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DIFFUSION METHODS IN THE DEFECTOSCOPIC STUDY OF SELECTIVE MEMBRANES

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Introduction

Operational properties of selective polymer membranes are determined by the structure of the material and the quality of its surface layers. Deviations from the required chemical composition, density fluctuations and the presence of microdefects lead to a decrease in the operation efficiency of the polymer membranes. As changes of transport properties of the membranes, taking place in the course of their operation, can lead to a discontinuity in the membranes functioning, accidents with serious consequences can happen, especially in the medical application of membrane separators.

For this reason, methods for checking quality of the membranes during their operation and investigating changes in their transport properties have been developed. Methods discovering the early stages of the membrane errosion are of special importance. By using information obtained by these methods, the membrane separators can be repaired in time and accidents can be prevented.

In this communication the principles of the diffusion methods for checking the operation and transport properties of selective membranes are given, and the possibilities of these methods are demonstrated.

Principle of Methods

The pulse method for the gas permeability measureraent (1) is based on the measurement of a gas concentration pulse passed through the membrane. The gas mixture to be separated or a special gaseous probe are inserted at the input of the membrane in time t_0 The expression for the gas concentration pulse of a rectangular shape passing through the membrane is given by the authors in another contribution to these Proceedings (2) .

For cases when for the normalized flux we have $J_m/J_\infty<0.3$ ($J_0= C_0D/l$), the diffusion coefficient can be determined as

$$D = J_m l^2/5.922\ J_\infty \Delta t$$

If an infinitely thin gas pulse $\Delta t\rightarrow 0$ is inserted at the input of the membrane, the output gas flux can be expressed by Eq.(1)

$$J(t) = 2C_0 D\Delta t l^{-1} \sum_{n=1}^{\infty} (-1)^n n^2\pi^2 D l^{-1} \exp\left\{-(n\pi/l)^2 Dt\right\} \qquad (1)$$

which can be written in the form normalized with respect to the peak area as

$$f(t) = 2\sum_{n=1}^{\infty} (-1)^{n+1} n^2 B \exp\left\{-n^2 Bt\right\} \qquad (2)$$

where $B = \pi^2 D/l^2$.

The time T which is necessary for attaining the maximum flux on the membrane output ($T = t_m$-t_o) is related to the parameter $U = D/l^2$. The diffusion coefficient D can be determined from Eq.(3)

$$D = l^2/10.9\ T \tag{3}$$

In this way, any change of the diffusion coefficient, caused e.g. by changes of the membrane structure, the deposition of substances at the membrane input, variations of the membrane thickness, etc., lead to variations of T (with respect to the standard value T_{st} determined previously). The appearence of the deviation ΔT can be considered as a signal of the defect of the membrane separator. The sign plus or minus of the deviation $\Delta T = T\text{-}T_{st}$ gives the first information about the cause of the defect. If ΔT exceeds the limit ΔT_{lim} repair of the membrane separator should be undertaken. The main advantage of this method consists in its simplicity.

Another independent method of investigation of the operation ability of the membrane separator is based on the measurement of the gas pulse height (1).

The diffusion coefficient can be expressed by Eq. (4)

$$D = 0.2442\ J_m\ l/C_0 \tag{4}$$

where $C_0 = \Gamma p$; Γ is the solubility constant of the gas in the material of the membrane, p is the partial pressure of the gas at the membrane input.

The parameter J_m (height of the gas pulse) can be advantageously used for the characterization of the "rapid" membranes (small thickness, higher operation temperatures), where the parameter T can hardly be evaluated with a sufficient accuracy because of the apparatus inertia.

The simultaneous evaluation of J_m and T is of special interest, as both the kinetic parameter (D) and the thermodynamic parameter (Γ) of the membrane system may be determined simultaneously.

Moreover, the accompanying processes, such as the gas trapping in the polymer matrix, can be quantitatively estimated by means of this method: the rate constant of the reaction can be obtained by analyzing the shape of the output gas pulse.

Application of Methods

Several examples of the application of the pulse gas method for gas permeability measurement are given below.

Let us suppose that isolated point defects arise, randomly distributed in the bulk of the polymer membrane. In the course of their random motion, molecules of the diffusing agent are trapped by the defects and excluded for a definite time interval from the diffusion process. This process, called "gas diffusion with reversible trapping", can be described by the following differential Eqs. (5)

$$\partial C_1 / \partial t = D\partial^2 C_1 / \partial x - k_1 N_2 C_1 + k_2^* C_2 \tag{5a}$$

$$\partial C_2 / \partial t = k_1 N_2 C_1 - k_2^* C_2 \tag{5b}$$

where C_1 and C_2 are the concentrations of the diffusing agent in the diffusion channels and the traps, resp.; k, and k_2 are the rate constants of the gas trapping and release, resp. (k_2*=k_2N_2); N_1 and N_2 are the concentrations of the diffusion channels and traps, resp. (N_1+N_2 = N) , the equilibrium constant of the trapping reactions $K = k_1/k_2$ (the 1st order chemical reaction kinetics is used for the description of the trapping of gas molecules by the matrix and subsequent release of the gas) .

As can be seen from Fig. l, isolated point defects in the membrane cause a significant distortion of the gas pulse shape.

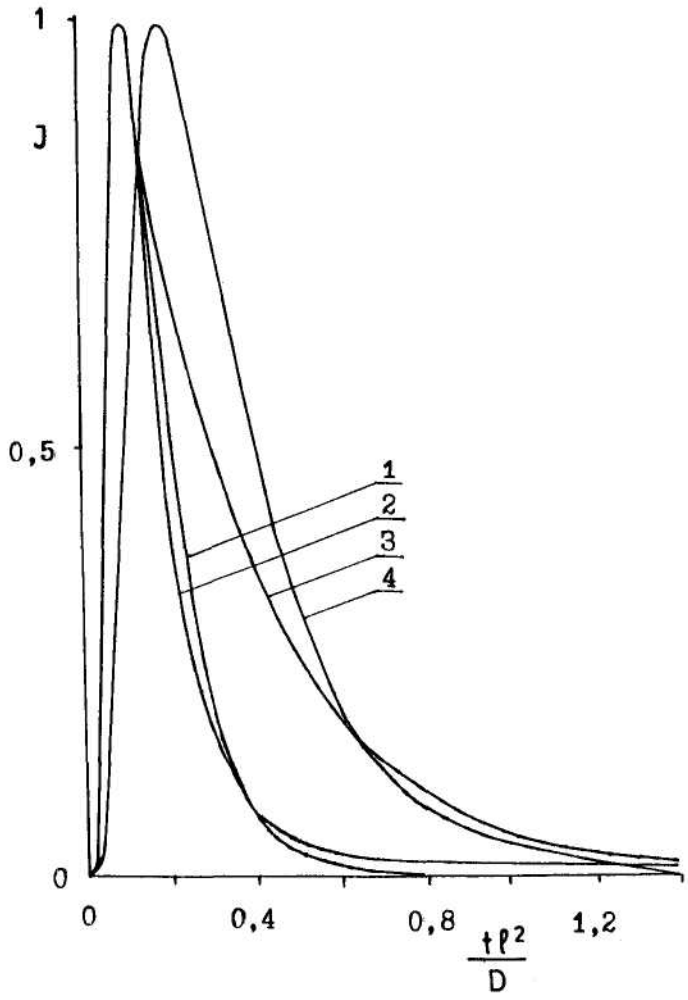

Fig. 1. Distortion of an infinitely short gas pulse after the passage through the membrane containing dispersed point defects. (The values $D/l^2 = 1$, $K = 1$ were used for the computer simulation of the curves.) Curve 1 - corresponds to the mechanism of classical diffusion without gas trapping. Curves 2 - 4 represent various gas trapping expressed by the rate constant values $k_1^* = k_1 N_2 = 1; 10; 100$ and $k_2^* = k_2 N_1 = 1; 10; 100$, resp.

It follows from Fig.1 that for low concentration, N_2, of the point defects the position of the peak maximum does not change, but "tags" appear on the curves. The parameters k_1 and k_2, which can be determined by analyzing the curve shape, characterize the non-homogeneity of material of the polymer membrane. The position of the peak maximum is shifted towards a higher time in cases of increased defect concentration. The effective diffusion coefficient, evaluated from Eq. (6), decreases as a result of the defect formation in the membrane.

The effective diffusion coefficient can be evaluated as

$$D_{\text{eff}} = D/(1 + K N_2/N) \qquad (6)$$

The defect of the polymer membrane structure can lead to the formation of channels where molecules of the diffusing agent can penetrate. In this case the transport of the gas in the defective membrane can be described by the multichannel diffusion mechanism. In Fig. 2 we demonstrate changes of the shape of the gas pulse after a passage through the polymer membrane where a diffusion mechanism via two channels is supposed. As follows from Fig.2, the position of the peak maximum is shifted towards a lower time and the height of the peaks increases when the concentration of the structure damage is more intense. (The relation $D_1 = 2D_2$ between the two diffusion coefficients in the individual channels was supposed.)

The changes of the defect state of the polymer membrane in the dynamic conditions (e.g. during the aging of polymeric materials or by an increase in thickness of the membrane) can be investigated by means of the pulse method using a special gas probe. Radioactive nuclides of inert gases, such as Rn-222, Kr-85 or Xe-133, are advantageously used as gas probes for the defect state of a polymeric membrane. The high sensitivity of detection of radioactive nuclides makes it possible to use very low concentrations of the gases, so that no influence on the diffusion of the gas mixture to be separated can be supposed.

In Fig.3, the results of the application of an inert gas probe in the investigation of the changes in the polymeric material are demonstrated. Curve 2 represents the original pulse of the inert gas (Rn-222), curves 2 and 3 represent the distorted pulses of the gas after the passage through either a stable or an unstable polymer membrane.

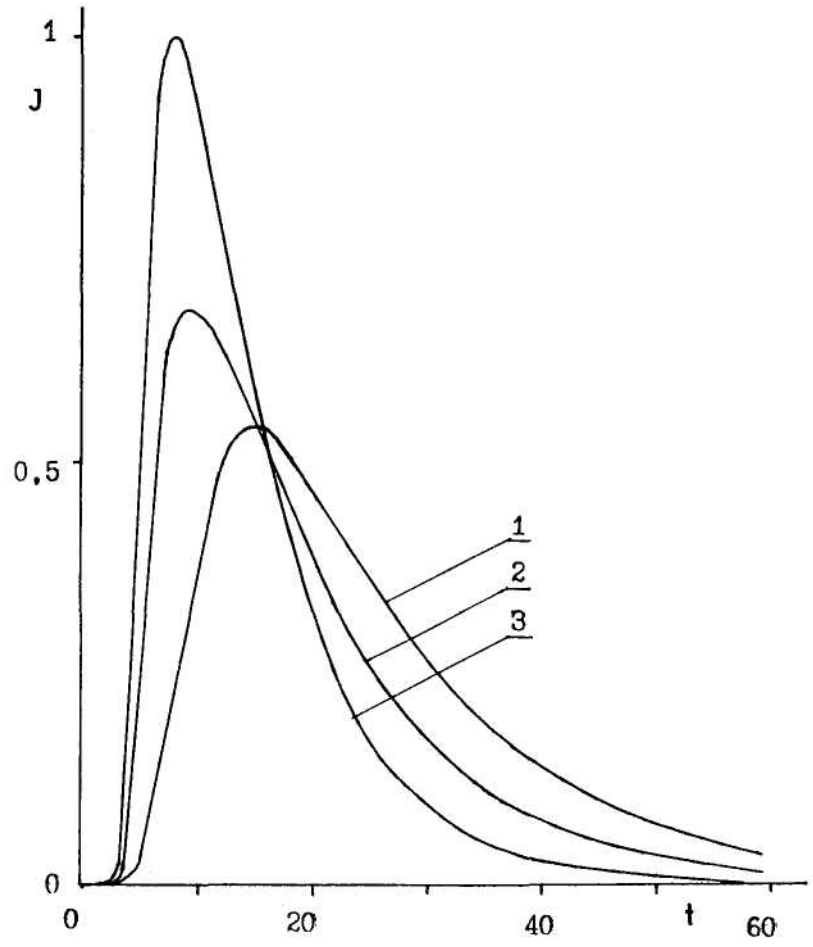

Fig.2. Distortion of an infinitely short gas pulse after the passage through the membrane containing two diffusion paths. The mechanism of a parallel diffusion is supposed (where $D_1 = 2D_2$) , the concentration of the defects, expressed as the volume ratio in the computer simulation of the curves 1 - 3, was 0.2; 0.4; 0.6, resp.

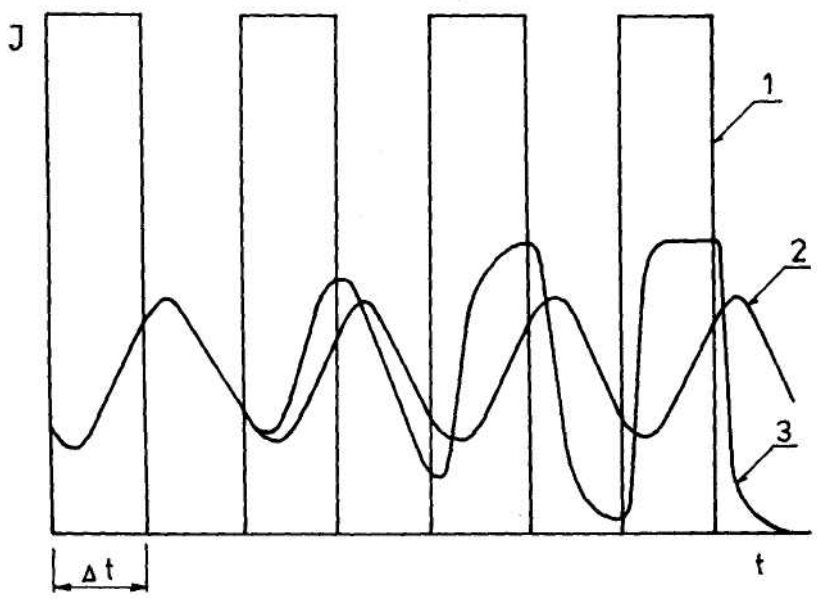

Fig.3. Experimental results of the inert gas probe method using a set of rectangular pulses of Rn-222. Curve 1 - values of the inert gas concentration at the membrane input. Curves 2 and 3 -changes of the inert gas flux at the membrane output in case of a well-stable and unstable membrane, resp.

Conclusion

By means of this method the quality and operation properties of the membrane can be investigated continuously in the course of the operation of the membrane separator. The height and width of the gas pulse, as well as the inert gas used as the probe can be varied during the defectoscopic investigation of the membrane. Even a mixture of inert gases can be used as the probe of the defect state of the material. The evaluation of the results shown in Fig.3 is described elsewhere (1, 2).

References

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