# INVESTIGATIONS INTO THE POROSITY OF CAPILLAR SYSTEMS

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The dependence on time of the diffusion of an electrolyte into tubes of known cross section and length was followed by conductivity measurements. Comparing the results with the corresponding theoretical relation, the length and the cross section of the tubes were calculated and found to be in good accordance with their real dimensions. The method was applied to a capillar system of unknown porosity, thus permitting the tortuosity factor to be determined.

Since the already classic work of MANEGOLD [1], the study of the porosity of capillar systems was the object of numerous investigations [2—5]. This problem is of high practical importance, being closely related with the permeability of foils, dyestuff films and other anticorrosive coatings. The permeability of rocks may be important from the point of view of oil field exploration.

The porosity of a capillar system is due to capillar tubes and holes of different diameteres and directions. The porosity is generally characterized by the quotient of the volume of these cavities and the total volume of the porous system. As the internal cavities and capillaries of the system are of different cross sections, lengths, ramification, etc., therefore a single numerical characteristic will not always be sufficient for describing the porous system, and further data are desirable. The tortuosity factor (see *e.g.* FATT [6]) is a step in this direction.

In an earlier paper [7] we described a method of determining the porosity by measuring the electric conductivity. We applied this method, based on the mentioned results of MANEGOLD and FATT, to measure the porosity of dyestoff films with the aid of a conductivity cell. In this cell the electrolyte of conductivity $x_0$ between two platinum electrodes in the distance $l$ was divided into two parts by a dyestoff film of thickness $l_x$. To obtain the total resistance, the resistance of the electrolyte enclosed in the capillaries of the dyestoff film has to be added to the resistance of the electrolyte divided by the film. Therefore, if the conductivity measured in the cell containing the film is $x_f$, the porosity due to the capillaries traversing the film can be expressed by

$$\varepsilon = \frac{x_f}{x_0 - x_f} \frac{l_x}{l}. \tag{1}$$

If all capillaries were perpendicular to the surface of the film, the porosity given by Eq. (1) would be equal to the exact value of the quotient of the total cross section of the capillaries traversing the film and the total surface area of the film. Thus the capillaries in an electric insulator could be characterized by a single figure.

However, this characteristic does not give information about the course which the capillary, starting from one surface of the film, takes to arrive to the opposite surface. It seemed therefore desirable to elaborate a method capable to yield more, though not full, information on the porous system. We tried to find a method giving also the true, or at least the mean length of the capillaries traversing the film. Starting from FATT's quoted investigations, we modified the method based on the measurement of electric conductivity to permit the so-called tortuorsity factor to be determined, too. The method essentially consists in measuring the time dependence of the diffusion of the electrolyte into the porous system.

The diffusion of an electrolyte into a tube of given cross section and length through both ends of the tube can be exactly followed theoretically. Thus it is possible to express the time dependence of the conductivity of the electrolyte present in the tube by a closed formula [8]. On the other hand, the changes in time of this conductivity can be measured by the cell mentioned above.

### Description of the apparatus

In our measurements we used a cylindrical cell, containing electrolyte of known concentration divided by the sample to be examined, and closed on both ends by platinum electrodes. This cell was connected with a conductometer type RADEL-KISZ OK—102.

### Investigations on plexiglass samples

To check the theoretical formula, we used plexiglass discs, provided with perforations of known dimensions, to separate the electrolyte in the cell. The discs, closely fitting into the cell, were made of a plexiglass plate of 9.73 mm ($\pm 0.4\%$) mean thickness. In each disc a cylidrical hole of 1, 2 or 4 mm diameter was drilled perpendicularly to the surface (samples No. 1, 2 and 3, respectively), while sample No. 4 contained 13 holes of 1 mm diameter. The holes were filled with 1% agar gel. The samples prepared in this way were placed between the two parts of the cell, previously filled up with 1% agar gel containing $0.1N$ KCl. The measurements were made at $24 \pm 2\,°C$. Fig. 1 shows the time dependenc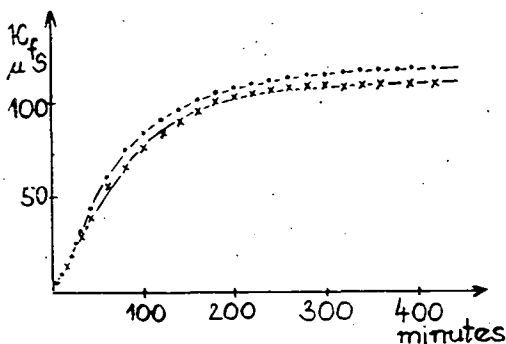e of the conductivity of the cell separated by sample No. 1. The upper curve gives the results of the measurements made at 24 °C, the lower curve those at 22 °C. The time dependence of the measurements with samples No. 2 and 3 was very similar. Figure 2 shows the results obtained with sample No. 4, containing 13 holes, at 24 and 23 °C, respectively.

On the base of theoretical considerations [8], the relative conductivity was calculated. Denoting by $\varkappa_\infty$ the conductivity evolved in the cell after a long time and show-



*Fig. 1.* Time dependence of conductivity
for sample No. 1

ing no further changes, the relative conductivity is defined as the quotient $\sigma_r = \varkappa_f / \varkappa_\infty$. The mean values of the relative conductivities obtained with different samples are plotted in Fig. 3 as a function of time. In order to compare this curve of relative conductivity with the theoretical curve, the former has to be reduced. Let us read from the theoretical curve some values of $\sigma_r$ and the respective values of the independent variable $\tau$. As $\tau$ depends on the diffusion constant $D$ of the electrolyte, the length $l$ of the tube and the time $t$ according to

$$\tau = D\left(\frac{\pi}{l}\right)^2 t, \qquad (2)$$

the corresponding time $t$ can be read from the measured curve of relative conductivity pertaining to the same value of $\sigma_r$. Some corresponding data are listed in Table I. From these, the values of $l$ can be calculated using Eq. (2) (column 4 in Table I). The mean of the values of $l$ obtained in this way was 9.53 mm. This differs from the true length of the tube by 0.2 mm ($\sim$2%). Using the mean value of $l$, the relative conductivity $\sigma_r$ can be plotted as a function of $\tau$. This plot, together with the theoretical curve, is shown in Fig. 4.
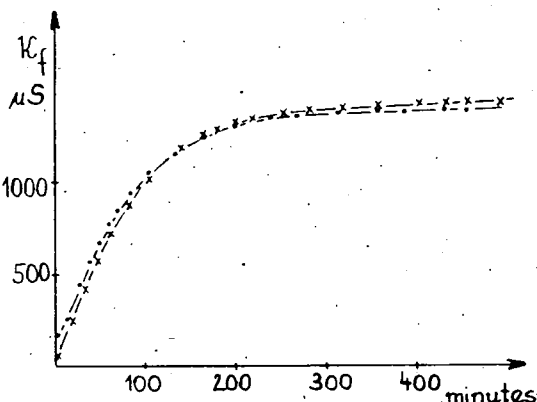


Fig. 2. Time dependence of conductivity for sample No. 4



Fig. 3. Mean values of relative conductivity obtained with different samples as a function of time

It can be seen that the kinetic determination of the conductivity results in a good approximation of the length of the tube.

Table I

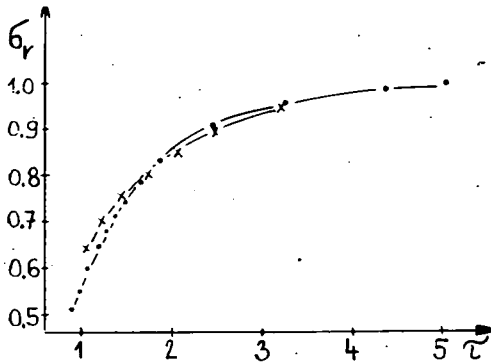| $\sigma_r$ | $\tau$ | $t$ minutes | $l$ mm |
|---|---|---|---|
| 0.70 | 1.31 | 100 | 9.23 |
| 0.75 | 1.48 | 117 | 9.39 |
| 0.80 | 1.69 | 139 | 9.58 |
| 0.85 | 1.97 | 165 | 9.67 |
| 0.90 | 2.34 | 199 | 9.74 |
| 0.95 | 3.06 | 252 | 9.59 |

Fig. 4. Measured and theoretical curve of relative conductivity as a function of $\tau$: × measured curve; ● theoretical curve
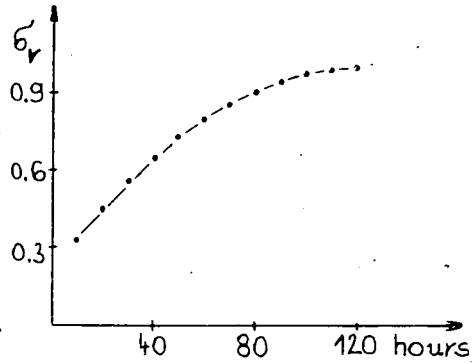


Fig. 5. Time dependence of relative conductivity of Sarmatian limestone

The $\varkappa_\infty$ read from the measurement can be considered as identical with the $\varkappa_f$ in Eq (1). By measuring also $\varkappa_0$ the porosity $\varepsilon_k$ can be calculated using Eq. (1) (see Table II). This $\varkappa_0$ is the conductivity of the cell containing no sample if the distance of the electrodes of the cell filled with 1% agar gel containing 0.1N KCl is the same as in measuring $\varkappa_f$. The porosity can be determined also by filling the hole of the sample with the same electrolyte as used in the cell. In this case the value of $\varkappa_f$ can be read and the porosity $\varepsilon_s$ can be calculated immediately after filling the cell. In Table II, column 1 gives the diameter of the holes in the sample, and column 2 the porosity $\varepsilon_g$ calculated from the diameter of the holes.

*Table II*

| Diameter of holes mm | $\varepsilon_g$ | $\varepsilon_s$ | $\varepsilon_k$ |
|---|---|---|---|
| 1 | 0.0020 | 0.0021 | 0.0022 |
| 2 | 0.0082 | 0.0078 | 0.0075 |
| 4 | 0.0330 | 0.0278 | 0.0273 |
| 13×1 | 0.0269 | 0.0281 | 0.0275 |

*Table III*

| $\sigma_r$ | $\tau$ | $t$ hours | $l$ mm |
|---|---|---|---|
| 0.55 | 0.98 | 29 | 44.5 |
| 0.60 | 1.03 | 35 | 44.8 |
| 0.65 | 1.16 | 41 | 48.9 |
| 0.70 | 1.31 | 47 | 49.0 |
| 0.75 | 1.48 | 54 | 48.8 |
| 0.80 | 1.69 | 60 | 48.6 |
| 0.85 | 1.97 | 66 | 47.4 |
| 0.90 | 2.34 | 77 | 47.0 |
| 0.95 | 3.06 | 94 | 45.3 |

*Measurements on a sample of Sarmatian limestone*

A sample of 8.6 mm mean thickness, prepared of Érd limestone, was studied. The disc was boiled in distilled water to fill the pores. The cell was filled with 0.1 $N$ KCl solution. The time dependence of the relative conductivity is shown in Fig. 5.

The mean length of the capillaries in the limestone was determined as in the case of the plexiglass samples (Table III). The length $l$ obtained was 46.9 mm.

Dividing this by the thickness of the sample, the value 5.5 was obtained for the tortuosity factor. We also determined the porosity $\varepsilon$ applying Eq. (1), obtaining the value 0.0085.

### References

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## ИЗУЧЕНИЕ ПОРИСТОСТИ КАПИЛЛЯРНЫХ СИСТЕМ

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Изучена диффузия электролита в капилляр известной длины и сечения определением электропроводности в зависимости от времени. Сопоставлением полученных данных и теоретических соотношений были рассчитаны длина и сечение капилляра, которые получились соответствующими действительным размерам. Метод был распространён на капиллярную систему с неизвестными параметрами и таким образом нам удалось рассчитать для нее параметр пористости.