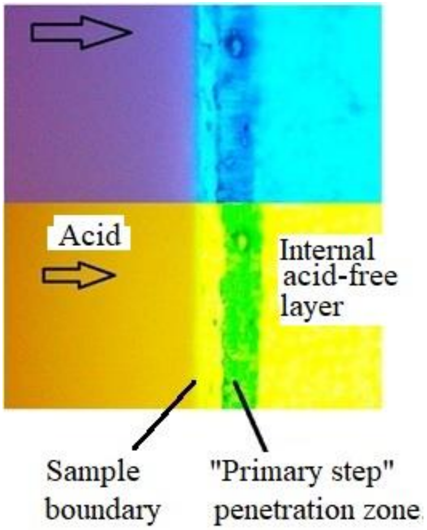

Figure 8. Comparison of the zones of penetration of 60% HEDPA in the epoxy formulation at 80°C for 2160 h for the two ranges of luminescence excitation and detection: UV-UV 330–400 nm and vis-vis 420–485 nm. An Altami LUM-1-LED luminescent digital microscope. The arrow indicates the direction of acid diffusion.

The "primary" internal region is observed for the first time and is probably related to a noticeable dissociation of NTPA and HEDPA by the second stage [111, 112] and to the plastifying effect of this class of compounds.

Thus, a two-step profile illustrates the possibility of a more complicated models of penetration of particular HCM characterized by dissociation by both the first and second stages and by a plastifying effect.

2.2.4.2. HCM penetration boundary

An abrupt boundary of acid penetration is detected by various methods, particularly by drop indicators based on acid–base or luminescent indicators applied onto a face cut/chip of polymer samples exposed to corrosive media [113].

Moreover, for a number of polymers, a difference can be detected in the luminescence of the material in the acid penetration region and in the initial polymer, which also determines the diffusant penetration boundary.

The abrupt boundary of penetration of nonvolatile acids observed by luminescent methods also coincides with the marker element distribution profile, *e.g.*, of phosphorus for phosphoric acid, sulfur for sulfuric acid, determined using the method of local X-ray spectral analysis [94, 95]. For volatile inorganic and organic acids, abrupt diffusion profiles are recorded using the interference microtechnique [114].

An abrupt stepwise profile, though it differs from a smooth Fick diffusant distribution, moves in a sample according to the classical $X \sim \sqrt{t}$ relationship [94, 95, 98]. It will be described in more detail in the section dedicated to the model of diffusion with binding.

An effect of the presence of an abrupt broken profile of the diffusant distribution separating the surface swollen layer from the internal layer of the original polymer is [103] the detected universal relationship between the overall weight gain and the relative acid penetration depth (Figure 9).

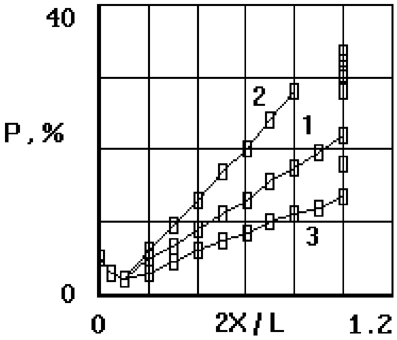

Figure 9. Effect of the relative acid penetration depth ($2 \cdot X/L$, where L is the sample thickness) on the weight gain (P, %) of the epoxy formulation in corrosive media: (1) 30% H_2SO_4, 343 K, 1–100 h; (2) 1–70% CH_3COOH, 343 K, 27 h; (3) 1–23.8% HCl, 293 K, 1200 days.

2.3. HCM diffusion models in reactive resins

2.3.1. Background

Analysis of the entire set of available experimental data on the sorption, distribution profiles, and kinetics of variation of penetration and weight gain in HCM allows one to conclude that it is reasonable to describe the diffusion process in such systems using models with binding [2]. Let us consider the diffusion models with HCM binding using the simplest example of a single-component diffusant.

2.3.2. Diffusion model with binding

The regularities of this mechanism are that irreversible diffusant binding occurs at the abrupt diffusion boundary; a sorbed molecule leaves the diffusion process and the diffusion transport is observed only in the range between the sample boundary and the abrupt diffusion boundary.

Mathematically, the above process can be described [116] by the following system of diffusion kinetic equations:

$$\frac{\partial c}{\partial t} = -D_1 \frac{\partial^2 c}{\partial x^2}$$

$$\begin{aligned} c &= C_0 \quad \text{at} \quad x = 0 \\ c &= 0 \quad \text{at} \quad x = X \end{aligned} \tag{3}$$

$$-D_1 \frac{\partial c}{\partial x}\Big|_{x=X} = E\frac{dX}{dt}$$

where c is the concentration of the diffusing compound dissolved in the material with spent functional groups; E is the concentration of chemically reactive functional groups in the polymer; X is the reaction zone coordinate that changes with time.

The solution of this system of equations (3) for unbound acid [117] takes the form (4):

$$c = c_0 \left[1 - \frac{erf(x\sqrt{4Dt}\,)}{erf\beta}\right] \tag{4}$$

for $0 < x < X$, $0 < t < t^*$

and $C = 0$

for $x > X$, $t > 0$.

Here, the reaction zone movement is described by the equation:

$$X = \beta\sqrt{4Dt} \tag{5}$$

where t^* is the time of movement of the moving boundary through the membrane; β is a numeric parameter determined from the equation:

$$\sqrt{\Pi}\,\frac{\exp(-\beta^2)}{erf\beta} = \frac{E}{c_0}\beta \tag{6}$$

where $erf\,\beta$ is the error function.

Here, the distribution of the total concentration (of the free and bound acid) can be presented as:

$$c_{tot} = E + c_0 \left[1 - \frac{erf(x\sqrt{4Dt}\,)}{erf\beta}\right] \tag{7}$$

at $0 < x < X$

and $C_{\text{tot}} = 0$

at $x > X$.

According to the above experimental data for sulfuric and formic acids (Figure 2 and Figure 3), the acid concentration gradient in the diffusion zone is negligible. In this case, $C_0/E \ll 1$ and expression (6) can be reduced to:

$$\beta = \sqrt{c_0/2E} \tag{8}$$

Substituting (8) into (3), we obtain:

$$X^2 = \frac{2c_0 D}{E}t \tag{9}$$

or

$$\lambda^2 = \frac{2c_0 D}{E} \tag{10}$$

Thus, the model of diffusion with binding allows one to qualitatively describe the above main regularities of acid diffusion into reactive resins, namely:

- the presence of a stepwise profile of diffusant distribution with an abrupt diffusion boundary,
- the Fickian character of the boundary movement: $X – t^{0.5}$;
- the relationship of the main diffusion-sorption parameters: D, C_0, E.

As it is seen from equation (10), a decrease in the permeability of materials based on reactive oligomers and polymers capable of binding the medium is favored by a decrease in D and C_0 (it is significant that we speak of the diffusion coefficient and solubility of a material with “spent” functional groups, *i.e.*, a material chemically modified by the medium) and an increase in the concentration of chemically reactive polymer groups participating in the binding.

2.3.3. Diffusion of a HCM/water binary system

The above approach determining the fundamental regularities of interactions between acids and a material containing residual reactive groups focuses on the “strong” acid–polymer interaction. At the same time, irreversible sorption on the residual groups of a reactive resin is not the only type of specific interaction in the systems under consideration.

The above description of the diffusion process did not explicitly take into account that the diffusant (aqueous electrolyte solution) is a bicomponent system with specific (solvation) interaction between its components. In particular, the values of constants D, C_0, and E in Equation (10) do not explicitly imply, *e.g.*, the dependence of the permeation constant on the concentration of the outside acid solution.

At the same time, determination of the correlation between the permeation constant and the properties of the outside electrolyte solution is of great practical importance. Let us consider whether Equation (10) can be used for this purpose.

There are two main equally popular approaches for the explanation of the concentration dependence of D: the free volume model [56] and activated diffusion model [42]. The latter approach is preferable in the description of highly polar systems.

The effect of the outside solution concentration in the activation theory can be considered on the basis of the following equation:

$$D = D_0 \exp[-\frac{E}{RT}] \exp[-\frac{\Delta G\text{st}}{RT}] \quad (11)$$

where ΔG_{st} is the additional contribution to the activation energy equal to the energy of destruction (formation) of solvates in the internal solution.

The fundamental problem of the activation theory is the composition of the solvate from which the HCl molecule “jumps” into the surrounding polymer matrix.

As regards thermodynamics, the composition of the electrolyte sorbed by the polymer is a complex function of the composition of the medium and the properties of the matrix. It should be determined by the minimum energy principle, *i.e.*, by the process that is most favorable for the system: replacement of the acid molecule by an equivalent amount of water molecules or vice versa. This problem has no theoretical solution to date.

In this connection, two models of solvate composition in polymers appear to be justified:

1) The composition of the solvate in the polymer is the same as the composition of the outside electrolyte solution. This viewpoint was suggested by A.L. Shterenzon [23] in an analysis of acid sorption by nonpolar hydrophobic polymers.

It is easy to show that with account for the expression for ΔG_{st}:

$$\Delta G_{\text{st}} = N\Delta\mu_w + \Delta\mu_{ha} = RT\ln[(P_w/P_w^0)^N](P_{ha}/P_{ha}^0)] \tag{12}$$

where N is the outside solution concentration expressed by the ratio of the number of moles of water per mole of acid.

From equations (10)–(12), an expression for the dependence of the penetration rate constant on the component vapor pressures (activities) follows:

$$\lambda^2 = \frac{2k\,P_{ha}}{E} D_0 \exp[-\frac{E}{RT}][(P_w/P_w^0)^N](P_{ha}/P_{ha}^0)] \tag{13}$$

Thus, according to equation (13), the described model of diffusion transport of acids in the case of irreversible binding and under the condition of existence of associates in the polymer with the composition similar to that of the outside solution predicts a linear dependence between log λ and $[(P_W/P_W^0)^N(P_{ha}/P_{ha}^0)]$. The corresponding data are presented below (Figure 10).

2) The composition of solvates from which acid molecules "jump" can be considered unvaried in a certain concentration range.

This concept is supported by the fact that acid penetration always occurs with faster penetration of water, *i.e.*, into a polymer pre-saturated by water. Here, it appears probable that the number of water molecules in a hydrate is also approximately constant and is determined by the permissible size of the cavity available for solvate formation around the "acquired" functional group of the cross-linked polymer.

Under the conditions of equilibrium with the outside solution, the free energy of solvate formation can be presented as follows:

$$\Delta G_{\text{st}} = RT\ln[(P_w/P_w^0)^n](P_{ha}/P_{ha}^0)^m] \tag{14}$$

where m and n are the numbers of acid and water molecules in the internal solvate (m, n = const).

Substituting expressions (14) and (11) into equation (10) for hydrates constant composition, we have:

$$\lambda^2 = \frac{2k\,P_{ha}}{E} D_0 \exp[-\frac{E}{RT}][(P_w/P_w^{0})^{n}][(P_{ha}/P_{ha}^{0})^{m}] \tag{1}$$

Figures 10 and 11 below show the plots of the rate constant of HCl penetration from HCl solutions with different concentrations on the reduced activity in the models of solvates with a variable and constant composition.

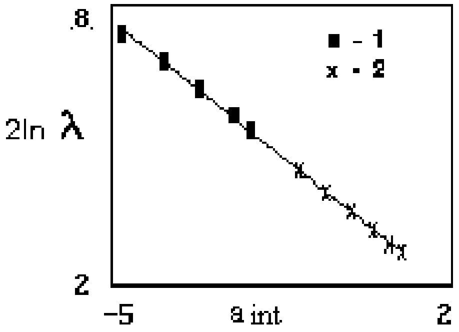

Figure 10. Dependence of the logarithm of the rate constant of HCl penetration into an epoxy material on the integral activity of the outside HCl solution in the concentration range of 5–33% in the constant-composition solvate model: (1) 20°C, (2) 70°C.

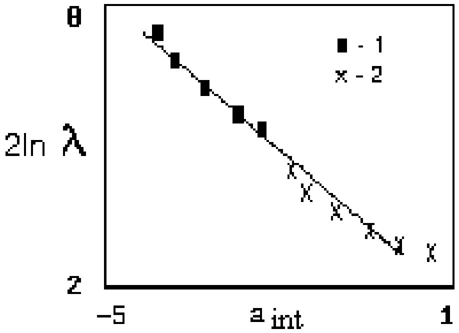

Figure 11. Dependence of the logarithm of the constant of HCl penetration into an epoxy material on the integral activity of the outside HCl solution in the concentration range of 5–33 % in the variable-composition solvate model: (1) 20°C, (2) 70°C.

One can see that using solvate formation models allows one to describe HCl penetration into epoxy materials from solutions with different concentrations using a single dependence. A more accurate description is obtained using the model of constant-composition solvates.

A satisfactory description of the dependence of penetration constant λ on reduced activity is also observed for H_2SO_4 in the range of average acid concentrations (20–68 %) [107].

2.3.4. On the possibility of describing diffusion using the effective diffusion coefficient

From a practical standpoint, in addition to the effect of the temperature and outside solution concentration of the diffusion of electrolytes into coating materials, it is of particular interest in the case of multicomponent systems whether the components have a mutual effect on the penetration into polymer materials.

In the steady-state mode, according to the thermodynamic approach [118], the flow density of the electrolyte (acid) from the aqueous solution through a coating can be presented in the form of a sum of flows related to the acid concentration gradient C_A and water concentration gradient C_W:

$$-J_a = D_{aa}\frac{d\,c_a}{dx} + D_{aw}\frac{d\,c_w}{dx}\ , \tag{16}$$

where D_{aa} is the partial diffusion coefficient of the acid (with respect to the acid concentration gradient) and D_{aw} is the partial diffusion coefficient of the acid with respect to the water concentration gradient.

The flow of water is determined similarly. Thus, the flows of compounds in the case of multicomponent diffusion are generally interdependent. However, it was shown in studies on the penetration of gases and high-concentration acid solutions that the acid flow through hydrophobic polymer films (polyolefins, fluoroplastics, polyesters) is determined only by the partial vapor pressure of the acid [12, 53], which can be interpreted as evidence of independence of acid and water penetration. At the same time, it is known that in some cases, the permeability coefficients from a dry gas phase and from an aqueous solution can differ by an order of magnitude [54]. Moreover, there are well-known experiments on the counterdiffusion of acid and water into polymer films: the time of acid breakthrough through a film, when water is present on the opposite film side, considerably exceeds the breakthrough time in case of diffusion into a dry inert gas [58]. Besides, one should point out that the conclusion on the possible independence of penetration of components of aqueous electrolyte solutions contradicts the concepts of interaction between an electrolyte and water resulting in solvate formation. The above contradictions also led to a hypothesis about the presence of two diffusion coefficients, steady-state and nonsteady-state ones, in the systems under consideration [86], which contradicts the basic physicochemical concept of diffusion.

We believe that systematization of the concepts of diffusion of electrolyte solutions into anticorrosion polymers can be performed on the basis of the concept of solvate formation. This concept in the case of the systems under consideration is the second-important concept after the one of specific sorption on residual functional groups of the polymer determining both the nonsteady-state and steady-state diffusion in the systems in question.

One should point out that it is the concept of solvation in the course of diffusion of aqueous solutions that allows establishing the relationship between the concentrations of the diffusing components. Within the model of constant-composition solvates, the concentrations of acid C_a and water C_w in the polymer can be presented as follows:

$$c_a = c_{af} + k_p c_{af} c_{wf}^{\ n}$$

$$c_w = c_{wf} + n k_p c_{af} c_{wf}^{\ n},$$

where C_{af} is the concentration of "free" (non-solvated) acid in the polymer and C_{wf} is the concentration of "free" (non bound in solvates) water in the polymer.

One can show that in this case the initial equation (14) for the overall acid flow takes the form:

$$-J_a = [D_{aa} + D_{aw}(\frac{n k_p c_{wf}^{\ n}}{1 + k_p c_{wf}^{\ n}})](1 + k_p c_{wf}^{\ n})\frac{d c_{af}}{dx} \tag{17}$$

The main conclusion following from equation (17) is that acid diffusion from aqueous solutions into polymers can be described using the single-component diffusant model with a concentration-dependent effective diffusion coefficient. This conclusion confirms the feasibility of the above description used in the analysis of diffusion with binding.

Analysis of equation (17) shows that acid transport generally depends on the flow of the second component, *i.e.*, water. The effect depends on the outside solution concentration: the contribution of water to the acid transport is the largest in dilute solutions. Here, the water flow from the solution is greater than from a dry gas. For concentrated acid solutions, C_{wf} tends to 0 and therefore equation (17) assumes the form:

$$-J_a = D_{aa}\frac{d c_{af}}{dx} = D_{aa} k_a \frac{d h_a}{dx},$$

where k_a is the acid sorption constant; h_a is the partial acid vapor pressure.

In other words, acid transport in the case of concentrated solutions will be determined only by the acid vapor pressure, which agrees with the experimentally observed results.

2.3.4.1. Effect of impurities on mass transport

Polar groups in polymer macromolecules play the role of binding centers and slow down the penetration of electrolytes towards the support being protected. However, incorporating polar groups into a polymer within solvents, plastifiers, stabilizers, fire retardants, antistatic agents, surfactants, finishing agents, and other polar compounds can result in enhancement or initiation of diffusion transport of acids through the coating film [42].

It was shown [68] that cyclohexanone or acetone enhances the permeability of fluoroplastic F-42 or polyethylene HDPE for 30% sulfuric acid solutions by 1–2 orders of magnitude, whereas sulfuric acid does not penetrate hydrophobic polymers upon replacement of polar solvents with toluene. Similarly, dichloroethane enhances the diffusion of sulfuric and hydrochloric acid.

This phenomenon requires that the absence of noticeable amounts of migrating polar components in the ready coating is guaranteed in the choice of compositions and temperature modes used in the creation of anticorrosion coatings.

3. Multilayer composite coatings

The presented review of diffusion studies on hydrophobic and hydrophilic polymers allows their advantages and drawbacks for anticorrosion protection to be pointed out.

Hydrophobic coatings can be efficiently used in nonvolatile electrolytic media since they have low solubility and permeability in such media. For volatile electrolytes, the breakthrough time of a hydrophobic coating is negligible and the breakthrough of the corrosive medium to the support quickly destroys the polymer/metal adhesive bonds. The application of hydrophobic coatings is nearly always accompanied by the use of hydrophilic primers, primers, and adhesion activators.

Hydrophilic coatings based on reactive resins prevent the acid breakthrough to the support, since abrupt breaking profiles, both single- and two-step ones, exclude the existence of diffusion forefronts owing to the chemical reaction of the polymer’s ionogenic groups with the acid. Hydrophilic polymers provide support isolation both from nonvolatile and volatile acids, in contrast to hydrophobic matrices. Hydrophilic compounds in the form of mastics, filler pastes, enamels, and paints create a monolithic seamless barrier after solidification of the applied coating layer.

Despite all the advantages of hydrophilic materials, they are still inferior to hydrophobic polymers as regards the stability to exposure to extremely corrosive media, especially those with oxidative activity. An efficient solution is to combine layers of hydrophobic and hydrophilic materials in the same coating.

Using rational thicknesses of hydrophilic reactive resins allows avoiding the degradation of their mechanical stability, especially in the adhesion defect zones [119, 120], and eliminating an increase in the internal stress owing to removal of shrinkage when the medium penetrates the polymer [121].

3.1. Model of HCM transport in bilayer composite coatings

Analysis of HCM diffusion in a composite coating consisting of layers of hydrophobic and hydrophilic materials primarily requires choosing an approach to its mathematical description.

The problem of solving one- and multidimensional diffusion and thermal conductivity problems for the transfer of single-component diffusants or heat through a single layer has been developed rather well and implemented in algorithms and applied software [122, 123].

However, for multicomponent diffusants or for multilayer coatings, the conditions of the problem are considerably complicated and there are as yet no generalizing algorithms or programs.

Mathematically, the problem of transport of an *n*-component medium through an *l*-layer flat coating in the absence of chemical reactions in layers can be formulated in general by the following system of equations:

$$\begin{aligned}
\frac{\partial C_i^{(1)}}{\partial \tau} &= \frac{\partial}{\partial X_1}\left(\sum_{j=1}^{n-1} D_{ij}^{(1)} * \frac{\partial C_i^{(1)}}{\partial X_1}\right)\\
\frac{\partial C_i^{(k)}}{\partial \tau} &= \frac{\partial}{\partial X_k}\left(\sum_{j=1}^{n-1} D_{ij}^{(k)} * \frac{\partial C_j^{(k)}}{\partial X_k}\right)\\
\frac{\partial C_i^{(l)}}{\partial \tau} &= \frac{\partial}{\partial X_l}\left(\sum_{j=1}^{n-1} D_{ij}^{(l)} * \frac{\partial C_j^{(l)}}{\partial X_l}\right)
\end{aligned} \qquad (18)$$

where $i = 1...n$; $k = 1…l$; $D_{ij}^{(k)}$ is the diffusion coefficient of the *i*-th component owing to the presence of the concentration gradient of the *j*-th component in the *k*-th layer; $C_j^{(k)}$ is the concentration of the *j*-th component in the *k*-th layer in the point with coordinate X_k.

It is known that the above system of equations can be solved only provided that some necessary initial and boundary conditions and dependences $D_{ij}^{(k)}(C, X)$ are provided.

Owing to the complexity and interrelationship of the values, no general analytical solution exists. However, an analytical solution can be obtained in some specific cases, *e.g.*, where diffusion coefficient *D* is independent of the concentration for a single-component diffusant penetrating a bilayer coating. In this case, both the delay time and the steady-state flow are independent of the order of the layers [124] and a combination of two layers of different hydrophobic materials does not result in a decrease in diffusion permeability.

For more complicated cases, if a concentration dependence exists, the solution can be obtained numerically. As shown in [42], in this case, one could expect an increase in delay time θ for a nonsteady-state diffusion region and a decrease in steady-state transport flow J_{st}.

The permeability of a bilayer coating can be decreased even further by alternating layers with different chemical affinity to the diffusant, particularly in a bilayer coating consisting of an outside layer of a chemically inert hydrophobic polymer and an internal layer of a polymer capable of chemical interaction with the diffusant.

Let us use the following layer numbering in multilayer systems:

- index 1 corresponds to the outside layer, *i.e.*, the one facing the corrosive medium and thus the first to contact this medium;
- the underlying layers will have sequentially numbered indices.

Let us use the following notations:

D_1 is the diffusion coefficient in the first hydrophobic layer;
l_1 is the thickness of the first layer;
c_1^0 is the equilibrium solubility of the medium in the material of the first layer;

$c_1^{(s)}$ is the diffusant concentration in the first layer at the interface between the first and second layer;
D_2 is the diffusion coefficient in the second layer;
X is the diffusant penetration depth into the second layer, *i.e.*, the distance between interface 1–2 and the acid penetration boundary into the second layer material;
E_2 is the chemisorption capacity of the second layer material;
$c_2^{(s)}$ is the diffusant concentration in the second layer at the interface between the first and second layer: $c_2^{(s)} = k_g \cdot c_1^{(s)}$.

For steady-state transport, the system assumes the form:

$$\begin{gathered} J_1 = -D_1 \frac{d\,c_1}{d\,l_1} = -D_1 \frac{c_1^0 - c_1}{l_1} \\ J_2 = -D_2 \frac{d\,c_2^{(s)}}{dX} \\ J_3 = E_2 \frac{dX}{dt} \\ c_2^{(s)} = k_g c_1^{(s)} \\ J_1 = J_2 = J_3 \end{gathered} \tag{19}$$

Solution of the system of equations in differential form is:

$$\frac{dX}{dt} = \frac{D_2 k_g c_1^0}{E_2[X + l_1(D_2/D_1)k_g]} \tag{20}$$

In integral form:

$$X = \sqrt{\frac{2D_2 k_g c_1^0}{E_2} t + \left(\frac{D_2}{D_1} k_g l_1\right)^2} - \frac{D_2}{D_1} k_g l_1 \tag{21}$$

As one can see from analysis of the equations obtained, in the absence of the outside layer equation (21) is reduced to the well-known equation for diffusion with a chemical reaction [22, p. 74]:

$$X_0 = \sqrt{\frac{2D_2 k_g c_1^0}{E_2} t} \tag{22}$$

With account for the fact that $\frac{D_2}{D_1} k_g = \frac{P_2}{P_1}$, one could expect that application of an additional outside layer would be efficient and justified in the case where its permeability is comparable with the permeability of the primary coating, though not of the initial material but of the material chemically modified by the corrosive medium.

It is easy to show that equation (21) with account for (22) can be reduced to a simpler form:

$$\frac{X^2 - X_0^2}{X} = 2 l_1 \frac{P_2}{P_1} \tag{23}$$

where X is the front penetration depth into the reactive resin layer in a composite coating and X_0 is the front penetration depth into the reactive resin layer in a single-layer coating.

Thus, the reduced penetration depth $Y = (X^2 - X_0^2)/X$ of a chemically active media into a bilayer coating with the above structure is proportional to outside layer thickness l_1 and inversely proportional to the permeability of the internal layer material P_1.

Experimental results of studying acid penetration into composite coatings in the coordinates “reduced rate constant of penetration into the reactive resin layer” – “thickness of the outside hydrophobic polymer layer” are shown below (Figure 12).

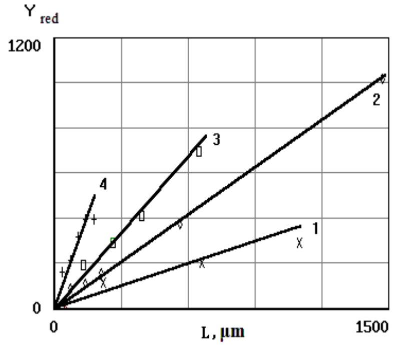

Figure 12. Dependence of reduced penetration rate constant Y_{red} (μm/h$^{0.5}$) for 35.6 % HCl at 50°C into an epoxy material with its surface modified by films of polyethylene HDPE (1), polypropylene PP (2), modified fluoroplastics F-26 (3) and F-2m (4) on the film thickness.

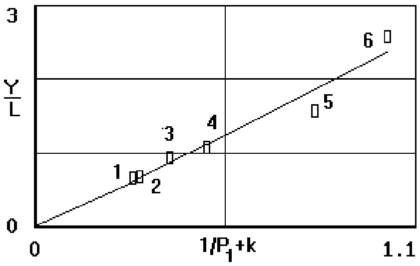

Figure 13. Dependence of reduced penetration rate constant $Y_{\text{red}} = (X^2 - X_0^2)/X$ divided by the thickness L of the surface polymer film (μm/h$^{0.5}$/μm) on the effective diffusion resistance of a surface film with unit thickness [Pa·h/g·10^4]. The medium is 35.6 % HCl; 50°C. The epoxy material surface is modified by films of polyethylene HDPE (1), polypropylene PP (2), fluoroplastics F-26 (3), F-4 (4), F-4mb (5), and F-2m (6).

As one can see from the above data (Figure 12), the dependence of the reduced depth or penetration rate constant on the thickness of the upper modifying layer for each of the studied polymers is linear, as indeed follows from the presented concept.

One should point out that the model under consideration is based on the linear sorption by materials of both layers. While this model is quite justified in the case of hydrophobic polymers, it may be more reasonable to use sorption models with specific interaction for hydrophilic polymers with reactive groups. It is interesting to note that if other sorption models are used, *e.g.*, sorption with Langmuir filling of active centers, the basic form of the equation describing reduced penetration remains practically unchanged; only an additional constant factor appears that changes the line slope:

$$\frac{X^2 - X_0^2}{X} = 2P_2\left(1 + K_g\frac{c_1^0}{c_m^0}\right)^{-1}\frac{l_1}{P_1} \tag{24}$$

The model under consideration also predicts the existence of a unique dependence between the reduced penetration depth and diffusion resistance for bilayer coatings with an upper layer of different polymers.

As one can see from the data (Figure 13), the same linear dependence between the reduced penetration depth and diffusion film resistance is indeed observed, but the resulting straight line is shifted with respect to the origin of coordinates by $+k$, which may be interpreted as the appearance of a certain additional diffusion resistance in the system.

The effect of additional diffusion resistance may be due to various reasons, *e.g.*, a change in the interlayer structure [125], potential drop at the interface where an additional insulating layer is present, *etc*.

In the literature, experimental data are available confirming that the permeability of multilayer coatings is not an additive sum of the permeabilities of individual layers [126] and depends on the order of layers with respect to the diffusant flow. For example, the diffusion coefficient and permeability coefficient of ethanol in an ethanol/polyethylene/polyvinyl chloride (E/PE/PVC) system are 1.3 to 2.0 times smaller than in the E/PVC/PE system.

Coating structures consisting of a layer of polar polyvinylbutyral PVB under a layer of hydrophobic polyethylene PE and polytrifluorochloroethylene PTFCE also efficiently block corrosive medium [65]. Modification of such a coating with anionic AN-1 and cationic KU-1 ion exchange resins enhances the concentrations of selectively bound corrosive medium cations and anions.

Interlayer adhesion can produce an additional effect on the permeability of binary coating films [125]. For a lavsan/PE laminate, the impermeability time is 8.6 times higher than the sum of the impermeability times of individual films.

Aside from laminates, nonadditivity is also characteristic of surface-modified polymer films, *e.g.*, polyethylene HDPE after surface treatment with fluorine [126, 127]. The surface HDPE layer treated with fluorine to a 15–50 μm depth attenuates the polyolefine permeability for heptane, oil products, and paint-and-lacquer materials 10–100 fold.

With account for the above effect of the sorption regularities and contribution of additional diffusion resistance, equation (24) assumes a more general form:

$$\frac{X^2 - X_0^2}{X} = 2\frac{P_2}{(1+b)}\left(\frac{l_1}{P_1} + k\right) \tag{2}$$

where *b* and *k* are constants accounting for the regularities of sorption and effect of additional diffusion resistance.

From the practical point of view, the results under consideration, first, mean that combining layers of different polymer coatings permits the polymer coating permeability to be decreased considerably. Introduction of an additional layer or partial replacement of one material with another one, *e.g.*, with a thickness as small as 100–200 μm allows the penetration depth to be decreased tenfold, which is equivalent to an increase in the time-to-breakthrough by a factor of hundreds (Figure 14).

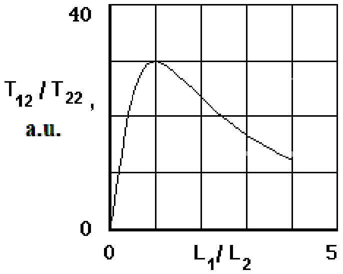

Figure 14. The extremal dependence of time to breakthrough of a composite bilayer epoxy coating with an upper hydrophobic layer (T_{12}) compared to a single-layer epoxy coating T_{22} with the same thickness on the ratio of layers' thicknesses *L*. Diffusant: 36 % HCl, *t* = 50°C.

Second, combining layers of a hydrophobic material and a material that can bind the medium in a single coating allows one to simultaneously solve the problem of full elimination of breakthrough of the most corrosive volatile components at the initial stage of coating operation.

4. Conclusion

Studies on the diffusion transport of acidic corrosive media in anticorrosion coatings allow formulating a concept of creating multilayer coatings with gradient structures manifesting selective interaction and binding corrosive medium components.

The suggested approach [107] distinguishes three zones with different functionalities in the coating structure:

- The top (finishing) layer that directly contacts with the corrosive medium. It is recommended to use hydrophobic chemically inert polymer as a polymer matrix for top layer. Due to its inert origin media solubility is low and the acid distribution in the layer has a smooth Fickian diffusion profile. Top layer modification imparts additional special properties to the coating, such as conductivity, abrasion resistance, wettability, *etc*.
- The main (inner) coating layer that determines the barrier and mechanical properties of the coating; as the moderately hydrophilic polymer matrix contains reactive

groups, with ability of binding of most aggressive components of media. The diffusion profile of the acid distribution in the layer is abrupt and stepwise. Main layer works as selective membrane.

- The primer coating layer that is applied directly onto the protected metal. Due to above mentioned selective properties of main coating layer, the primer coating works under much lighter corrosion attack as exposure only to water, dissolved oxygen, and chemically inert gases. Its main goal will be to provide stable adhesion to metal.

This approach allows one to create coating systems with high chemical stability for solving many corrosion problems. Examples of practical implementation of the diffusion model of multilayer or gradient coatings used in multicomponent highly corrosive media can be found in [3, 6, 11, 94, 95, 128, 129, 130].

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