Impregnation and Polymerization of Vinylic Monomers in Porous Media.   I. Kinetics of Impregnation

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Synopsis

In this work, we have studied the mechanism and kinetics of penetration of monomers and of liquids of low molecular weight into porous media such as asbestos cements. Although the phenomenon is physically different from a molecular diffusion, the kinetics of impregnation are well represented by Fick's laws of diffusion.   We observe an excellent agreement between the experiment and the theoretical equation as long as the degree of impregnation does not exceed 80%.   If, in order to represent this, we use a simplified model introducing a flow governed by Poiseuille's law through a bundle of capillaries of the same diameter, we obtain a parabolic law which is verified up to only 55%.   We have demonstrated the physicochemical parameters which influence the kinetics of impregnation.   The results can be summarized by the following empirical equation:

$$D = \frac{D^* \gamma \cos \theta r^3}{\epsilon \eta}$$

where η represents the viscosity of the liquid, γ the surface tension, θ the angle of contact, r the average radius, and ϵ the porosity; D^* appears as a constant equal to 2.0×10^9 cm^{-2}.   The standard deviation of its determination is 0.14×10^9 cm^{-2}.

INTRODUCTION

Most building materials derived from concrete and cement are characterized by a relatively high degree of porosity.   The presence of pores results from the removing of water in the course of setting.

Various authors[1-6] have taken advantage of this open, porous structure to introduce polymeric resins into stony building materials.   They have observed, particularly in the case of cements and concrete, a truly spectacular increase in flexural resistance, capable of reaching 500%.   These first unexpected and remarkable results have created considerable interest in the study and development of these composites.

The industrial application of these organomineral materials poses relatively complex problems.   These problems result, more particularly,

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from the difficulty of introducing polymers into the porous system, owing to the high viscosity of polymeric resins. The most simple method for obtaining these composite materials is by means of impregnation with monomers, which, by reason of their limited viscosity, penetrate relatively rapidly into the network of pores. The monomers are subsequently polymerized in situ.

A first aim of the present work was to determine the physicochemical parameters which govern the penetration of monomeric liquids into porous media. This is the subject of part one of the publication (present paper). In a second part, we shall study the kinetics of polymerization inside the pores.

The porous material chosen for this study is an asbestos cement. The manufacturing methods for this stony material make it possible to obtain a very homogeneous porous structure. By varying the lime/silica weight ratio, one can obtain a range of materials of varied porosities and average radii.

THEORETICAL AND PHYSICAL ASPECTS OF THE PHENOMENON OF IMPREGNATION

The spontaneous penetration of liquids into porous media is a result of the phenomenon of capillarity. It is well known that the introduction of a liquid of surface tension γ into a capillary of radius r gives rise to a force normal to the section of the capillary. Its value is expressed as follows:

$$f = 2\pi r\gamma \cos \theta \tag{1}$$

where θ is the contact angle between the capillary wall and the liquid. To this force corresponds a capillary pressure

$$P = \frac{2\gamma \cos \theta}{r}. \tag{2}$$

This pressure is inversely proportional to the radius r of the capillary. In the case of small-diameter pores, the capillary pressure can reach extremely high values. Thus, with vinylic monomers characterized by a very low value of the contact angle θ, the capillary pressure normally attains values in the range of 50 atmospheres for pores of 100 Å diameter.

The thermodynamic potential of the liquid in the porous medium is given by Kelvin's equation:

$$\mu = \mu_0 - P\bar{V} = \mu_0 - \frac{2\bar{V}\gamma \cos \theta}{r} \tag{3}$$

where $\bar{V}$ is the molecular volume of the liquid. This expression can be determined from the work brought to the system by the penetration of the liquid into the pore.[7] It shows, in particular, that the thermodynamic potential of the liquid varies in inverse proportion to the radius of the pore;
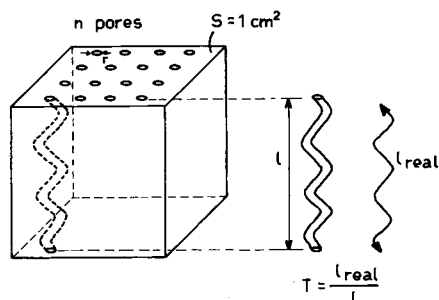
Fig. 1. Idealized representation of the porous system.

at equilibrium, therefore, the liquid goes preferentially in pores of small diameter.

The penetration of liquids into porous media may be considered as a phenomenon of flow, and it can be admitted that the phenomenon is governed by laws analogous to these established for the flow in a cylindrical tube.

The basic law concerning laminar flow is Poiseuille's law, which expresses the flow of a liquid through a tube of radius r and length l in function of the pressure exerted on the tube and the viscosity η of the liquid. In the present case, the motive pressure is capillary pressure, and the rate of flow through a section of the tube is expressed by

$$\frac{dv}{dt} = \frac{\pi r^3 \gamma \cos \theta}{4l\eta}. \tag{4}$$

It is possible to represent the porous structure of the material by means of a simplified model in which the medium is composed of a bundle of n pores per unit of section whose radii are equal to the average radius (Fig. 1). When the liquid has penetrated for a distance l into the porous medium, the length covered in reality in the porous system is Tl, where T represents the tortuosity coefficient or the deviousness factor of the pores. The rate of flow of the liquid through one unit section of the porous material is given by

$$\frac{dV}{dt} = \frac{\epsilon r \gamma \cos \theta}{4T^2 l \eta}. \tag{5}$$

This formula was obtained by taking into account the fact that the number of pores per unit of section, n, is linked with the porosity ϵ and with the pores radius by

$$n = \frac{\epsilon}{T \pi r^2}. \tag{6}$$

We conclude, therefore, that the rate of flow through a unit section of the porous material must be directly proportional to the porosity, to the pores radius, to the surface tension, and to $\cos \theta$; and inversely propor-
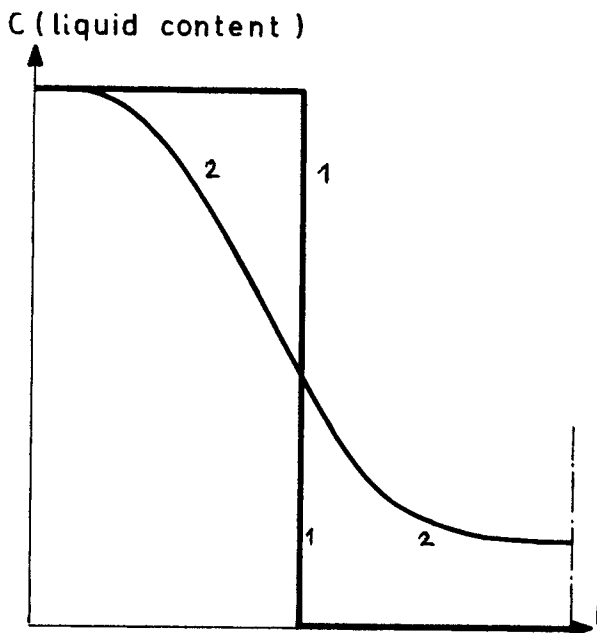
C (liquid content)

Fig. 2. Theoretical contours of liquid content in relation to depth of penetration at time t: curve 1, according to Poiseuille's law of flow;   curve 2, according to Fick's law of diffusion.

tional to the length penetrated into the medium, to the viscosity, and to the square of the tortuosity coefficient.

By integrating eq. (5), we obtain a formula for the kinetics of penetration of liquids into the porous medium:

$$V^2 = \frac{\epsilon r \gamma \cos \theta t}{2T\eta} \tag{7}$$

where V represents the volume of liquid which has penetrated at time t per unit section of a plate of infinite dimension and perpendicularly to this section.

In the simplified model which we have just discussed, the impregnation front of the liquid is very narrow (Fig. 2, curve 1).   In real materials, such as asbestos cement, characterized by a relatively broad pore size distribution, the diffusion border is more diffuse (Fig. 2, curve 2).   The linear rate of penetration into the porous medium which can be deduced from formula (5) is, indeed, proportional to the radius of the pores; and in the case of asbestos cement, we must consider that the rate of penetration into wide pores is from 10 to 100 times more rapid than into pores of size equal to the average radius.   In this case, we may assume that liquids penetrate into the porous medium through the pores of greater dimension, from which they spread progressively toward pores of smaller dimension.

This new model leads us to consider the penetration of liquids into porous media more like as a diffusion phenomenon. This formalism has already been used by some authors[8] in order to study the movements of water in porous media during drying.

The mathematical theory of diffusion is based on the hypothesis that the rate of transfer of the diffusing substance through the unit section is proportional to the gradient of concentration measured perpendicularly to the section.

When a gradient of concentration exists between the contiguous elements of volume of a porous medium, an exchange of matter takes place according to Kelvin's law, through the common interface in such a way as to minimize the chemical potential of the diffusing liquid. It is possible to assume that the rate of flow is proportional to the gradient of concentration between the two elements of volume. In these circumstances, we obtain a mathematical expression identical in form to Fick's first law:

$$F = -D \frac{\delta c}{\delta x} \qquad (8)$$

where F is the flux, that is to say, the rate of transfer of matter per unit of section, c is the concentration of the diffusing substance, x is the spatial coordinate measured perpendicularly to the section, and D is the coefficient of diffusion.

The physical situation associated with the movement of liquids in porous media is very different from a molecular diffusion in an homogeneous system. The exchanges do not take place on a molecular scale but result from transfers through preferred passages constituted by the pores. At this level, we cannot talk of a gradient of concentration since only one possibility exists: a section of the pore either contains or does not contain liquid.

When considering the porous medium as a whole, one can take a sort of statistical approach, and define by c the quantity of liquid present in the various pores of a unit volume element. It should be noted, however, that this quantity is not a concentration in the strict physicochemical sense, because the liquid is not distributed uniformly throughout the whole element of volume since it is restricted to the pores.

In this work, one shall observe that impregnation is satisfactorily described by Fick's law. In fact, there is an analogy with the case of diffusion in homogeneous media because of the existence of a difference of overall "concentration."

The basic equation of diffusion is usually expressed in the form of Fick's second law:

$$\frac{\delta c}{\delta t} = D \frac{\delta^2 c}{\delta x^2}. \qquad (9)$$

The latter is deduced from Fick's first law, when one considers the variation in concentration of a substance which diffuses by two opposing faces of a right-angled parallelepiped.[9]

Expression (9) can be integrated for a unidirectional diffusion through a plate of infinite section. Considering the initial conditions, namely, zero concentration of the diffusing substance in the plate and constant around it, we obtain[10]:

$$\frac{V(t)}{V(\infty)} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2\pi^2} \exp\left(-D(2n+1)^2\pi^2 t/L^2\right) \qquad (10)$$

where the quantities $V(t)$ and $V(\infty)$ represent, respectively, the volumes of matter that have penetrated into the plate at time t and at infinite time, and L is the thickness of the plate.

It is possible to calculate the coefficient of diffusion D from the times of half-impregnation, by limiting the summation to the first two terms. This calculation gives the following result:

$$t_{0.5} = \frac{0.049\, L^2}{D}. \qquad (11)$$

Starting from expression (7) deduced from Poiseuille's law, we can also calculate an expression for the time of half-impregnation:

$$t_{0.5} = \frac{\epsilon L^2 T \eta}{2r\gamma \cos\theta}. \qquad (12)$$

Comparison of the two expressions (11) and (12) is interesting, as it enables us to reckon the physicochemical parameters which ought to influence the coefficient of diffusion D. The latter should be directly proportional to the surface tension γ, to the average radius r, and to $\cos\theta$, and inversely proportional to the viscosity η, to the porosity ϵ, and to the tortuosity coefficient T.

The influence of these parameters will be investigated systematically in the experimental study that follows. It is to be noted that the only factor which is not directly accessible in the experiment is the tortuosity coefficient.

EXPERIMENTAL

The experimental study of the penetration of monomers and liquids of low molecular weight into porous media was carried out on plates of asbestos cement manufactured on a filter press. The sheets were autoclaved for 8 hr under a steam pressure of 10 kg/cm². This manufacturing process produces almost isotropic sheets. By changing the lime–silica proportions, we were able to obtain plates whose average radius varied from 86 to 965 Å and whose porosity, expressed in volume fraction, was between 0.22 and 0.36. These parameters were determined by mercury porosimetry (Carlo Erba AG 25, pressure 2000 kg/cm²).

We studied the kinetics of unidirectional impregnation of a parallel-epiped of asbestos cement. The samples measured $4 \times 0.8 \times 0.65$ cm, except in the first series of experiments. The four faces parallel to the 4-cm edge were made impervious by coating with an epoxy resin (Ciba FZ 260).

The extent of the progress of impregnation was measured by dilatometry. The sample was previously subjected to a 12-hr annealing at 120°C in the dilatometer. After degassing, the impregnating liquid was introduced under vacuum into the bulb of the dilatometer. The impregnating liquids were distilled twice, and 1‰ benzoquinone was added to the monomers in order to avoid any polymerization during measurement. This very small amount of inhibitor does not alter either the surface tension or the contact angle of the liquid.

The surface was determined by the capillary ascension method. As it was impossible to measure the angle of contact between the liquid and the asbestos cement, we assumed that the latter was equal to the contact angle between the liquid and a thin plate of glass. We determined this value by the Mozzo method.[11]

EXPERIMENTAL RESULTS

Method of Expressing the Results

Figure 3 shows the experimental kinetics obtained at 25°C for a uni-directional impregnation of a specimen of asbestos cement of porosity 0.29 and average radius 148 Å.

We observe that agreement with eq. (10), calculated on the basis of Fick's law, is excellent up to a degree of impregnation of 80%. The parabolic law deduced from Poiseuille's equation (7) is verified only up to a degree of approximately 55%.

The divergence observed between experimental points and Fick's law could result from the limited size of the sections of penetration of the im-
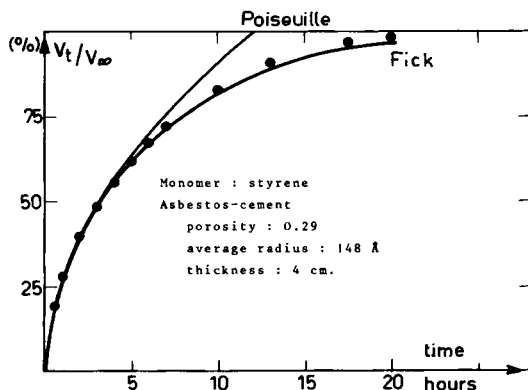

Fig. 3. Comparison of the experimental kinetics with the expressions deduced from Poiseuille's and Fick's laws.

TABLE I
Influence of Thickness of Sample on Coefficient of Diffusion
and on Impregnation Time[a]

Monomers	Thickness, cm	$D \times 10^5$, cm²/sec	Time, min	
			50% impregn.	90% impregn.
Styrene	4	6.81	192	916
	2	6.80	48	229
	1	6.81	12	57
Vinyl propionate	4	5.78	226	1079
	2	5.80	56	269
	1	5.79	14	67

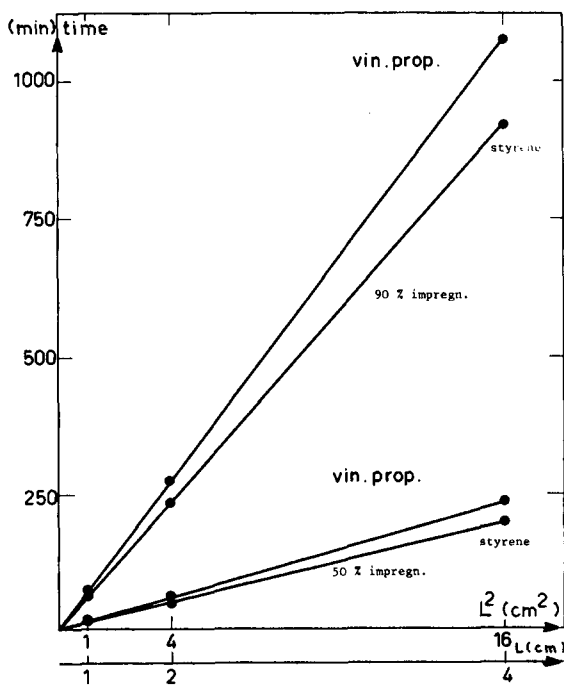[a] $r = 148$ Å, $\epsilon = 0.29$, $T = 25°C$.

Fig. 4. Experimental results giving impregnation time in relation to the thickness of the asbestos cement (porosity, 0.29; average radius, 148 Å).

pregnating liquid into the sample, namely, this divergence could result from the disturbing effect of the impervious walls of the sample.

The experimental kinetics already departs from the parabolic equation at an impregnation degree of 55%. This result, in our opinion, arises from the diffused nature of the impregnation border. From an impregnation degree of 55% upward, it is likely that the impregnation borders coming from each end of the specimen interfere with each other (Fig. 2). This explains the slowing down of the kinetics as compared with the parabolic law.

In a second series of experiments, we studied the influence of the thickness of the sample on the penetration by styrene and vinyl acetate. The diffusion coefficients were calculated from eq. (11). The results of these experiments, reported in Table I and Figure 4, show that the impregnation times are proportional to the second power of the thickness of the specimen and that the coefficients of impregnation are independent of this thickness.

This first series of data shows that Fick's law is more suitable for expressing the results than the parabolic law deduced from Poiseuille's law.

Influence of Physicochemical Characteristics of the Impregnating Liquids

We first of all studied the influence of viscosity on the kinetics of impregnation. The asbestos cement used was identical to that used in the first series of experiments.

The introduction of small quantities of polymer into the corresponding monomer does not alter the surface tension or the angle of contact (Table II, columns 5 and 6) to any appreciable extent. On the other hand, the viscosity is very sensitive to the introduction of small quantities of polymer, and we were able to vary the viscosity in proportions of 1 to 18.

The kinetic results are expressed in Figure 5 for the styrene–polystyrene solution, and in Figure 6 for the vinyl acetate–poly(vinyl acetate) solution. In Table II, the different physicochemical parameters of these systems are shown, as well as the coefficients of diffusion. We observe that the product of the viscosity times the coefficient of diffusion (Table II, column 7) is a constant.

In another series of experiments, we varied the nature of the impregnating liquid with a view to study the influence of surface tension and the contact angle on the kinetics of impregnation. The results of this series of
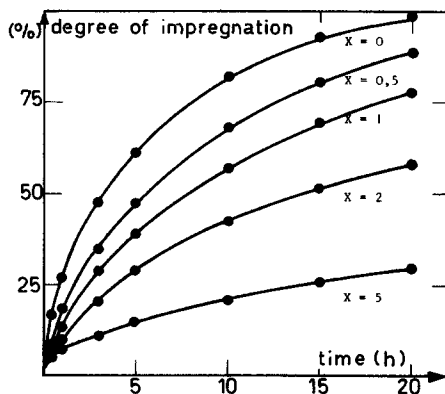

Fig. 5. Kinetics of impregnation of asbestos cement. Porosity, 0.29; average radius, 148 Å; thickness, 4 cm; impregnating mixture, styrene–polystyrene $(100 - X)$.

TABLE II
Impregnation by Solutions of Polymer in its Monomer

| Monomer, g	Polymer, g	$D \times 10^6$, cm²/sec	η, ctps	γ, dyn/cm	cos θ	$D_\eta \times 10^7$, cm/sec²	$D^* \times 10^9$, cm^{-2}
Styrene, 100	polystyrene, 0	6.81	0.69	29.0	0.79	4.71	1.84
Styrene, 100	polystyrene, 0.5	4.27	1.10	28.9	0.80	4.71	1.82
Styrene, 100	polystyrene, 1	2.84	1.64	28.9	0.80	4.65	1.83
Styrene, 100	polystyrene, 2	1.51	3.12	28.8	0.79	4.71	1.85
Styrene, 100	polystyrene, 5	0.38	12.3	28.7	0.79	4.67	1.84
Vinyl acetate, 100	poly(vinyl acetate), 0	3.58	0.39	22.9	0.31	1.41	2.11
Vinyl acetate, 100	poly(vinyl acetate), 2	1.87	0.75	23.0	0.32	1.41	2.03
Vinyl acetate, 100	poly(vinyl acetate), 5	0.87	1.62	22.9	0.31	1.41	2.11

$r = 148$ Å, $\epsilon = 0.29$, $T = 25°$C.
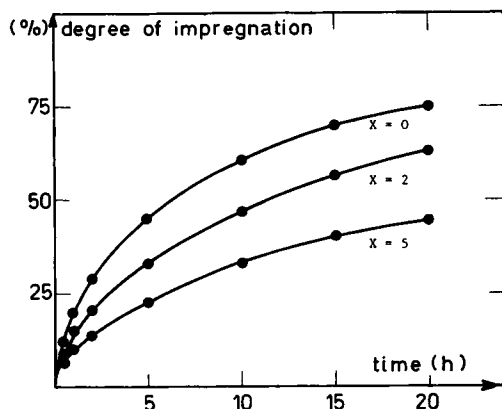
Fig. 6. Kinetics of impregnation of asbestos cement.   Porosity, 0.29; average radius,148 Å; thickness, 4 cm; impregnating mixture, vinyl acetate-vinyl polyacetate (100 − X).
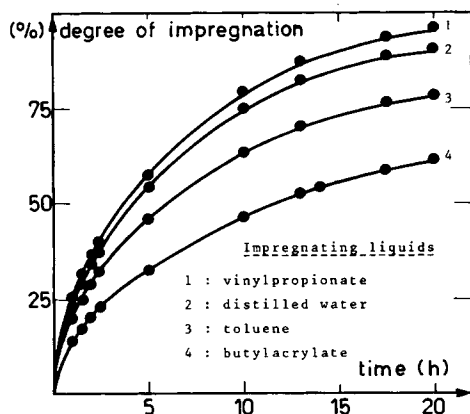

Fig. 7. Kinetics of impregnation of asbestos cement.   Porosity, 0.29; average radius, 148 Å; thickness, 4 cm.
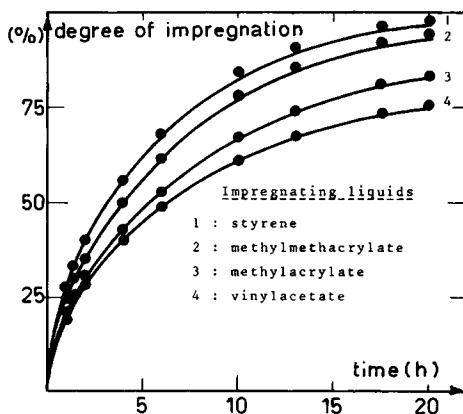

Fig. 8. Kinetics of impregnation of asbestos cement.   Porosity, 0.29; average radius, 148 Å; thickness, 4 cm.

TABLE III
Impregnation by Various Liquids

	$D \times 10^6$, cm^2/sec	η, ctps	γ, dyn/cm	$\cos \theta$	$\dfrac{D\eta/\gamma}{\cos\theta} \times 10^8$, cm	$D^* \times 10^{-9}$, cm^{-2}
Monomer						
Styrene	6.81	0.69	29.0	0.79	2.06	1.84
Vinyl propionate	5.78	0.45	24.0	0.55	1.99	1.77
Methyl methacrylate	5.73	0.51	26.6	0.50	2.19	1.96
Vinyl acetate	3.58	0.39	22.9	0.31	1.99	1.77
Butyl acetate	1.89	0.79	26.1	0.31	1.84	1.64
Methyl acetate	4.08	0.44	23.9	0.37	2.05	1.83
Simple Liquids						
Distilled water	5.50	0.75	72.4	0.26	2.19	1.96
Toluene	3.78	0.54	26.8	0.36	2.13	1.91

$r = 148$ Å, $\epsilon = 0.29$, $T = 25°C$.

experiments, which included monomers and simple liquids, are reported in Figures 7 and 8.

Table III shows the diffusion coefficients calculated from the kinetics and the physicochemical parameters of the different liquids. We notice that, within the limits of experimental accuracy, the product $D\eta/\gamma \cos \theta$ remains constant. We may conclude from this that the coefficient of diffusion varies in direct proportion to the surface tension and to the angle of contact and in inverse proportion to the viscosity. However, we shall note that while the viscosity η can be varied independently of the contact angle θ and surface tension γ, the latter could not be varied independently of the viscosity η. Therefore, the dependence on θ and γ is not unequivocal.

Influence of Porosity and Radius of the Pores

The study of the influence of the pores' radius and of the porosity on the kinetics of impregnation was carried out using asbestos cements whose average radius varied from 86 to 965 Å and whose porosity varied from 0.22 to 0.36. It is unfortunately not possible to vary independently these two parameters. As impregnating liquid, we chose styrene and solutions of polystyrene in styrene for specimens of high average radius, in order to increase the accuracy of results. These tests were carried out at a temperature of 25°C on samples 4 cm thick.

Table IV gives the results. We observe that the product $D\epsilon/r^3$ is practically constant. From these experiments it is shown that the coefficient of diffusion is directly proportional to the third power of the average radius and inversely proportional to the porosity. Let us recall that, on the basis of Poiseuille's law, one might have expected a proportionality of the coefficient of diffusion equal to the first power of the average radius.

TABLE IV
Impregnation of Asbestos Cement of Various Mean Radii ($T = 25°C$)

Sample code	Mean radius, Å	Porosity ϵ	$D \times 10^5$, cm^2/sec	$\dfrac{D\epsilon}{r}$, cm/sec	$\dfrac{D\epsilon}{r^2} \times$ 10^{-6}, sec^{-1}	$\dfrac{D\epsilon}{r^3} \times$ 10^{-11}, cm^{-1} sec^{-1}	$D^* \times$ 10^{-9}, cm^{-2}
Styrene							
1092	86	0.22	2.1	5.4	6.2	7.3	2.2
1005	148	0.29	6.8	13.3	9.0	6.1	1.8
1087	258	0.30	38.5	44.8	17.4	6.7	2.0
1100	488	0.30	256	157	32.2	6.6	2.0
1083	671	0.32	632	301	44.9	6.7	2.0
1084	671	0.36	500	268	40.0	6.0	1.8
1080	965	0.33	1960	670	69.5	7.2	2.2
Styrene–Polystyrene Solution (100–5)							
1005	148	0.29	0.38	0.74	0.5	0.34	1.8
1084	671	0.36	32	17.2	2.6	0.38	2.0
1080	965	0.33	107	36.6	3.8	0.39	2.1

TABLE V
Impregnation by Styrene at Different Temperatures

T, °C	$D \times 10^5$, cm^2/sec	η, ctps	γ, dyn/cm	$\cos \theta$	$D\eta/\gamma \cos \theta \times 10^8$, cm	$D^* \times$ 10^{-9}, cm^{-2}
5	5.33	0.86	28.4	0.79	2.05	1.8
25	6.81	0.69	29.0	0.79	2.06	1.8
35	7.14	0.60	26.6	0.77	2.04	1.8
75	9.68	0.39	23.5	0.76	2.13	1.9

$r = 148$Å, $\epsilon = 0.29$.

Dependence on Temperature

We also studied the influence of temperature on the coefficient of diffusion. These tests were carried out on an asbestos cement of average radius 148 Å and of porosity 0.29. The results of this study are shown in Table V. We see that the modifications of the coefficient of diffusion result essentially from the variation in viscosity of the impregnating liquid. The coefficient of diffusion remains directly proportional to the surface tension and to the contact angle and inversely proportional to the viscosity.

DISCUSSION OF RESULTS AND CONCLUSIONS

In this investigation, we have studied the kinetics of penetration of liquids of low molecular weight and of monomers into asbestos cements. The overall kinetics are quite satisfactorily expressed by Fick's law of diffusion despite the fact that the phenomenon is very different from a molec-

TABLE VI
Coefficients of Tortuosity in Relation to the Radius of the Pores

Code	Radius, Å	Coefficient of tortuosity
1092	86	60
1005	148	24
1087	258	7
1100	488	2.1
1083	671	1.1
1084	671	1.2
1080	965	1.0

ular diffusion. We find an excellent agreement between the experimental points and the theoretical as long as the degree of impregnation does not exceed 80%.

If, in order to represent the phenomenon, we make use of a simplified model, introducing a flow governed by Poiseuille's law through a system of capillaries of diameter equal to the average radius, we obtain a parabolic law which is applicable as long as the degree of impregnation does not exceed 55%.

It must be pointed out that the parabolic law corresponds to a sharp penetration border (Fig. 2). The divergence we observe above 55%, with regard to this law, is very likely induced by the relatively wide distribution of the radii of the pores. Pores of large diameter are filled up more rapidly, and this results in a rounding off of the angles of the liquid content versus depth curve, giving it a shape closer to the curves described by Fick's law. The variation observed above 55% degree of impregnation with regard to the parabolic law could also result from the mutual disturbance of the two advancing impregnation areas, coming from each end of the sample.

The parabolic law deduced from Poiseuille's equation permits us to estimate the coefficient of tortuosity of the pores. Knowing the half-impregnation times $t_{0.5}$, we can calculate the coefficient of tortuosity with the aid of formula (12):

$$T = \frac{2r\gamma \cos \theta t_{0.5}}{\epsilon L^2 \eta}. \qquad (13)$$

Table VI gives this set of results. The calculated values of the coefficients of tortuosity of asbestos cements of a radius greater than 488 Å are reasonable. For pore radii below 300 Å, the calculated coefficients are abnormally high. This shows that Poiseuille's model does no longer hold. We must therefore conclude that the flow of liquids in pores less than 300 Å cannot be considered as "Poiseuillian."

The formalism deduced from Fick's law appears to be better applicable to the expression of the experimental results. The kinetic study can be reduced to the determination of a coefficient of diffusion. We have identified the physicochemical parameters which have an effect on the value

of this coefficient of diffusion, namely, the viscosity η, the surface tension γ, the angle of contact θ, the average radius r and the porosity ϵ. The results as a whole can be summarized by the following empirical equation:

$$D = \frac{D^*\gamma \cos \theta r^3}{\epsilon\eta}. \tag{14}$$

In this expression, D^* appears as a constant equal to 2.00×10^9 cm^{-2}. The standard deviation in its determination for the whole set of results is equal to 0.14×10^9 cm^{-2}. This empirical equation allows us to calculate with an excellent degree of accuracy the kinetics of impregnation.

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