

# Evaluation of Results of Simplified Determination Methods of Polymer Membrane Permeability to Vapors

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## Synopsis

The permeability coefficients for some selected systems comprising a polymer membrane and organic vapors were measured by means of simplified methods. The aim was to evaluate the suitability of these methods for permeability determination of polymer membranes under average conditions of use. The results obtained by various methods were compared and analyzed taking into account permeation models associated with different apparatus and operation principles as well as different measuring conditions. For similar mass transfer models, permeability coefficient values of the same order and close accuracy of the measurement were obtained.

## INTRODUCTION

Determination methods of polymer membrane permeability to vapors, such as the sorption or the divided diffusion cell method, have, besides many advantages, also some serious disadvantages.<sup>1</sup> For example, the currently applied methods are not suitable for quality inspection of manufactured polymer membranes, mainly due to the complicated measuring apparatus operating under high vacuum and also the time-consuming and expensive procedure. Also the measuring conditions, mainly the long-lasting reduced pressure, imply that the results obtained by means of such methods, no doubt interesting from the purely scientific point of view (e.g., for studying the transfer mechanism or polymer structure), are not very useful for practical purposes. In practice, the polymer membranes "operate" within a given environment comprising, besides the penetrant tested, other substances such as water vapor and air components which may influence the polymer membrane properties and consequently change the parameters characterizing the transfer process.

It is therefore necessary to develop simplified methods of determination of the permeability of polymer membranes to organic vapors that should be both simple and inexpensive and result in data suitable for practical purposes. This would be achieved if the measurements are performed under conditions close to those under which the given polymer membrane is expected to be used. Such methods are the weighed cell method, the electrochemical method, and the capillary evaporation method. Each of these methods has been applied in our investigations, and the results were published in earlier works.<sup>2-5</sup>

In the weighed cell method,<sup>2</sup> analogous to the obligatory standards for the determination of polymer membrane permeability to water vapor,<sup>6</sup> a weighing bottle of a special design filled with a sorbent and tightly closed at the top with

a disc of the tested polymer membrane is placed within a chamber filled with vapors of a given substance, e.g., in a desiccator. From the increase in the mass of the bottle, weighed at predetermined time intervals, the permeability coefficient  $P$  and the vapor transmission rate (permeability)  $P^*$  may be calculated. Alternatively, the weighing bottle is being filled with liquid and placed within a conditioning chamber, e.g., an air washer. The decrease in the bottle mass due to evaporation of the liquid and the vapor penetration through the polymer membrane forms the base for the calculation of  $P$  and  $P^*$ .

In the electrochemical method the vapor from the gaseous phase penetrates into the electrolyte layer between the polymer membrane and the measuring electrode. The electrode signal, recorded as a potential change<sup>4</sup> or reduction (oxidation) current,<sup>3</sup> is proportional to the penetration rate of the penetrant mass into the electrolyte.

In the capillary evaporation method,<sup>5</sup> to a limited space closed at one side tightly with a disc of the tested polymer membrane are soldered, a calibrated glass capillary filled with liquid and a mercury manometer. Owing to the evaporation of the liquid within the closed space, the pressure of the vapors increases and simultaneously penetration takes place of the vapor through the polymer membrane into the surroundings. At the moment when the liquid evaporation rate and the vapor penetration rate equalize, a stationary state is being achieved, accompanied by a regular decrease in the liquid column in the capillary and a constant positive gauge pressure  $\Delta p$  within the cell. These values are sufficient for the calculation of  $P$  and  $P^*$ .

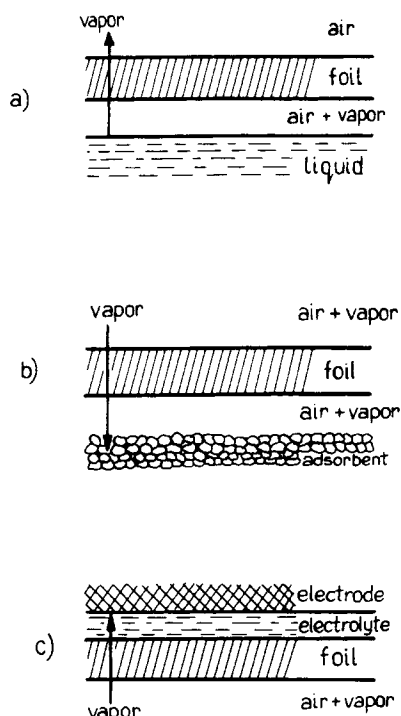


Fig. 1. Vapor permeation schemes through polymer membranes in simplified methods: (a) weighed cell with liquid evaporation method and capillary evaporation method; (b) weighed cell method with vapor adsorption by means of an adsorbent; (c) electrochemical method.

Figure 1 illustrates cross sections of systems in which a mass transfer takes place, with the denotation of phases and interfacial boundaries for the applied measuring methods. The figure shows that, besides the diffusion resistances within the polymer membrane, additional diffusion resistances due to the presence of air at both sides of the tested polymer membrane or of air and electrolyte in case of the electrochemical method occur in all the simplified methods.

## RESULTS AND DISCUSSION

To compare and evaluate the results of the  $P$  and  $P^*$  determinations by means of the different simplified methods, measurements were performed for some selected systems comprising polymer membranes and organic vapors. The results obtained are presented in Table I. Owing to the high permeability of the polyethylene (PE) membrane, the permeability coefficients for  $\text{CCl}_4$  and  $\text{CHCl}_3$  could not be determined by the capillary evaporation method as the manometer indicated practically no positive gauge pressure. Therefore, in Table I only the permeability values of these substances are presented. For their calculation the pressure may be neglected. On the other hand, the permeabilities of the Estrofol T 19 and Teflon membranes were not determined by the electrochemical method. For these membranes, because of their very low permeability, the sensor signals were at the internal noise level.

The results presented in Table I show good agreement of the  $P$  and  $P^*$  values in the PE/ $\text{CCl}_4$  and PE/ $\text{CHCl}_3$  systems obtained by the electrochemical and the weighed cell (adsorption) methods, whereas the parameters for the same systems obtained by means of the other methods differ significantly, namely, by one order of magnitude in the weighed cell (adsorption) method and by two orders of magnitude in case of the capillary evaporation method. Attention should be paid to the very good agreement of the results, particularly  $P^*$ , obtained by the weighed cell (adsorption) and the capillary evaporation methods in case of the following systems: Estrofol T-19/ $\text{CH}_3\text{OH}$ , Estrofol T-19/ $\text{CCl}_4$ , and Teflon/ $\text{CCl}_4$ . Simultaneously, substantially larger differences in the  $P$  value were observed. It seems that these differences are due to many factors which may be identified

TABLE I  
Permeability Coefficient  $P$  and Vapor Transmission Rate  $P^*$  Determined by Simplified Methods at 293 K

Membrane type and penetrant	Membrane thickness $\mu\text{m}$	Weighed cell method				Capillary evaporation method		Electrochemical method	
		Evaporation		Adsorption		$P \times 10^9$	$P^*$	$P \times 10^9$	$P^*$
		$P \times 10^9$	$P^*$	$P \times 10^9$	$P^*$				
Polyethylene, $-\text{CCl}_4$	35	15	2080	1.6	219	—	15	14	1900
Polyethylene, $-\text{CHCl}_3$	35	22	4070	7.1	1300	—	11	25	4600
Estrofol T-19, $-\text{CH}_3\text{OH}$	20	0.20	10.2	0.018	0.95	0.043	1.0	—	—
Estrofol T-19, $-\text{CCl}_4$	20	0.012	2.77	0.0074	1.73	0.013	2.0	—	—
Teflon, $-\text{CCl}_4$	20	0.012	2.72	0.0061	1.44	0.0048	1.5	—	—

$P$  in  $(\text{cm}^3/\text{S.T.P.}/\text{cm})/\text{cm}^2\text{-sec-Torr}$ ,  $P^*$  in  $\text{g}/(\text{m}^2\cdot 24 \text{ hr})$

through analysis of the penetrant's concentration distribution (partial pressure) at different points of the measuring apparatus. Diagrams of the penetrant gradients along the permeation path for each method are presented in Figure 2. The broken line represents the "ideal" distribution of concentrations which would be the result only of the diffusion resistance of the polymer membrane. The concentration difference  $\Delta c$  corresponding to that distribution is being used in the calculation of the permeability coefficient  $P$ . In all the methods it is assumed that at one side of the membrane the partial pressure of the penetrant is approximately equal to zero. It is assumed that on the other side of the membrane the vapor pressure is approximately equal to (1) the saturated vapor pressure at measuring temperature in the weighed cell method, (2) the partial pressure of the vapor in the mixture (inert gas + vapor) introduced into the measuring system in the electrochemical method, and (3) the positive gauge pressure measured in the measuring chamber in the capillary evaporation method.

From the above assumptions and from Figure 2 it becomes evident that the concentration gradient assumed in the calculations is in practice a resultant of

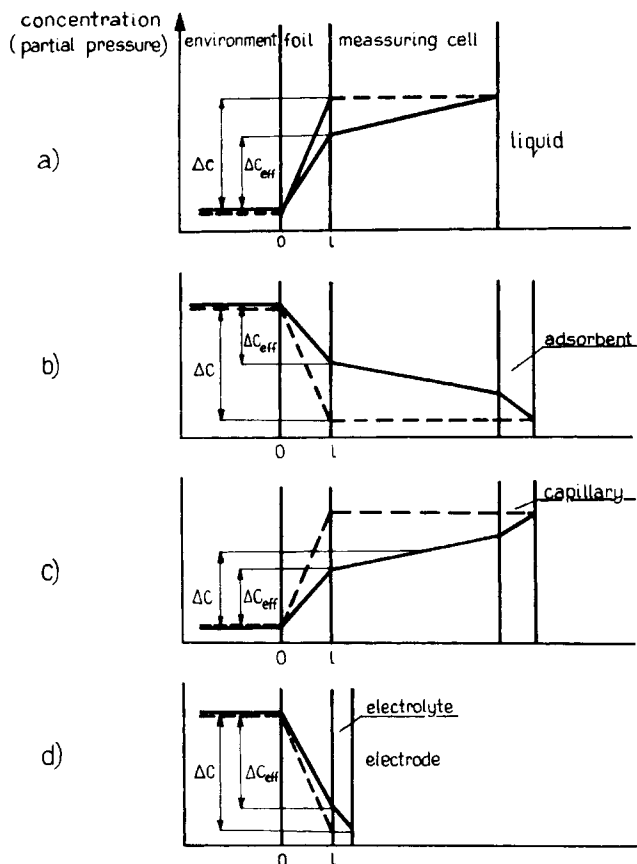


Fig. 2. Concentration distribution of penetrating vapor in the following methods: (a) weighed cell through evaporation method; (b) weighed cell through adsorption method; (c) capillary evaporation method; (d) electrochemical method.

the concentration gradients due to the occurrence within the measuring systems of diffusion resistances of the stationary air layer, the diffusion resistances inside the sorbent capillaries or inside the electrolyte layer, or the vapor diffusion resistances within the capillary above the liquid meniscus. The diffusion resistance of the polymer membrane and the corresponding true concentration decrease the  $\Delta c_{\text{eff}}$ ; thus, only a part of the  $\Delta c$  is assumed in the calculations. The above-mentioned diffusion resistances depend to a large extent on the geometric parameters of the measuring apparatus, as for example the distance of the liquid meniscus from the membrane in the weighed cell through evaporation method; the ratio of the measuring chamber diameter to the capillary diameter in the capillary evaporation method; the electrolyte layer thickness in the electrochemical method; or the thickness of the adsorbent layer, its capillary structure, and the characteristics of the adsorption isotherm in the weighed cell through adsorption method.

It may be concluded that the results of the  $P$  determinations for organic vapors through polymer membranes obtained by means of the different simplified methods are as a general rule different from the true permeability coefficients. Moreover, there are differences between the results. Nevertheless, these methods may be very useful for practical purposes. The conditions under which the determinations by these methods are performed are very close to the average conditions under which the membranes are used. The simplicity of this apparatus and the low cost of the determination procedure are also important.

The necessity to standardize the applied apparatus and to determine the measuring ranges for the individual methods applied must however be stressed. This would allow comparison of the results obtained in different laboratories and also to determine unequivocally the permeability of the polymer membranes which in turn would facilitate the proper selection of membranes by their users.

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