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Separation of Liquid Organic Mixtures by Diffusional Permeation Through Non-porous Polymer Membranes

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The physicochemical aspects of a new method of separation of organic liquids by diffusional permeation through non-porous polymer membranes are discussed. The process is assumed to consist of 5 successive steps: transport of material from the liquid to the membrane surface, sorption by the surface layer of the membrane, diffusion through the membrane, desorption from the opposite side of the membrane, and evaporation of the desorbed molecules into the gas (or vapour) phase. The influence of the polymer structure (polyethylene, polypropylene) on the separation process is discussed, and possible modifications of the membrane by solvent treatment, unidirectional mechanical stress, cross-linking by radiation-chemical and photochemical methods, and grafting of other polymers are considered. The effects of the composition of the initial mixture, of the nature of the compounds to be separated, and of temperature are also discussed.

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I. INTRODUCTION

Separation processes are extremely important in the chemical industry. New and increasingly complex problems concerning the separation of mixtures are often encountered, which traditional methods (fractional distillation, adsorption, absorption, fractional freezing, extraction) are powerless to solve. New methods of separation have therefore been proposed and developed, such as counter-current crystallisation, preparative chromatography, separation by ion-exchange resins and molecular sieves, and gel chromatography.

Separation by permeation through membranes is one of these newer methods. All variants of this technique rely on the selective transfer of materials through a semipermeable partition. The driving force of the process can be a temperature gradient, a concentration gradient, or a pressure gradient. Some processes use polymer membranes (reverse osmosis, ultrafiltration, diffusional permeation), others use porous glass or metal membranes, or metal foils. The nature of the processes within the membrane can vary quite considerably. For example, the separation of hydrogen by palladium alloy membranes relies on the unique properties of the palladium crystal lattice; ultrafiltration processes rely on the properties and on the molecular size of substances dissolved in water; separation by means of porous glasses depends almost entirely on the size of the solute molecules.

It is clear, from recent review articles dealing with various separation methods based on membranes[1-11], that diffusional permeation through non-porous polymer membranes is the method most widely used for separating mixtures of liquid organic compounds. The separation of organic liquids by ultrafiltration under high pressure (up to 100 kg cm^{-2}) through porous polymer membranes is unacceptably slow, and is complicated by irreversible changes in the membrane during operation[12,13].

We shall therefore confine our discussion to the separation of organic mixtures by diffusional permeation through non-porous polymer membranes. In the Western literature this method of separation is usually termed "permeation" or (less frequently) "pervaporation". The principle of the method, the essential differences from other methods of separation, and possible applications on an industrial scale were first discussed between the late 1950's and the early 1960's[14-18].

This review aims to explain (on the basis of published data) the main features of this method of separation and to assess the influence of various factors on the rate of permeation of materials through a membrane and on the selectivity of the separation process.

II. FIVE-STAGE MECHANISM FOR THE PERMEATION OF SUBSTANCES THROUGH THE MEMBRANE

The separation of substances by permeation through polymer membranes is carried out as follows: the liquid mixture, heated to the required temperature, is placed in contact with a thin polymer membrane (usually 50 to 100 μm thick). The material which passes through the membrane is removed by pumping or in a stream of inert gas. The permeation of a liquid through a membrane consists of the following 5 steps: 1) transfer of material from the centre of the liquid flow to the surface of the membrane, 2) sorption by the surface layer of the membrane, 3) diffusion through the membrane, 4) desorption from the opposite surface of the membrane, 5) transfer from the desorption layer of the membrane surface to the gas (or vapour) phase.

It is not always possible to resolve all 5 stages: for example, stages 1 and 2, and also 4 and 5, are sometimes combined by adding their resistances[19,20].

In order to simplify the terminology we shall assume that the membrane is located horizontally, and that its upper surface is in contact with the liquid and its lower surface with the vapour. We begin with a discussion of the 5 individual stages, and of the way in which each stage affects the overall process.

1. Transfer of Material from the Centre of the Liquid Flow to the Surface of the Membrane

This stage consists essentially in the transport of matter and heat to the surface of the membrane. It has fundamental significance both in the permeation of pure substances, when concentration polarisation cannot arise†, and in the separation of multicomponent mixtures. Hence, vigorous stirring of the liquid is advisable, as was suggested in some of the early papers[21-23]. A more recent paper[24] shows that the rate of permeation can be raised very considerably by increasing the speed of the stirrer.

It is stated[21-23] that a Reynolds number in the liquid of 2300 is sufficient to bring the resistance of stage 1 to a minimum. However, this conclusion may be true only for rates of permeation below 10 kg m^{-2} h^{-1}, and should be tested experimentally at the higher mass flows currently of interest (up to 50–60 kg m^{-2} h^{-1}).

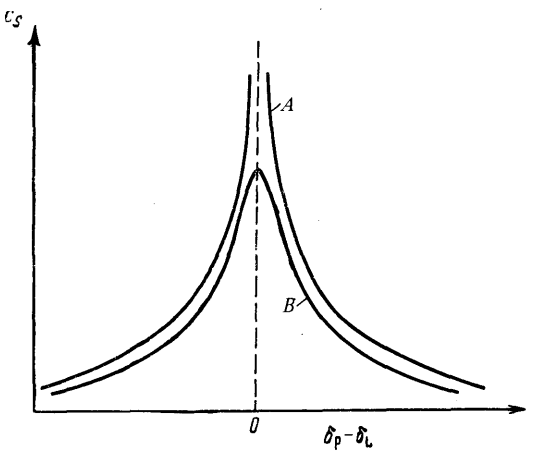


Figure 1. Influence of the Hildebrand solubility parameter on the solubility of liquids in a polymer: δ_P is the solubility parameter of the polymer, δ_L is the solubility parameter of the liquid, *A* is the curve for a linear amorphous polymer, *B* is the curve for a cross-linked or crystalline polymer.

2. Sorption by the Surface Layer of the Membrane

Sorption of the liquid by the polymer membrane is an essential step in the process, because substances which are not sorbed by the membrane (i.e. which are insoluble in it) are incapable of permeation. The dissolution of a liquid in a polymer is described by the Hildebrand solubility parameter. The smaller the difference between the solubility parameters of the liquid and of the polymer, the greater is the solubility (see Fig. 1).[10,25-28] For example, the solubility parameter δ for polyethylene is 7.7–8.4 $(cal\,cm^{-3})^{1/2}$, and for benzene and n-hexane, which are readily soluble in polyethylene, the parameter is 9.2 and 7.3 respectively (all values for 25°).[27]

Long[29] suggested that an equilibrium is rapidly set up at the liquid–polymer interface during the permeation of toluene, methylcyclohexane, and n-heptane through polypropylene membranes. He writes $c_1 = c_S$, where c_1 is the concentration of the permeating substance in the upper layer of the membrane and c_S is the solubility of the permeating substance in the polymer. According to Long, the solubility of hydrocarbons increases with temperature, reaching values of 0.17, 0.23, and 0.34 g per g of dry polymer for n-heptane, toluene, and methylcyclohexane respectively at 60°. Kim and Kammermeyer[30] have measured the concentration profiles during permeation of organic liquids through membranes, and have compared their results with experimentally measured equilibrium concentrations of dioxan in Nylon and dioxan, n-hexane, and benzene in polyethylene. They report that the true concentration of the permeating substance in the upper layer of the membrane is close to (but slightly lower than) the equilibrium value.

Michaels and coworkers[31] measured the solubility of xylene isomers in high-pressure and low-pressure polyethylene: at 25° the solubility of *o*-, *m*-, and *p*-xylene in high-pressure polyethylene is 0.169, 0.136, and 0.118 g per g of dry polymer respectively.

An unsuccessful attempt to measure directly the sorption of liquid benzene by polyethylene membranes has been reported[32]: the results were erratic, and in some cases the membrane lost weight as a result of the extraction of some of its material by the benzene.

The difficulties attending direct experimental measurements of sorption equilibrium have been stressed by Paul[33], who proposed an indirect method of measuring c_S based on the "time-lag" method[34]. In this method, two separate experiments are made on the permeation of the same substance through the membrane: in one experiment, the permeation is monitored from the time when the dry membrane first makes contact with the liquid to the time when equilibrium is established, in the other experiment the permeation is monitored under steady-state conditions. Fick's second law equation had been previously solved for the special case of a concentration-independent diffusion coefficient[35], and also for the general case when the diffusion coefficient is a function of the concentration of the permeating substance in the membrane[33]. A mathematical analysis of the experimental results, using these equations, yields the required value of c_S.

Fels[36] has described an interesting method of measuring equilibrium sorption: by using an electro-balance, he determined c_S for n-heptane and cyclohexane vapours at different activities, and hence he calculated c_S for the liquids by extrapolation. The only drawback of this method is the very laborious experimentation involved.

As we have already pointed out, substances which are not sorbed by the membrane cannot be transmitted through it. However, an exception to this rule is possible, at least in principle: substances which in the pure form are very slowly transmitted through a given membrane may acquire a higher solubility in the membrane, and be readily transmitted, when mixed with other substances which can diffuse rapidly through the same membrane[37]. Effectively, the substance which is readily soluble in the polymer retains the ability to dissolve the substance which in the pure form is insoluble in the polymer, and is thus able to "entrain" it. Furthermore, a very soluble material can expand the structure of the polymer and plasticise

†Concentration polarisation is the increase in concentration of the less rapidly diffusing component, in the boundary layer of liquid adjacent to the surface of the membrane, observed with inadequate stirring.

it[3,10,25,26,37-41], thus assisting the migration of other substances through the membrane. The plasticising effect can be detected also when all the components of a mixture are readily sorbed by the polymer: the rate of permeation of the mixture is usually greater than the "additive" value, calculated from the composition of the mixture and the rates of permeation of the individual components[36,41-43]. The abnormally high rate of permeation of mixtures (benzene–n-hexane, benzene–cyclohexane, n-hexane–cyclohexane) through a polyethylene membrane is also explained[42] by assuming an increased activity of the components, resulting from intermolecular interaction, which enables the molecules to penetrate more readily into the polymer structure, thus raising the concentration of each component in the outermost layer of the membrane beyond the level corresponding to the permeation of an ideal mixture. A decrease in the activity of the components (and therefore in the rate of permeation) as compared with ideal behaviour is another possibility.

Thermodynamic calculation of the sorption isotherm is not possible at the present time, and therefore the isotherms must be determined experimentally.

The sorption of one liquid component is complicated to such an extent by the presence of another component that it is impossible, as a rule, to predict the sorption behaviour of a mixture from a knowledge of the data relating to the individual components. Values of c_1 applicable to the separation of binary and more complex mixtures by permeation through a membrane are not available in the literature.

3. Diffusion Through the Membrane

The third stage of permeation through a membrane is diffusion under the influence of the concentration difference between the upper and the lower surface layer or, more precisely, under the influence of the activity difference. The activity in the polymer can be calculated by the Flory–Huggins equation

$$\ln a_p = \ln V_p + (1 - V_p) + \chi(1 - V_p)^2 \qquad (1)$$

where a_p is the activity of the material dissolved in the polymer, V_p is its volume fraction in the polymer, and χ is the interaction parameter. According to existing data, χ is a function of temperature and concentration, but in most systems it varies over a narrow range (from 0.3 to 0.8). For example, for benzene and an ethylene–propylene copolymer $\chi = 0.65$, and for n-hexane and the same polymer $\chi = 0.3$;[44] for the benzene–polyethylene system $\chi = 0.68–0.90$;[45] for xylene and polyethylene $\chi = (-0.48 + 318/T) \pm 0.2$ where T is temperature in °K.[46]

If the swelling of the membrane in the permeating liquid is appreciable (over 1%) the diffusion coefficient D_c increases exponentially with the concentration of the liquid in the polymer, and the activation energy for diffusion ED_c decreases linearly[10,25,26,28-30,36,47]:

$$D_c = D_0 \exp(\gamma c), \qquad (2)$$

$$E_{D_c} = E_{D_0} - \gamma' c. \qquad (3)$$

In these equations c is the concentration of the permeating substance in the membrane and γ and γ' are constants. As the concentration is increased, ED_c can decrease by 10 kcal mole^{-1},[10] and D_c (in the case of hydrocarbon diffusion through polyethylene membranes) can increase from 10^{-11} to 10^{-7} cm^2 s^{-1}.[25,26,41]

Long[29] has determined experimentally the values of D_0 and γ in the equation

$$G = \frac{D_0}{\alpha l}(e^{\gamma c_s} - 1) \qquad (4)$$

for the permeation of toluene, methylcyclohexane, and n-heptane through polypropylene membranes. In this equation α is a constant and l is the thickness of the membrane. Eqn. (4) was derived on the assumption that Eqn. (2) applies, that $c_1 = c_s$, and that the concentration at the lower surface of the membrane is $c_2 = 0$. From his experimental results Long was able to calculate the concentration profile across the membrane.

Kim and Kammermeyer[30], starting from Fick's second law and assuming an exponential dependence of the diffusion coefficient on concentration (Eqn. (2)), obtained the following equations for calculating the concentration profile in the membrane and the diffusion coefficient applicable to the permeation of a liquid through a membrane (assuming $c_2 = 0$):

$$\frac{dc}{dl} = \left(\frac{1}{l}\right)^2 \frac{1 - e^{\gamma c_1}}{(1 - e^{\gamma c_1})\, l + e^{\gamma c_1}}, \qquad (5)$$

$$\frac{dD}{dl} = D_0(1 - e^{\gamma c_1}). \qquad (6)$$

In these equations $0 \leqslant l \leqslant 1$. The authors concluded that the diffusion coefficient decreases linearly across the thickness of the membrane, as required by Eqn. (6). The mean (effective) diffusion coefficient $\bar{D}$ is defined as

$$\bar{D} = \frac{D_0}{c_1} \int_0^{c_1} e^{\gamma c}\, dc. \qquad (7)$$

The assumption that $c_2 = 0$ is usually admissible when the space below the membrane is continuously evacuated.

Kim and Kammermeyer[30] measured the concentration profile across the membrane and the permeation of water and dioxan through Nylon membranes and n-hexane, benzene, and dioxan through polyethylene membranes (see Fig. 2). The experimental technique consisted in using a pack of 15–25 tightly pressed thin layers as the membrane; after the experiment the pack was dismantled and the concentration of the permeating substance in each layer was determined.

Experimental determinations of the diffusion coefficient followed by graphical analysis of the results by the "time-lag" method have been reported. The method relies on measurements of the penetration of liquid through the membrane from the instant when the liquid is brought into contact with the dry membrane[48,49]. The main shortcoming of this method, according to the authors themselves, is that the error in the calculated diffusion coefficient is always several times greater than the error in the experimentally measured rate of permeation.

Fels and Huang[50] measured the diffusion coefficient by observing desorption from previously swelled membranes. They modified Fick's second law for the assumption of "volume-additive" swelling, i.e. that the increase in volume of the polymer is uniquely determined by the dissolution of liquid in it (as had been previously confirmed experimentally for the dissolution of benzene and n-hexane in polyethylene[51]), and they arrived at the equation

$$\frac{dc}{dt} = \frac{\partial}{\partial l}\left[\frac{D_c}{(1 - V_p)} \frac{\partial c}{\partial l}\right]. \qquad (8)$$

They used this equation in their next paper, devoted to a theoretical interpretation of the effect of the initial composition of the mixture on the separation of benzene and

n-hexane by permeation through a polyethylene membrane[26]. We shall summarise their arguments below.

The theoretical approach of Fels and Huang[25,26,50] is based on Fujita's suggestion[52] that free volume is present within the polymer. This term is analogous to the concept of "holes" during thermal fluctuations, and denotes the total fraction of free volume in the polymer. The free volume is a function of temperature and of the concentration of solutes in the polymer, and can be presented in the form

$$f(V_p, T) = f(0, T) + \beta(T)V_p \qquad (9)$$

where $f(V_p, T)$ is the free volume at given values of T and V_p, $f(0, T)$ is the free volume of the dry polymer, and $\beta(T)$ is a proportionality coefficient. When $V_p = 0$ we obtain the intrinsic free volume of the polymer, and when $V_p = 1$ the free volume of the diffusing substance. According to Fujita

$$\ln\frac{D_T}{D_c} = \frac{V_p}{[f(0, T)]^2/[B_d \cdot \beta(T)] + [f(0, T)/B_d] \cdot V_p} \qquad (10)$$

where B_d is an arbitrary parameter corresponding to the smallest "hole" needed for diffusional transport, and D_T is the thermodynamic diffusion coefficient

$$D_T = \frac{D_c}{(1 - V_p)}\frac{\partial \ln V_p}{\partial \ln a_p} . \qquad (11)$$

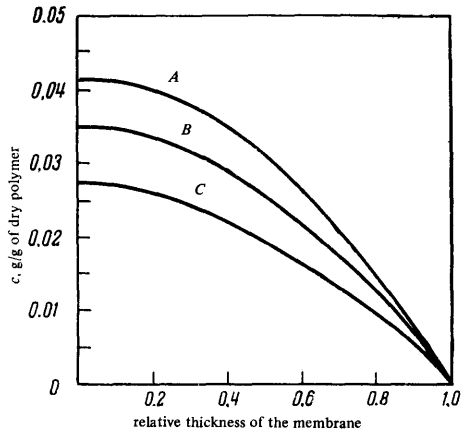


Figure 2. Concentration profiles during permeation of a liquid mixture through a membrane[30]. Membrane of high-pressure polyethylene, 0.0432 cm thick, separation temperature 35°, A is n-hexane, B is benzene, C is dioxan. c_S of the three components 0.043, 0.044, and 0.039 g/g of dry polymer respectively.

Michaels and coworkers[28] have measured, by two methods, the diffusion coefficient in polypropylene before and after treatment in a solvent at high temperature. (The effect of solvent treatment is discussed below.) The first method depends on calculating the rate of permeation (G) through the membrane by Fick's second law:

$$Q = \bar{D}_Q c_1 \qquad (12)$$

where $Q = Gl$. Since the thickness of the membrane is constant, we can calculate $\bar{D}_Q$ from the experimentally measured quantities G and c_1 (assuming that $c_2 = 0$). The second method is a calculation based on experimental observations of sorption and desorption of the same substances by the membrane:

$$\bar{D}_a = \frac{\bar{D}_{abs.} + \bar{D}_{des.}}{2} \qquad (13)$$

where $\bar{D}_{abs.}$ is the mean diffusion coefficient determined from absorption experiments, and $\bar{D}_{des.}$ is determined from desorption experiments.

Table 1. Comparison of diffusion coefficients obtained from membrane permeation experiments (Eqn. (12)) and from sorption–desorption experiments (Eqn. (13))[28]. $T = 40°$.

Permeating substance	$10^7\bar{D}_Q$, cm^2 s^{-1}			$10^7\bar{D}_a$, cm^2 s^{-1}		
	polypropylene membrane, untreated	polypropylene membrane treated 24 h in *p*-xylene at		polypropylene membrane, untreated	polypropylene membrane treated 24 h in *p*-xylene at	
		80°	100°		80°	100°
Toluene	3.7	9.1	12.6	1.4	3.0	3.3
Methylcyclohexane	3.1	5.5	8.2	1.1	1.6	2.4
Iso-octane	0.5	2.7	5.9	0.6	1.0	1.6

Numerical values of diffusion coefficients are listed in Table 1. Michaels and coworkers[28] ascribe the discrepancy between diffusion coefficients determined by different methods to the fact that in absorption and desorption the diffusion coefficient depends on time as well as on concentration.

Fels[36] reported some measurements of the diffusion coefficient of hydrocarbons in polyethylene by experiments on the absorption of vapours at different activity.

During the diffusional permeation of a multicomponent mixture through a membrane, resulting in separation of the mixture, we cannot assume that the components of the mixture diffuse independently of each other (in parallel flows, as it were). Intermolecular interaction, which is present in the original solution, is undoubtedly complicated by the interaction between the components of the mixture and the membrane material (i.e. the polymer[25,26,42,43,36,53,54]). The diffusion coefficients will depend not only on the concentration of each substance diffusing through the membrane, but also on their physicochemical interactions with each other and with the polymer. This interaction will undoubtedly influence also the concentration profile of the various components across the membrane[37].

Fels and Huang[25,26] suggest two basic reasons for the deviation from additive (i.e. ideal) behaviour of the rate of permeation of a benzene–n-hexane mixture: liquid–liquid interaction, and the plasticising effect of the solutes on the polymer (the presence of a second liquid component in the polymer alters the activity and hence the plasticising effect of the first). A similar view is put forward by Krewinghaus[41], who studied the separation of a benzene–cyclohexane mixture by permeation through modified polyethylene membranes: he treats benzene as a "stronger plasticiser" than cyclohexane.

No information on the diffusion coefficients which apply to the permeation of binary or multicomponent mixtures through a membrane is available in the literature.

4. Desorption from the Lower Surface of the Membrane and Transport from the Desorption Layer to the Gas (or Vapour) Phase

These two stages of the permeation process cannot easily be separated on the basis of published work, and we shall consider them jointly.

Substances which have permeated through the membrane are desorbed from the lower surface, forming a layer of liquid. In principle, however, we could choose experimental conditions such that no liquid is formed on the lower surface of the membrane, and the permeating substances are immediately removed as vapours (for example, by suitably evacuating or heating the space below the membrane). These are exactly the conditions which are most often chosen in practice. Permeation through a membrane can take place at a useful rate also if evaporation from the lower surface is hindered, e.g. if the lower space is maintained at atmospheric pressure or at low temperature: in this case the desorbed liquid simply drains off the lower surface of the membrane [53, 37, 55, 56].

In order to clarify the role of stages 4 and 5 in the separation process, we shall write Fick's second law equation in the form

$$G = -D_c \frac{c_2 - c_1}{l} . \qquad (14)$$

We shall assume that the absorption and desorption processes are fast, and $c_1 = c_S$, but $c_2 = c_g$, where c_g is the equilibrium concentration of the permeating species in the lowest layer of the membrane, corresponding to the concentration of the same species in the vapour. Eqn. (14) becomes

$$G = D_c \frac{c_s - c_g}{l} . \qquad (15)$$

In Eqn. (15) c_S and c_g depend essentially on the temperature, on the composition of the mixture, and on the physicochemical properties of the permeating substances. Furthermore, $c_g = f(p)$, and $p = f(P, t_V)$, where P is the total pressure below the membrane, t_V is the temperature of the vapour, and p is the partial pressure of the permeating substance below the membrane. Hence, $c_g = f(P, t_V)$, and changes in P or in t_V influence p and therefore also c_g. An increase in p produces an increase in c_g, a decrease in the concentration gradient across the membrane, and hence a decrease in the rate of permeation through the membrane, as has been observed experimentally [37, 53, 55, 56]. A change in P or in t_V affects not only the rate, but also the selectivity of the separation. For example, the separation coefficient of a mixture, defined as

$$\alpha = \frac{Y_A}{Y_B} \Big/ \frac{X_A}{X_B} \qquad (16)$$

(where $Y_A(Y_B)$ is the concentration of component A(B) in the mixture permeating through the membrane, $X_A(X_B)$ is the concentration of the same component in the original mixture), can be varied from 1.68 to 1.17 simply by varying P and t_V at constant liquid temperature [53, 56] in the case of the two close-boiling hydrocarbons n-heptane and iso-octane (50 : 50% mixture). Similar results were reported by other workers [57].

The effect of vapour pressure on the rate of permeation and on the selectivity of the separation of toluene–isobutanol mixtures [37] is illustrated in Fig. 3. (the special features of the separation of hydrocarbon–alcohol mixtures are discussed below.)

At P = 760 mmHg it is possible to increase p (by heating the space below the membrane) to such an extent that the rate of permeation almost vanishes. Conversely, by cooling the space below the membrane (still keeping P = 760 mmHg) we can lower p and therefore also c_g, and in this way the rate of permeation can be made comparable to the rate obtained in a fairly good vacuum (of the order of 10 mmHg) [37, 53, 55]. Unambiguous experimental confirmation of the sensitive dependence of the rate of permeation on vapour pressure [57] and on total pressure and vapour temperature [55, 56, 58] has been given in the literature.

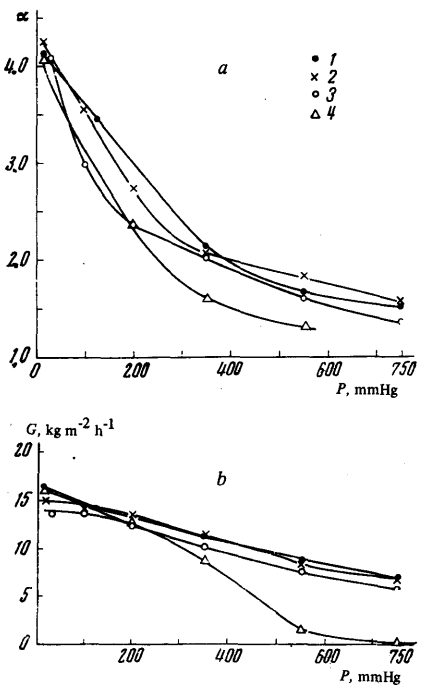


Figure 3. (*a*) Rate of permeation of a 50 : 50% toluene–isobutanol mixture against vapour pressure [37]. Temperature t_T of the heater jacket for the vapour space below the membrane: *1*) 15, *2*) 30, *3*) 50, *4*) 80°; temperature of the liquid 79°. (*b*) Separation coefficient of a 50 : 50% toluene–isobutanol mixture against vapour pressure [37]. Conditions as for Fig. 3*a*.

Ghosh and Rawat [57] have shown that an increase in vapour pressure from 20 to 160 mmHg results in a sharp fall in selectivity of the separation of n-heptane–iso-octane, benzene–cyclohexane, toluene–iso-octane, toluene–methylcyclohexane, and toluene–n-heptane mixtures. In the last three of these mixtures they observed an inversion of the separation: under different conditions the mixture permeating through the membrane may be

enriched in one or the other component. Inversion of the separation of benzene and n-hexane has also been reported [55,58].

Generalising our consideration of the five-stage mechanism of permeation of liquids through polymer membranes, we must stress the need to make proper allowance for each of the stages. Failure to do so may result in serious errors, lack of reproducibility, and incorrect design of apparatus for large-scale operation.

III. INFLUENCE OF POLYMER STRUCTURE AND POSSIBLE MODIFICATIONS OF THE MEMBRANE

Since polyethylene and polypropylene membranes are used almost exclusively at present for the separation of organic liquids by diffusional permeation, we shall not consider other types of membrane in this review.

Several workers have shown [59-63] that in crystalline polymers (such as polyethylene and polypropylene) diffusion is confined almost entirely to the amorphous regions. The permeability of crystalline regions towards gases (He, CH_4) is 2–3 orders of magnitude lower than the permeability of amorphous regions.

Increasing the degree of crystallinity leads to a drastic lowering of the rate of permeation of liquids through the membrane [31,53,64,65], since the permeation of liquids also takes place in the amorphous regions to a large extent. Since dissolution also is largely confined to the amorphous regions, and the diffusion coefficient varies exponentially with the concentration of the liquid in the polymer, decreasing the proportion of amorphous material causes a sharp decrease in the diffusion coefficient.

In a crystalline polymer the amorphous regions are separated by crystalline regions, which thus limit the volume fraction of the polymer available for diffusional permeation. Diffusion takes place along irregular, tortuous channels. Some of the amorphous regions may be close-ended, and not available for continuous permeation. There may also be very narrow channels, which are blocked by the diffusing material.

Not only does the presence of crystalline regions create geometric barriers and lower the rate of permeation, but (even more important) these barriers affect different substances to different extents, as shown by the different rates of permeation of chemically similar but structurally different substances. For example, the rate of permeation of normal alkanes decreases with increasing chain length [1,43,53,55]; iso-alkanes permeate more slowly than normal alkanes [1,43,53]; the xylene isomers [28,31], and benzene and cyclohexane [41,53,54,56], permeate at different rates.

In their paper on the separation of the xylene isomers [31] Michaels and coworkers treat polyethylene as a special type of molecular sieve, in which the intercrystalline pores are filled with amorphous material. On this basis they were able to explain the effect of a "conditioning" treatment on the polymer (lengthy immersion of the membrane in one of the xylene isomers at 50–60° (low-pressure polyethylene) or 90–100° (high pressure polyethylene)). They suggest that during the heat treatment of the membrane the crystals are rearranged without significant change in the degree of crystallinity (for temperatures up to 100°). A more ordered structure, with larger crystals, is formed, the molecules of the xylene isomer acting as "templates" for the reconstruction of the crystalline regions. After this conditioning treatment, the rate of permeation and the selectivity of the separation of the xylene isomer used as a template are significantly increased.

Michaels and Hausslein [46] explain the difference in the sorption capacity for *p*-xylene of polyethylene membranes prepared in different ways by distinguishing between elastically effective and elastically ineffective parts of the amorphous regions. In this model the activity coefficient of the compound dissolved in the polymer is given by the Flory–Renner equation

$$\ln a_p = \ln V_p + (1 - V_p) + \chi(1 - V_p)^2 + \frac{\langle\alpha\rangle_0^2 f \rho V_p (1 - V_p)^{1/3}}{M_c} \qquad (17)$$

rather than by the Flory–Huggins equation (1). In Eqn. (17) $\langle\alpha\rangle_0$ is a geometric factor, taken [46] to be unity, f is the weight fraction of elastically effective polymer, ρ is the density of the unswelled polymer, and M_c is the average molecular weight of the elastically effective regions.

The term elastically effective refers to polymer chains firmly attached to both ends to a cross-linked or to a crystalline region. Polymer chains fixed at one end only, short molecules, and tangles of loose polymer chains are non-elastic. The authors prepared polyethylene membranes with different degrees of crystallinity and different amounts of elastically effective polymer by cooling the membranes from 160° at different rates to 50° (in a dry ice–acetone mixture, in a few minutes, or over a period of 4 hours). Some membranes were mechanically stretched at 40°. The higher cooling rates gave larger amounts of elastically effective polymer. Heat treatment at 130° of samples previously cooled in dry ice–acetone mixture lowered the proportion of elastically effective polymer. Stretching at 40° gave the highest proportion ($f = 0.88$ g g^{-1}) of elastically effective amorphous polymer.

Elastically effective and elastically ineffective regions behave quite differently during dissolution and diffusion. The diffusing molecule can easily draw apart the ineffective, loose regions of the polymer, but it experiences considerable resistance to migration in the regions where the polymer molecules are anchored and elastically effective. As a result, the solubility of the permeating substance in the membrane and its diffusion coefficient are both lowered, but the effect on the diffusion coefficient is much greater than the solubility effect. This is because the diffusion coefficient is an exponential function of the concentration of diffusant in the polymer. For example, the solubility of hydrocarbon vapours in membranes which have been stretched at low temperatures is decreased 2–3 fold, whereas the diffusion coefficient is decreased by a factor of 10–1000.

In a more recent paper, Michaels and coworkers [28] apply the concept of an elastically effective polymer to the conditioning effect on polypropylene membranes of different solvents (methylcyclohexane, *p*-xylene, *o*-xylene, iso-octane, toluene) at temperatures between 60 and 100°. They re-examine their earlier model of the conditioning effect, in which the solvent molecules act as "templates" for the reorganisation of the crystalline regions [31,66], and they show experimentally, for example, that the rate of permeation of iso-octane is substantially increased (4-fold) after treating the membrane in a solvent composed of much smaller molecules (toluene). They also show that the smaller the difference between the Hildebrand solubility parameters of the polymer (polypropylene) and the solute, the lower is the temperature at which the polymer will dissolve. Solvent treatment is thought to involve 2 processes: 1) partial melting of the crystalline regions in the polypropylene and 2) recrystallisation to

give larger crystals. In the resulting structure the amorphous regions are less intimately constrained, less crowded by the crystalline regions, and therefore the proportion of elastically effective polymer is decreased and the diffusion coefficient and rate of permeation are increased. However, the selectivity of the separation is found to vary in inverse proportion to the rate of permeation‡, in contrast to earlier findings[31,66].

A preliminary comparison of polyethylene and polypropylene membranes[28,67] indicates that the diffusion coefficient and the rate of permeation are somewhat higher in the latter. Since the solubility in the two polymers is practically the same, it is concluded that more direct "paths" are available for molecular migration in polypropylene. The greater selectivity of polypropylene towards the separation of xylene isomers is ascribed to greater stiffness of the chains, lower mobility of polymer segments, and greater sensitivity to the size and shape of the permeating molecules in polypropylene.

We must stress that comparisons between polyethylene and polypropylene membranes are arbitrary to a large extent, because both the rate of permeation and the selectivity of the separation are extremely sensitive to the degree of crystallinity and other parameters of the polymer.

Michaels and coworkers[68] have discussed the possible advantages of thermal modification of the membranes; they have also considered modification by mechanical treatment (including unidirectional stretching at low temperatures)[41,69-71] and by solvent treatment[72,73].

They have shown that unidirectional cold stretching (at a temperature well below the melting point) produces drastic changes in the properties of the membrane[41,70,71]. The degree of crystallinity hardly changes at all, but the solubility of the permeating compounds is significantly decreased, the diffusion coefficient falls sharply, so does the rate of permeation through the membrane, and the selectivity of the process is increased. An annealing treatment after unidirectional cold stretching practically restores the original rate of permeation, but at some cost in selectivity (which remains, nevertheless, higher than the selectivity of the original, non-oriented membrane).

These observations are explained as follows. Low-temperature unidirectional stress extends the polymer chains, producing narrow, compressed amorphous channels. The "mobility" of the polymer decreases, and additional barriers to molecular migration in the polymer are produced, leading to a sharp decrease in the rate of permeation. At the same time, the significance of the size and shape of the migrating molecules becomes even more important, and therefore the selectivity of the separation is improved. For example, unidirectional cold stretching of polyethylene membranes at 35° increases the separation coefficient (see Eqn. (16)) of a 50 : 50% mixture of benzene and cyclohexane from ~ 2 to 4, but the rate of permeation is reduced approximately 30-fold[41].

Krewinghaus[41] therefore confirms the previous suggestion, based on experimental observations[46], that unidirectional cold stretching produces a marked increase in the proportion of elastically effective polymer, and hence a very marked decrease in the diffusion coefficient.

One way of increasing the throughput of this method of separation is to work at higher temperatures: this raises the problem of the thermal stability of the membranes. The thermal stability can be increased, for example, by inducing cross-linking in polyethylene with various forms of ionising radiation[74]. High-pressure polyethylene membranes modified by u.v. irradiation in the presence of PCl_3 have been examined: the rate of permeation of toluene through membranes cross-linked by this technique was found to have risen to 40–60 kg m^{-2} h^{-1}, and the rate of permeation of toluene mixed with ~ 50% of alcohols had risen to 20–30 kg m^{-2} h^{-1}, without serious loss of selectivity[81]. Cross-linked polyethylene membranes can be used at 80–100°, and in some cases up to 120°, whereas the original membranes were rapidly degraded at 60–65°.

Siegel and Coughlin[75,76] subjected to γ-ray irradiation polyethylene membranes which had been previously immersed in a solvent (benzene, toluene, cyclohexane) for 48 h. The rate of permeation through a membrane modified in this way is increased by about a factor of 2. The authors consider that solvent treatment assists the growth of large crystals at the expense of the smaller crystals, giving rise to a more "open" structure and increasing the number of "amorphous holes". During the subsequent irradiation, the interaction of free radicals in the amorphous regions of the polyethylene results in cementation (or fixation) of a modified structure at the boundaries of the crystalline regions. It is suggested that this method of membrane modification should increase the selectivity of the membrane towards the solvent used for the initial swelling, but the suggestion has not yet been tested experimentally.

Rogers[77] was among the first to study the permeation of gases and vapours (N_2, CO_2, CH_3Br, n-hexane, benzene, methanol) through membranes modified by radiation-induced cross-linking of acrylonitrile, styrene, and vinyl acetate previously sorbed from a solution onto polyethylene.

Huang and Fels[78,79] used γ-radiation to graft styrene from methanol solution onto polyethylene membranes at 35°. The extent of grafting obtained was 5.16 and 26%. They found that as the amount of graft copolymer is increased from 0 to 26%, the coefficient D_0 (see Eqn. (2)) at 45° decreases from 4.49 to 0.90×10^{-8} cm^2 s^{-1} (for the permeation of n-hexane) and from 6.90 to 1.00×10^{-8} (for the permeation of benzene). The solubility of n-hexane is almost unaffected (from 0.228 to 0.245 cm^3 cm^{-3}), but the solubility of benzene is significantly increased (from 0.234 to 0.340 cm^3 cm^{-3} of dry polymer). The authors also studied the changes in free volume $f(V_p, T)$ (see Eqn. (9)), and found that in the polymer–n-hexane system this parameter decreases from 55 to 8% at 45° as the degree of copolymerisation is increased from 0 to 26%. Under similar condition, $f(V_p, T)$ for the benzene–polymer system decreases from 36 to 21%. The activation energies for the permeation of benzene–n-hexane and toluene–n-heptane mixtures through grafted membranes were calculated from the $G-T$ relationships. Increasing the amount of graft copolymerisation lowers the activation energy, and hence increases the rate of permeation (by a factor of 2–3). The observed increase in the separation coefficient α for benzene–n-hexane and toluene–n-heptane mixtures is explained by the lower mobility of the polymer chains after grafting, and by the increased importance of the geometrical parameters of the permeating molecules. The separation coefficient was increased, depending on the extent of graft copolymerisation, by 10–25%.

‡The selectivity of the separation of *p*- and *o*-xylene was defined[28] in terms of the ratio of the rates of permeation of the two isomers.

IV. DEPENDENCE OF THE RATE AND SELECTIVITY OF THE SEPARATION ON THE COMPOSITION OF THE MIXTURE

The rate of permeation through a membrane can be unequivocally calculated from the known rates of permeation and the composition of the mixture to be separated only in a few special ("ideal") cases, such as the separation of mixtures of alkane hydrocarbons [42,53]. In mixtures of hydrocarbons of different classes the rate of permeation is greater than the value expected from the rates of permeation of the individual components and the composition of the mixture. It is given by the equation

$$G_{AB} = G_A X_A \gamma_A + G_B X_B \gamma_B. \qquad (18)$$

where G_{AB} is the rate of permeation of the mixture, γ_A and γ_B are coefficients describing the deviations from additivity (or ideality) for the components A and B, defined as

$$\gamma_A = G_A^v / G_A X_A; \quad \gamma_B = G_B^v / G_B X_B$$

where G_A^p is the partial rate of permeation of the component A for the composition of the mixture and G_B^p is the same quantity for component B.

For an "ideal" mixture of alkane hydrocarbons $\gamma = 1$; for a benzene–n-hexane mixture the value of γ for benzene can be as high as 2.3 [48] or 1.8. [42,53]

As already pointed out, we cannot treat the permeation of the components as a case of parallel flows. The solubility in the membrane of the substances to be separated is affected by the intermolecular interactions of the liquids with each other and with the membrane material. The diffusion coefficients depend not only on the concentrations of all the species present in the membrane, but also on their physicochemical interactions within the polymer structure. The desorption process also is complicated by intermolecular forces. For these reasons, the mathematical description of the permeation of a complex mixture through a membrane is a very difficult problem, which can only be solved at present for a few of the simplest and most fully characterised systems.

Fels and Huang [25,26] attempted a theoretical interpretation of the effect of composition on the rate of permeation of a mixture, allowing for liquid–liquid interactions and for the plasticising effect of the solute molecules on the polymer structure. Starting from the exponential dependence of the diffusion coefficient on concentration, and from Fujita's free volume theory [52], they obtained equations for the rate of permeation of mixtures with different compositions. The required numerical values of $Dc = 0$, $f(0, T)$, $\beta(T)$, and Bd (see Eqn. (10)) were obtained experimentally for the benzene–n-hexane–polyethylene system by desorption experiments described in another paper [50]. The ratio between experimentally observed and calculated rates of permeation is 0.68–2.69 at 25° and 0.93–1.35 at 45°, depending on the initial composition. Fels and Huang ascribe the fairly large discrepancy between experiment and theory to the following effects: 1) inadequacy of the "free volume" concept, 2) the assumption that the concentration c_1 in the upper layer of the membrane has the equilibrium value c_S, 3) the unsupported assumption of a constant concentration ratio of benzene and n-hexane at any point in the membrane, 4) liquid–liquid interaction and liquid–polymer interaction.

Fels [36] points out that his earlier calculations [25,26] involved an elaborate mathematic programme and extravagant use of computer time. He developed a simpler method of calculating rates of permeation of mixtures from the composition of the mixture, the rate of permeation of the individual components, the diffusion coefficient, and the calculated free volume. The diffusion coefficient is determined from the absorption of vapours at different activities, using an equation proposed by Crank [35]:

$$1 - \frac{Q_t}{Q_\infty} = \frac{8}{\pi^2} \exp \frac{D\pi^2 t}{l^2} \qquad (19)$$

where Q_t is the amount of vapour absorbed in time t, and Q_∞ is the total amount of vapour absorbed when equilibrium has been established.

Table 2. Calculated and experimental rates of permeation of cyclohexane and n-heptane through a polyethylene membrane [36].

Temp., °C	Ratio of experimental to calculated rate of permeation for different amounts of cyclohexane in the mixture, wt.%							
	80		60		40		25	
	cyclo-hexane	n-heptane	cyclo-hexane	n-heptane	cyclo-hexane	n-heptane	cyclo-hexane	n-heptane
25	1.27	1.62	1.15	1.36	0.88	1.32	0.86	0.85
30	1.07	1.65	0.99	1.33	0.80	1.27	0.75	0.80

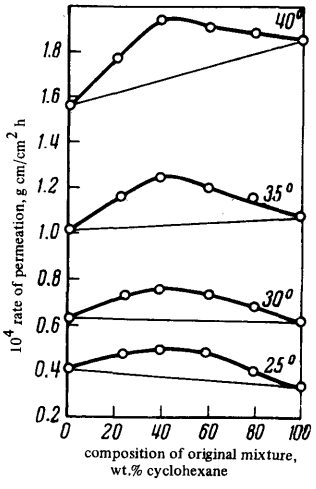


Figure 4. Rate of permeation of a cyclohexane–n-heptane mixture against composition of original mixture [36].

The ratios of experimental to calculated partial rates of permeation for cyclohexane–n-heptane mixtures of different composition are shown in Table 2. Fig. 4 shows experimental plots of the rate of permeation of a cyclohexane–n-heptane mixture as a function of composition.

This mixture does not deviate very strongly from "ideal" behaviour (indicated by the straight line joining the rates of permeation of the pure components). Hence, the results given in Table 2 are unacceptable. Nevertheless, the combined experimental and computational method proposed by Fels[36] has a great deal of merit, because it retains the strictly scientific and logical approach of the earlier attempt[25,26] to describe mathematically the separation of liquids by diffusional permeation through a membrane.

Krewinghaus[41] has tried to evaluate the combined plasticising effect of benzene and cyclohexane on polyethylene. He concludes that benzene is the "stronger" plasticiser, and he gives an empirical equation for the rate of permeation of a mixture with allowance for composition and for the plasticising effects of benzene and cyclohexane.

Several workers have reported (without comment) composition effects on the rate of permeation and selectivity during the separation of toluene–n-butanol mixtures (polypropylene membrane)[21,23] and benzene–isopropanol and benzene–methanol mixtures (polyethylene membrane)[32]. We should point out that whereas the separation coefficient α is usually less than 2 for mixtures of hydrocarbons (for example, benzene–n-hexane, n-heptane–iso-octane, benzene–cyclohexane, mixtures of xylene isomers, etc.), in mixtures of hydrocarbons and polar compounds (alcohols, acetic acid[23]) the separation coefficient is much higher (10–25, or even higher).

V. INFLUENCE OF THE NATURE OF THE COMPOUNDS TO BE SEPARATED

Although the influence of the nature of the compounds to be separated has been implicit in the whole of the preceding discussion, the subject is so important that we think it right to devote a special Section to it. It is the most complicated and the least clearly understood of all the problems which arise in the study of permeation. The difficulty stems from the fact that the permeation process takes place in several stages, and we must therefore consider a wide range of properties of the permeating liquids and of the polymer: boiling point, solubility in the other components of the liquid mixture and in the polymer, polarity, structure and size of the molecules, heat of evaporation, etc.

By analysing published data obtained under conditions such that $c_2 = 0$ and the resistance of steps 4 and 5 can be ignored, we can draw a number of general conclusions on the expected order of separation: 1) the lower members of a homologous series permeate faster than the higher members, 2) if two molecules have the same molecular weight and similar chemical nature, the one with the smaller cross-sectional area permeates faster, 3) if the only difference between the components is the degree of unsaturation, the more unsaturated species permeate faster, 4) the molecules which permeate fastest are those least likely to form hydrogen bonds with the material of the membrane.

The fourth conclusion is illustrated by the following example. The separation of chloroform–acetone mixtures with Teflon membranes is ascribed[80] to the fact that chloroform has an active hydrogen atom, and the fluorine atoms in Teflon have donor properties: as a result, hydrogen bonds are formed and the chloroform is held relatively firmly by the Teflon. In practice only acetone permeates through the membrane, and the chloroform is completely retained.

Most of the work on the separation of organic liquids by diffusional permeation through membranes has been done with hydrocarbons, whose rates of permeation through a given membrane are not very different. However, the separation of hydrocarbons from polar compounds (in particular, alcohols) is also a problem of great practical importance. Using the conventional polyethylene and polypropylene membranes, we would expect the rates of permeation of the hydrocarbon to be 2 orders of magnitude greater than the rate of permeation of the alcohol, leading to a very efficient separation of these mixtures. This expectation is not always borne out by experiment.

El'bert and coworkers[37] have suggested that the properties of the slowly permeating component are not the only factor (or even the main factor) determining the partial rate of permeation of the slow component (alcohol) when mixed with a fast permeating component (hydrocarbon) Hence, the properties of the slow component are not the only factor determining the selectivity of the separation. The solubility and the diffusion coefficient of the slow component are determined not only by the properties of this component and those of the polymer, but first and foremost by the concentration of the faster component at each point in the membrane and by its plasticising effect on the membrane. The fast diffusing substance, being dissolved in the membrane, appears to retain its power to dissolve the slowly diffusing substance, and is able to "drag" it across the membrane.

The same paper[37] describes an experimental study of the separation of a toluene–isobutanol mixture by permeation through polyethylene membranes modified by photochemical cross-linking. On cooling the space below the membrane, and raising the pressure from 20 to 760 mmHg, the selectivity of the separation is found to decrease very substantially. The following explanation is proposed: toluene is readily soluble in the polymer (according to Long, the solubility of toluene in polypropylene is 0.23 g g^{-1} of dry polymer at 60° [29]). Hence, the upper layer of the membrane, where the concentration is close to the equilibrium value, becomes essentially a gel with a high percentage of toluene, and the alcohol is dissolved by this gel rather than by the membrane material. On evacuating the space below the membrane (to a pressure of 10 to 20 mmHg) the concentration of toluene decreases sharply over the entire thickness of the membrane, and practically vanishes in the lower layer of the membrane[38]. In such a membrane (with a "damp" top layer and a "dry" bottom layer) the slowly migrating component has to pass from a region of extensively plasticised polymer, with a high concentration of fast diffusing solute, to a region where practically no plasticising has taken place. Thus, the geometrical barriers opposing migration of the alcohol increase throughout the thickness of the membrane. As a result, the partial rate of permeation of the alcohol is small, and the separation coefficients is acceptably high.

It is also pointed out[37] that on increasing the pressure below the membrane to 760 mmHg and cooling the space below the membrane the concentration profile across the membrane is greatly altered, and the concentration of the fast diffusing substance (toluene) is so high over the entire thickness of the membrane that the slowly diffusing substance (alcohol) is able to migrate across the membrane, which is now a gel (with a high concentration of plasticiser) over its entire thickness. In a "damp" membrane of this kind the geometrical barriers to migration of the alcohol are much lower than in a "dry" membrane.

As a result the separation coefficient of the toluene–isobutanol (50 : 50 wt.%) mixture decreases from 4.5 (at 15 mmHg) to 1.6 (at 760 mmHg).

The plasticising effect of hydrocarbons can be so marked that a hydrocarbon–alcohol mixture permeating through the membrane becomes enriched in the alcohol, although its individual rate of permeation through the membrane is 2 orders of magnitude lower [82].

Thus, a knowledge of the physicochemical properties of the compounds to be separated is far from sufficient to identify the order of the separation. We must also consider the way in which liquid–liquid and liquid–polymer interactions respond to changes in the experimental conditions, and first and foremost we must consider the temperature of the liquid and the temperature and pressure of the vapour.

VI. INFLUENCE OF TEMPERATURE OF THE LIQUID

As a rule, the rate of permeation through a membrane increases exponentially with the temperature of the liquid [17,21,23,28,53,56]. Michaels and coworkers [28] suggest 3 main reasons for the steep increase in rate of permeation: 1) activation of the molecules by the increase in temperature, 2) increased activity of the diffusing species in the polymer resulting from the lower compression, extension, etc. of the polymer chains in the amorphous phase (some decrease in the content of elastically effective polymer is also possible—this point is also stressed by Hausslein [83]), 3) the solubility of the permeating species in the polymer increases with temperature, and the diffusion coefficient is an exponential function of concentration.

The activation energy of the process of permeation through a membrane is usually in the range 7 to 10 kcal mole^{-1}.

Increase in the temperature of the liquid usually produces, in addition to a large increase in the rate of permeation, also a significant decrease in selectivity [17,21,31,28,37,42,56,69]. Michaels and coworkers [28] ascribe this effect to a decrease in the stiffness of the amorphous phase resulting from the combined solvent and temperature effects on the polymer: the polymer is plasticised, and the influence of geometrical barriers on the migration of molecules through the membrane becomes less marked.

Dytnerskii and Golovin [21] have shown, in the special case of the separation of an azeotropic mixture of toluene and n-butanol (containing 72 vol.% of toluene), that a reversible dependence of permeation rate on temperature is observed only if the polypropylene membrane is previously heated to the highest temperature in the experimental range.

Similar results were later reported by Michaels and coworkers [28], who consider that experiments at high temperature have an irreversible effect on the structure of the polymer by lowering the proportion of elastically effective polymer and partly releasing the internal stresses in the amorphous phase. It is pointed out that an increased rate of permeation of a given substance through a membrane can be obtained by previously subjecting the membrane to a high-temperature treatment in a solvent which does not need to be the same as the experimental liquid. For example, treatment of a polypropylene membrane at 60° in iso-octane, toluene, n-hexane, *p*-xylene, and methylcyclohexane increases the rate of permeation of iso-octane at 40° by factors of 2.07, 4.1, 3.58, 2.28, and 5.78 respectively. The selectivity of the separation is found to be somewhat lower after this treatment, in contrast to an earlier report [21] that the selectivity is unaffected.

Li and Long [84] measured the temperature dependence of the rate of permeation of a series of aromatic and non-aromatic hydrocarbons, acetic acid, methanol, water, ethyl methyl ketone, carbon tetrachloride, pyridine, and ethanol through polypropylene membranes. They also measured the effect of temperature on the permeation through Teflon membranes of n-heptane, toluene, ethanol, water, and on the permeation through Saran membranes of toluene, n-heptane, and ethanol. They found that when the permeation of non-aromatic hydrocarbons through polypropylene membranes at temperature in the range 10–70° is plotted as $1/T$ against $\ln G$ the curve shows a break at temperatures between 20 and 45°, corresponding to a sudden change in slope, and therefore also to a change in the activation energy of the permeation process. The break is not found in plots of the permeation of aromatic hydrocarbons through polypropylene membranes.

Chartov and coworkers [81] have shown that the rate of permeation of *o*-xylene and of a toluene–isobutanol (50 : 50%) mixture through photochemically modified polyethylene membranes is not an exponential function of temperature. The rate of permeation was measured at temperatures between 60 and 100° (for the toluene–isobutanol mixture) and between 60 and 120° (for *o*-xylene). The deviation from exponential behaviour is explained as follows: during photochemical cross-linking the new bonds are formed preferentially in the amorphous regions [85]. However, under the influence of a solvent and of elevated temperature we can expect partial dissolution of the crystalline regions, with formation of amorphous regions which are not cross-linked. Since the molecules diffuse through the amorphous regions of polyethylene, this process widens the permeation front, and furthermore the rate of permeation is different in the amorphous regions with and without cross-linking.

As already pointed out, an increase in temperature leads to an increased rate of permeation through the membrane, and at the same time it lowers the selectivity of the separation process. Hence, an optimum choice of temperature is most important since it allows the total area of the membrane to be decreased in industrial processes. It is stated [28] that the number of separation stages required to achieve a given degree of enrichment of one of the components is approximately inversely proportional to the logarithm of the separation coefficient (i.e. $\lg \alpha$), and the separation surface at each stage is inversely proportional to the rate of permeation (by raising the temperature), though accompanied by some loss of selectivity, could result in a decrease of the total working surface of the membrane required for an industrial apparatus. However, if $\alpha \simeq 1$ a small loss of selectivity, even if accompanied by a large increase in the rate of permeation, could greatly increase the number of separation stages required, and thus increase the total membrane area.

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The selectivity of separation methods based on diffusional permeation through polymer membranes is determined by a set of properties entirely different from those relevant to other methods of separation currently used in industry (fractionation, absorption, adsorption, crystallisation). Hence this method of separation could successfully be adopted industrially for the following operations:

1) separating mixtures of compounds of similar chemical nature and having similar boiling points (e.g. benzene and cyclohexane); 2) separating mixtures of isomers (for example, xylene isomers, normal and iso-alkanes); 3) separating various azeotropic mixtures (for example, mixtures of toluene and isobutanol, which form an azeotrope and boil at 110.6 and 108° respectively under atmospheric pressure).

Many different practical designs, and technological variants of the process, have been described. For example, "evaporation through a membrane" and "extraction through a membrane"[10], in which the substances migrating across the membranes are removed in a stream of air (or water vapour) or in a flow of inert solvent. Michaels and Bixler[10] point out that membranes suitable for use in the chemical and petrochemicals industry already exist. The main obstacle to the penetration of this method of separation into industrial practice is the unconventional design and operating mode of the necessary plant, which is radically different from traditional separation plant and therefore needs to be specially developed for the purpose.

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