Transport of organic penetrants through films of cellulose esters in transient regimes: a non-equilibrium thermodynamics analysis

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Transport equations are derived in the framework of the rational thermodynamics approach for membrane processes involving a dense (active) polymer layer. The influence of the deformation of the polymer matrix, formation of interacting species, changes in polymer configuration, etc., due to mixing of the penetrant and the polymer can be accounted for in the equations. Studies of permeation fluxes in the transient regime in which the membrane is suddenly put into contact with a solvent can give useful information on the behaviour of polymer–penetrant systems. Experimental results obtained for the transient permeation of alcohols and heptane through different cellulose ester membranes are reported and discussed in the framework of this approach.

(Keywords: transport equation; rational thermodynamics; polymer–penetrant system; transient regime; cellulose esters)

INTRODUCTION

Transport through dense membranes has often been described by equations of irreversible thermodynamics. However, irreversible thermodynamics (i.e. local-equilibrium theories[1]) does not account for some of the phenomena, such as those which are not explicitly related to known thermodynamic variables. In membrane processes, equations derived from irreversible thermodynamics are generally used to describe steady-state transport. These equations do not account for phenomena such as deformation of the polymer network and formation of interacting species as a result of the presence of permeants in the polymer, which are of particular importance in the transport of molecular species, especially in the transient regime. Rational thermodynamics, developed recently[2–6], has the advantage of (i) not being limited by linearity or closeness to equilibrium and (ii) being able to take into account various phenomena involved in non-linear mechanics of a continuum (e.g. deformation of a solid) and internal state changes of the component molecules. In a previous paper[6] we reported the use of the linearized version of this theory in the analysis of anomalous behaviour in the permeation of water vapour into plasticized poly(vinyl chloride)–starch blends. In this present work, the terms of the linearized equation are detailed and discussed with regard to their applicability to the polymer–penetrant system. The possibility of applying the developed approach to extract useful information from transient regime permeation measurements, which can then be used to improve membrane properties, is described. It should be mentioned that anomalous phenomena which may occur during a transient permeation (or sorption) were generally attributed to time-dependent phenomena[7–9]. However, the origin of these phenomena remains unclear and so far there is no available general framework for the analysis of such phenomena. Rational thermodynamics provide such a basis for the analysis of transient sorption and diffusion.

The transient permeation of alcohols (e.g. methanol, ethanol and n-propanol) and heptane through cellulose esters (such as cellulose acetate, cellulose triacetate, and cellulose butyrate) were measured by using the technique described in a previous paper[6], and the results are analysed according to the proposed approach.

EXPERIMENTAL

Membranes

Cellulose esters were purchased from the Eastman Kodak Corporation; cellulose acetate has an acetyl content of 39.4%. Dense membranes were made by first dissolving the chosen ester in an appropriate solvent (chloroform or dioxane), casting the solution onto a glass plate, and finally completely evaporating the solvent.

Procedure

The procedure used was similar to the one described previously[6]. However, due to the liquid nature of the penetrant, a cell, maintained at a constant temperature (30, 40 or 50°C), with an open face on the upstream side of the membrane, is rapidly placed in contact with the liquid being considered. The permeant vapour emanating from the downstream face was carried away by a stream of helium to the flame ionization detector of a gas chromatograph, the output from which was monitored until a constant signal was obtained.

The apparent diffusion coefficient D', which was defined

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in the previous paper[6], was calculated. However, in this paper we use the plot of this coefficient as a function of the extent of permeation, α, instead of the plot as a function of time[6]:

$$\alpha = J(t)/J_s \tag{1}$$

where $J(t)$ is the actual diffusion flux at time t and J_s is the steady state diffusion flux. This kind of plot enables us to directly compare the permeation behaviour of different penetrant–membrane systems (even when the time-scales for permeation are very different) and to locate the occurrence of different phenomena with regard to their own individual extent of permeation. When $\alpha = 1$, the system reaches the steady state of permeation. However, the steady state is also (slowly) reached at the end of the transient regime[6].

THEORY

Diffusivity

In studies of penetrant transport through membranes, the diffusion process is usually considered to be governed by Fick's law:

$$J = -D' \operatorname{grad} \rho \tag{2}$$

where J is the diffusion flux density, and D' is the diffusivity of the penetrant in the polymer. The latter is generally a tensor but for isotropic materials, it reduces to a scalar quantity. Equation (2) was originally formulated by analogy with thermal or electrical transport in a homogeneous medium at low penetrant concentrations. Under these conditions, D' is a measure of the mobility of the penetrant in the medium under consideration and the penetrant concentration ρ plays the role of a potential function (analogous to temperature or electrical potential), provided that the condition of diffusion equilibrium in the system, as specified above, is that of a spatially uniform ρ (i.e. $\operatorname{grad} \rho = 0$). The formalism of equation (2) has been applied somewhat indiscriminately to a wide variety of membrane–penetrant systems, often departing widely in various ways from the conditions indicated above. Polymeric membranes, in particular, may exhibit variations in properties due to a number of reasons. This should cause the physical meaning of the parameter D' to differ from the original one. It was shown that this parameter keeps its originally formulated meaning in the cases in which transport properties depend only on the penetrant concentration[7–12]. Therefore, we call D' the apparent diffusion coefficient in order to distinguish it from the original (i.e. Fick's) diffusion coefficient.

In the framework of rational thermodynamics the diffusivity D' consists of the following three terms[10,11]:

$$D' = D + L \operatorname{tr}\left(\boldsymbol{M}^{\mathrm{T}} \frac{\partial \boldsymbol{K}}{\partial \rho}\right) + Lk \frac{\partial A}{\partial \rho} \tag{3}$$

where D is the Fick diffusion coefficient:

$$D = L \frac{\partial g}{\partial \rho} \tag{4}$$

L is Onsager's coefficient, $\boldsymbol{M}$ is the related transformation tensor between concentration gradient and deformation gradient, $\operatorname{grad} B_{ijk} = M_{ij} \operatorname{grad} \rho_k$, $\boldsymbol{K}$ is the chemical potential tensor of elastic deformation, g is the chemical potential of the penetrant, A is the affinity (in the thermodynamics sense) of the internal state change (see Appendix), and k is the proportional coefficient of the concentration gradient. For gas diffusion, the last two terms in equation (3) are negligible, or even zero, as there is generally little deformation and only weak interaction between gas penetrant and polymer (i.e. $\boldsymbol{K} \approx 0$, and $A \approx 0$). Thus, in this special case D' reduces to the Fick diffusion coefficient, i.e. $D' \rightarrow D$.

Generally, the above-mentioned quantities are not constants but they are, in fact, the response functions of the following variables: the deformation tensor $\boldsymbol{B}$ of the polymer network and its gradient, $\operatorname{grad} \boldsymbol{B}$, the penetrant concentration ρ and its gradient, $\operatorname{grad} \rho$, and the temperature T and the internal state variable(s) β[5,11]:

$$\begin{aligned} g &= \hat{g}(\boldsymbol{B}, \rho, T, \beta) \\ \boldsymbol{K} &= \hat{\boldsymbol{K}}(\boldsymbol{B}, \rho, T, \beta) \\ \boldsymbol{M} &= \hat{\boldsymbol{M}}(\operatorname{grad} \rho, \operatorname{grad} \boldsymbol{B}) \\ A &= \hat{A}(\boldsymbol{B}, \rho, T, \beta) \\ k &= \hat{k}(\boldsymbol{B}, \rho, T, \beta, \operatorname{grad} \boldsymbol{B}) \end{aligned} \tag{5}$$

where the overscript $\hat{f}$ denotes the response function from the quantity f.

For L and k, the following conditions must be fulfilled:

$$L \geqslant 0; \qquad k \geqslant 0 \tag{6}$$

The last two terms of equation (3) correspond to the so-called non-Fickian diffusion contributions. The second term is the diffusion contribution which is caused by the elastic deformation of the polymer network, while the third term is the contribution which is brought about by internal state changes in the polymer–penetrant systems. These contributions to the penetrant transport come from the variations of the 2nd and 4th terms in the Gibbs energy equation (see Appendix, equation (Al)). Depending on the kinds of deformation and the nature of the internal state changes, their components may have either positive or negative effects on the Fick diffusion flux. The second term of equation (3) can also be written in the following form:

$$L \operatorname{tr}\left(\boldsymbol{M}^{\mathrm{T}} \frac{\partial \boldsymbol{K}}{\partial \rho}\right) = L \sum_i \sum_k M^{\mathrm{T}}_{ik} \frac{\partial K_{ki}}{\partial \rho} \tag{7}$$

From equations (2), (3) and (7), and depending on the positive or negative value of $M^{\mathrm{T}}_{ik}\, \partial K_{ki}/\partial \rho$, this component of the second term in equation (3) would have either a positive or negative effect, respectively, on the diffusion flux. For example, for an expansion or a compression deformation the component $M_{ii} \partial K_{ii}/\partial \rho$ is positive or negative, while for sliding or rotation the component $M^{\mathrm{T}}_{ik} \partial K_{ki}/\partial \rho$ may have a negative value (see Appendix). The second term of equation (3) has no effect on the diffusion process in the following cases: when the deformation of the polymer network is isotropic, i.e. $\boldsymbol{M} = 0$, or when the deformation of the polymer network is independent of the penetrant concentration change, i.e. $\partial \boldsymbol{K}/\partial \rho = 0$. This happens only in the case in which there is no elastic deformation when the penetrant enters the polymer.

The third term in equation (3) is generally a sum of different components:

$$Lk \frac{\partial A}{\partial \rho} = L \sum_i k_i \frac{\partial A_i}{\partial \rho} \tag{8}$$

i.e. the interaction of the penetrant with the polymer

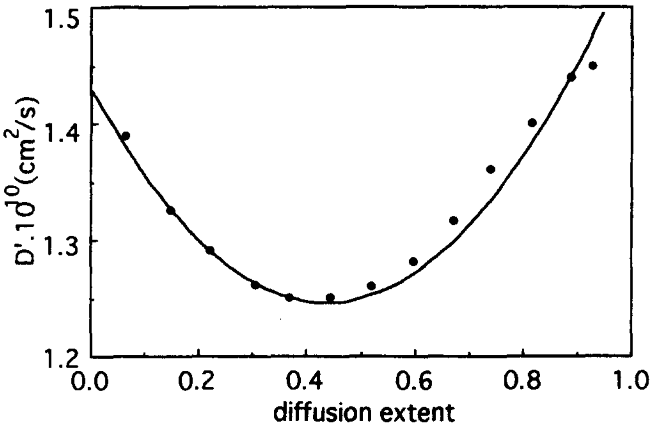

Figure 1 Plot of D' vs. diffusion extent α for the heptane/CTA system at 30°C

during the onset of diffusion may cause different independent internal state changes to occur. The penetrant not only causes the polymer network to swell (i.e. there are molecular chain configuration changes) but may also interact with polymer molecules to create secondary chemical species. For the case in which $\partial A_i/\partial \rho > 0$, the internal state change consumes energy. For example, a configurational change of the polymer chain caused by swelling usually requires some energy to transform the configuration in the stable state (at the lower energy level) to a configuration of a less stable (i.e. higher energy) state. As one can see from equations (3), (6), and (8), this component of the third term in equation (3) would have a positive effect on the diffusion flux. For the case in which $\partial A_i/\partial \rho < 0$, the change in the internal state of the polymer–penetrant system releases some energy (e.g. by the creation of secondary chemical species through the formation of weak bonds, such as hydrogen bonds, dipolar bonds, etc.). In this case the component of the third term in equation (3) would have a negative effect on the diffusion flux. If interactions between penetrant and polymer do not cause any internal state change, then $\partial A_i/\partial \rho = 0$, and in this case the third term of equation (3) has no effect on the diffusion flux.

Dynamic term related to internal state variables

From equation (5) it can be seen that all of the following quantities, namely the chemical potential of the penetrant, g, the chemical potential tensor of the polymer network elastic deformation, $\boldsymbol{K}$, the influence of the concentration gradient on the internal state changes, i.e. the proportional coefficient k, and the chemical affinity of the internal state changes, A, depend on the internal state variables β_i. Generally, internal state changes must be reflected in some dynamic changes, e.g. in the reorganization of molecular bonding in the system, while chemical reaction is reflected in the extent of chemical reaction. The parameter β_i is a function of a dynamic term which is related to the kinetic evolution of the internal state changes. In the membrane diffusion model, an appropriate procedure may be to consider the internal state variables to be a function of the extent of diffusion, $\alpha = J/J_s$ (the dynamic parameter), since the evolution of internal state changes are also reflected in a change in the extent of diffusion. As shown above, the diffusion flux is influenced by swelling and other processes involving internal state changes. When the diffusion flux reaches a constant value (i.e. the steady-state value, J_s), any internal state changes are terminated:

$$\beta_i = \beta_i(\alpha) \tag{9}$$

In many applications in which the system studied is close to equilibrium, the response functions are assumed to be linear. (This assumption was generally used in the Onsager equations.) By linearization from equations (5) and (9) one can obtain:

$$\begin{aligned} g &= g_0 + g_1\alpha \\ \boldsymbol{K} &= \boldsymbol{K}_0 + \boldsymbol{K}_1\alpha \\ k &= k_0 + k_1\alpha \\ A &= A_0 + A_1\alpha \end{aligned} \tag{10}$$

By substituting the quantities g, $\boldsymbol{K}$, k and A from equation (10) into equation (3) we can obtain:

$$D' = q\alpha^2 + r\alpha + t \tag{11}$$

where

$$\begin{aligned} q &= L\left(k_1\frac{\partial A_1}{\partial \rho}\right) \\ r &= L\left[k_0\frac{\partial A_1}{\partial \rho} + k_1\frac{\partial A_0}{\partial \rho} + \mathrm{tr}\left(\boldsymbol{M}^{\mathrm{T}}\frac{\partial \boldsymbol{K}_1}{\partial \rho}\right) + \frac{\partial g_1}{\partial \rho}\right] \\ t &= L\left[\frac{\partial g_0}{\partial \rho} + \mathrm{tr}\left(\boldsymbol{M}^{\mathrm{T}}\frac{\partial \boldsymbol{K}_0}{\partial \rho}\right) + k_0\frac{\partial A_0}{\partial \rho}\right] \end{aligned} \tag{12}$$

Equation (11) shows that the diffusivity D' varies with the extent of diffusion α according to a second-order function. The curve of D' *versus* α can be obtained by experimental measurements, from which the parameters q, r and t can be determined (see *Figures 1* and *2*). In *Figure 1*, the value of q is determined as 0.959 (i.e. >0), while in *Figure 2* q is found to be -11.43 (i.e. <0); this difference in sign clearly indicates the different nature of the interactions between different penetrants and the membrane material.

In practice, the $D'(\alpha)$ plot may have a more complicated pattern. It may be a higher-order function of the extent of diffusion, α, if the internal state change takes place far from the equilibrium condition, i.e. the response function cannot be considered to have a linear dependence on α, or if in the polymer–penetrant system there exist various independent processes of internal state changes with different time-delays and different intensities, and where D' represents the sum of all of these processes.

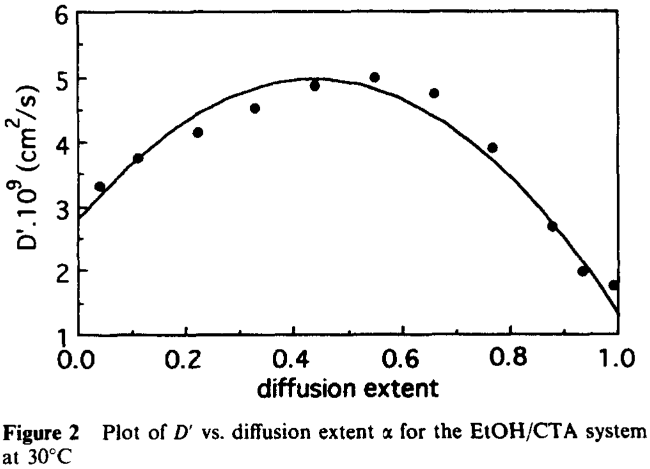

Figure 2 Plot of D' vs. diffusion extent α for the EtOH/CTA system at 30°C

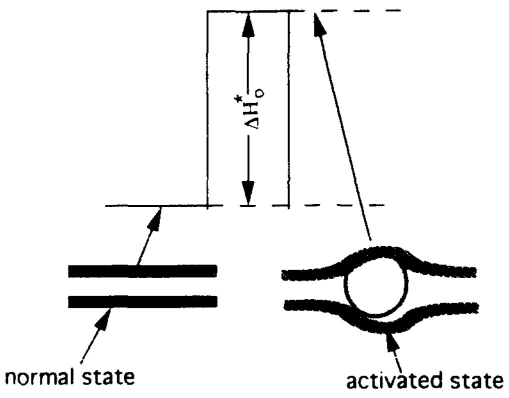

Figure 3 Schematic representation of the activation energy of diffusion in the 'jump theory'

RATIONAL THERMODYNAMIC RESULTS FROM THE POINT OF VIEW OF OTHER THEORIES

Macroscopic viewpoints of the problem

Many experimental studies, especially those concerning the diffusion of organic compounds in polymers, have showed that the diffusion processes do not obey Fick's law: the driving force for diffusion is not solely a concentration gradient, and the transport properties are not just functions of concentration[7-9]. All of these facts lead to suggestions of various other diffusion models, e.g. models of strain (-stress) dependence, models of time dependence, or models of spatial dependence, etc. However, each of these was successful in only describing some of the aspects. For instance, non-isotropic strong swelling gives rise to a strain driving force and to describe this phenomenon various strain models have been suggested[7,8]. From equation (3), the strain is described by using the second term, which gives, by a combination of equations (2) and (3)

$$J = D\,\mathrm{grad}\,\rho + L\frac{\partial \boldsymbol{K}}{\partial \rho}(\mathrm{grad}\,\boldsymbol{B}) \tag{13}$$

which can be rewritten in the following form:

$$J = D\,\mathrm{grad}\,\rho + LS \tag{14}$$

This equation corresponds well to the strain model first suggested by Crank, where S is called the stress deformation[7]:

$$S = \frac{\partial \boldsymbol{K}}{\partial \rho}(\mathrm{grad}\,\boldsymbol{B}) \tag{15}$$

Time evolution of the internal state variation of the polymer chain (represented by the internal state variable β) leads to the time dependence of the transport properties. From equation (3) one can write

$$\frac{\partial D'}{\partial t} = \frac{\partial D}{\partial t} + L\left[\frac{\partial A}{\partial \rho}\frac{\partial k}{\partial t} + k\frac{\partial}{\partial t}\left(\frac{\partial A}{\partial \rho}\right)\right] \tag{16}$$

This equation is similar to the one for the model of the structural relaxation process, suggested by Crank[7] and Petropoulos[9].

Anomalous diffusion may also be caused by non-uniform distribution of molecular configuration and morphology, i.e. gradients of the internal state variables which are different from zero (i.e. grad $\beta \neq 0$). This leads to a spatial variation of the transport properties, which can be described by using the third term of equation (3)[12]:

$$D' = D + k\frac{\partial A}{\partial \rho} \tag{17}$$

Microscopic viewpoints of the problem

From equation (3) we can consider D' to represent a frictional resistance of the diffusion medium against the driving force (i.e. the concentration gradient). From the microscopic viewpoint, molecular diffusion is regarded as a succession of random molecular jumps. Random walk theory yields[13]

$$D' = k\nu\lambda^2 \tag{18}$$

where k is a geometry related constant, λ is the mean jump length, and ν is the frequency of jumping which corresponds to the frequency at which a hole of a minimum required size can open up at an appropriate location. This frequency can be expressed in terms of either energy or volume fluctuation. Eyring's activation (or transition state treatment)[14] can be compared with the Arrhenius activation energy expression:

$$D' = D_0 \exp\left(-\frac{E}{RT}\right) \tag{19}$$

According to Brandt[15], E is the energy required to open up a cylindrical cavity, as depicted in *Figure 3*. For a given penetrant, E is a function of the geometrical parameters of the cavity (e.g. its diameter) and the flexibility of the polymer chain. If the polymer network is deformed then this process may lead to a deformation of the diffusion cavities. Therefore, the activation energy E may also be changed as a result of these deformations (shown in *Figure 4*). One can expect a decrease in the activation energy, when the formation of diffusion cavities is facilitated by the deformation of the polymer material. For instance, in case (a) (see *Figure 4*), expansion deformation may lead to a reduced activation energy, but in cases (b) and (c), for sliding and rotation deformations, respectively, these may both lead to increases in the activation energy. Equivalent to equation (19), equations (2) and (3) show that expansion deformation may have positive effects on the diffusion flux, while sliding and rotation deformations may have negative effects. From equations (2) and (3) we can say that if the internal state changes β_i require energy then this process

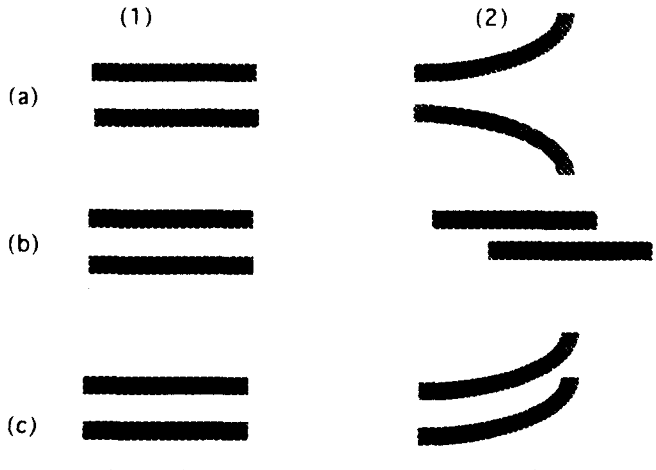

Figure 4 Schematic representation of the different types of deformation in a polymer network: (a) expansion; (b) sliding and; (c) rotation

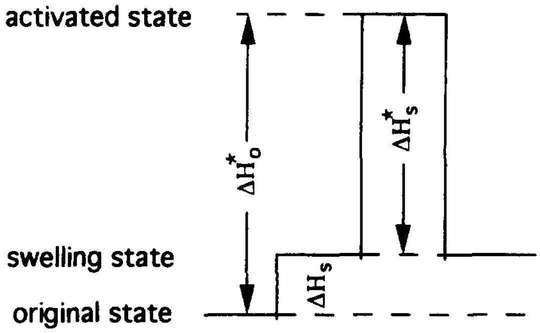

Figure 5 Schematic representation of internal state variation in a swelling process

may have positive effects on the diffusion flux, and since an internal process needs energy then the new configuration must be less stable than the original one. From the microscopic viewpoint, this is perfectly equivalent to the situation depicted in *Figure 5*, in which the decrease in the activation energy is due to the higher energy level of the new state in the transition state diagram. Similarly, equations (2) and (3) and analysis of the transition state show that an exothermal change in the internal state lead to an increase in the activation energy, and consequently a negative effect on the diffusion flux.

The alternative method of microscopic treatment is based on the so-called free volume theory^{16}:

$$D' = A\exp\left(-\frac{BV}{v_f}\right) \qquad (20)$$

where A and B are constants which depend on the molecular shape, V represents the minimum size of the hole required to permit a diffusion jump, and v_f is the fractional free volume of the polymer–penetrant system. As before, the effects of a penetrant on the diffusion process, as deduced from the rational thermodynamic treatment, can be found on the microscopic scale in the free volume theory. For example, expansion deformation leads to an increase in free volumes, i.e. an increase in diffusivity, and this is consistent with the predictions of equation (3). In a similar way, depending on the energy consuming or releasing nature of the process in the internal state changes which accompany the creation of new states of polymer configuration, the free volume of the system may be increased or reduced and this leads to increased or decreased diffusivity, as can be predicted quantitatively by equation (20).

In conclusion, we can say that there is no contradiction between the results of this approach and those which can be deduced from current diffusion theories. Moreover, it gives a general framework in which all types of behaviour can be accounted for.

POSSIBLE APPLICATION OF THE APPROACH TO MEMBRANE SEPARATION PROCESSES

The value of this approach lies in its ability to account for changes in a system with different parameters, and subsequently to be able to generate guidelines to improve membrane separation properties. In this section, we will consider the analysis of rational thermodynamics from this aspect.

A good membrane for practical purposes must show a combination of high selectivity and permeability. The membrane selectivity consists of two further fundamental parameters, namely solubility selectivity and diffusion selectivity. For a binary mixture of components A and B, the diffusion selectivity is determined by:

$$S_D = \frac{D'_A}{D'_B} \qquad (21)$$

It is well known that in the separation of organic liquid mixtures by pervaporation through dense membranes the interaction of penetrants with the membrane material usually leads to a swelling of the membrane, and in some cases it may result in the loss of membrane permselectivity. In other cases, strong membrane–permeant interactions may also lead to an increase in membrane permselectivity, with a reduced permeation flux. Therefore, it is important to know what may happen as the permeant penetrates and interacts with the membrane material: some of the above-mentioned processes may have very negative effects on the separation ability, even though the initial membrane characteristics were good. Furthermore, if one knows the nature of these processes (e.g. swelling, interaction exothermic or endothermic processes) one can enhance their positive effects and thus limit any negative effects on the separation ability. From equations (3) and (21), one can see that a suitable combination of all of these changes might be as follows. Regarding the low permeation component B, a better membrane is obtained when the sum of all of the changes that have arisen from the second and third terms in equation (3) is negative, or if it is positive, it must be very small. Under these conditions, one can increase the diffusion selectivity, or at least, the membrane does not lose its selectivity as a result of these processes. On the other hand, for the 'fast' permeant A, the sum of all the effects due to the last two terms of equation (3) should be positive, but not so large as to lead to an increase in undesirable effects on the slow component. If it is negative, then its magnitude must be very small. Therefore, a good material for separation of a given mixture must satisfy this given combination in order to obtain both a high permeability and selectivity. If this is not possible, then, again based on equation (3) one must find a suitable way to limit both the positive effects of the non-Fickian diffusion contributions on the transport of the slow component, and also the negative effects of the non-Fickian contributions on that of the fast component. The actual problem is to establish correlations between the chemical and physical structure of the polymer material and the way a permeant affects the material during its permeation. Different methods of polymer modification could then be used to change the behaviour of the material in permeation, such as crosslinking, polymer blending, grafting of groups or polymer chains, etc.

One method to identify the non-Fickian contributions consists of analysing the experimental curve $D'(\alpha)$. From the shape of the curve, one can deduce the type of process that is occurring, and from the derivatives $\partial D'/\partial\alpha$ one can estimate the intensity of this process. Using this information, one can set up a suitable combination or suggest a way to limit any undesirable effects. Various methods could be used to specify the nature of the phenomena involved in the change of the polymer–penetrant system during permeation (e.g.

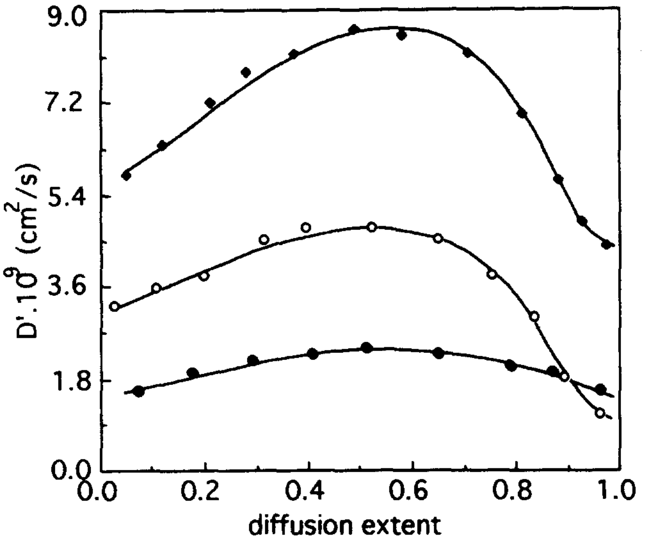

Figure 6 Plot of D' vs. diffusion extent α for the EtOH/CTA system at different temperatures: (●) 30°C; (○) 40°C and; (◆) 50°C

studies of the elastic deformation, swelling, weak chemical interactions, etc.). It is preferable, in fact, to use different methods to deduce the nature of the non-Fickian contributions.

All of these effects may occur in pervaporation, i.e. separation of liquid mixtures by selective vaporization through a dense polymer film. But for gas separations, the non-Fickian contributions are negligible, or even do not exist, so the question is how can one use the present approach for gas separation? One possibility is to artificially create non-Fickian processes by using an appropriate swelling agent to change the polymer, and then to 'freeze' the structure in the required state by an appropriate procedure. We have been using such a principle and promising results have been obtained in the application of membranes for gas separation.

The non-Fickian processes can also cause changes in the solubility of the penetrant in the membrane. This phenomenon is usually studied by using the Flory–Huggins approach in the framework of classical thermodynamics[17]. However, rational thermodynamics may also provide a means for studying it. The fact that the two phenomena can be studied in the same framework would make the analysis more coherent, and therefore the conclusions drawn would be more reliable.

RESULTS AND DISCUSSION

The diffusion experiments were carried out at different temperatures with pure methanol (MeOH), ethanol (EtOH), 1-propanol (1-PrOH), and heptane in various polymers, including cellulose acetate (CA), cellulose triacetate (CTA), cellulose acetate propionate (CP), and cellulose butyrate (CB). In addition, MeOH–EtOH and MeOH–PrOH mixtures in CTA membranes at 40°C were investigated. The experimental curves of $D'(\alpha)$ that were produced were then used to analyse the nature, intensity, and extent of the internal state processes with regard to the structure of the system. From a molecular structural viewpoint of penetrant and polymer, one can see that dipole interactions (and hydrogen bonding when it occurs) may arise between the OH group (polarity $= 5.7\,\mu\mathrm{C\,m^{-1}}$) of MeOH, EtOH and 1-PrOH and the -CO group (polarity $= 9.0\,\mu\mathrm{C\,m^{-1}}$) of CA, CTA, CP and CB. Swelling may be caused by a dipole induced interaction of the R radicals of the penetrants with the non-polar radicals and the backbone of the polymers.

As can be seen in all of the figures, the general features of the experimental curves that are produced (see *Figures 1, 2* and *6–12*) are consistent with the conclusions drawn from the rational thermodynamics analysis, i.e. dipole interactions between the polar OH groups of the alcohols and the polar CO groups of the polymers create more stable internal states than were originally created in the system. This leads to an energy release which is reflected by a negative value of the parameter q associated with the experimental curves of $D'(\alpha)$ (see *Figure 1* and also equation (11)). On the contrary, the interactions between the radicals of the penetrants with the polymer molecules lead to a swelling of the polymer chains; these processes need a certain amount of energy and the internal state is less stable than the original one. This is reflected by a positive value of the parameter q of the experimental $D'(\alpha)$ curves (see *Figure 2*). The parameter β represents internal state variations, i.e. molecular

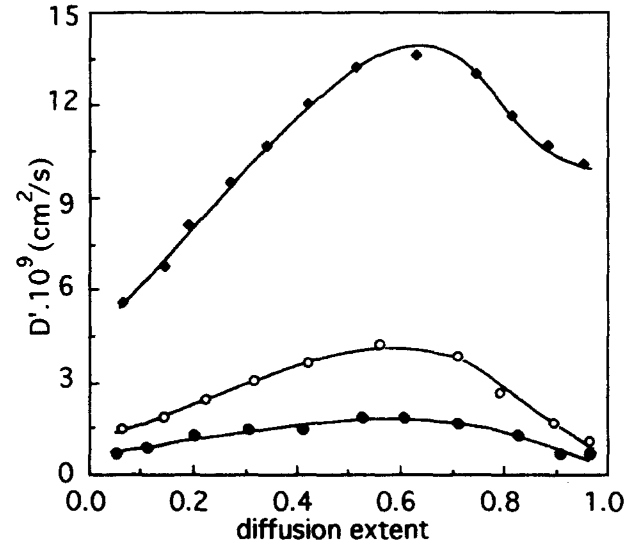

Figure 7 Plot of D' vs. diffusion extent α for the systems of EtOH with various cellulose esters at 30°C: (●) CA; (○) CTA and; (◆) CB

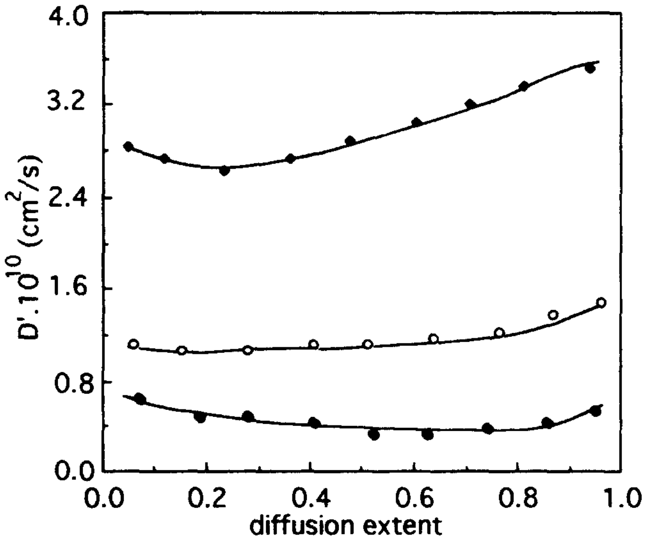

Figure 8 Plot of D' vs. diffusion extent α for the systems of heptane with various cellulose esters at 30°C: (●) CA; (○) CTA and; (◆) CB

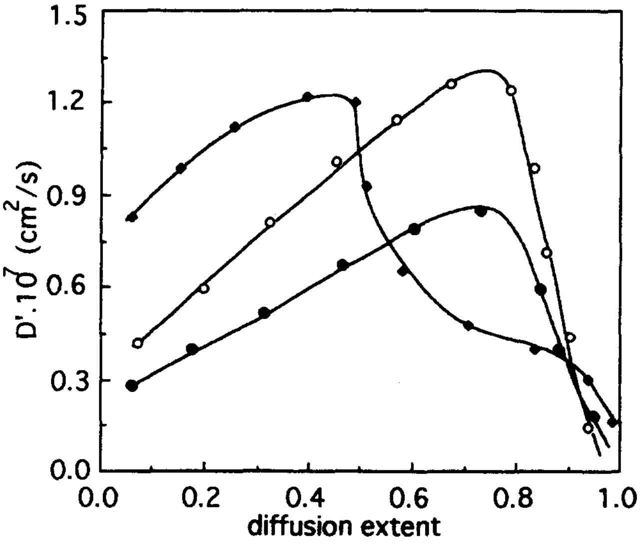

Figure 9 Plot of D' vs. diffusion extent α for the EtOH/CA system at different temperatures: (●) 30°C; (○) 40°C and; (◆) 50°C

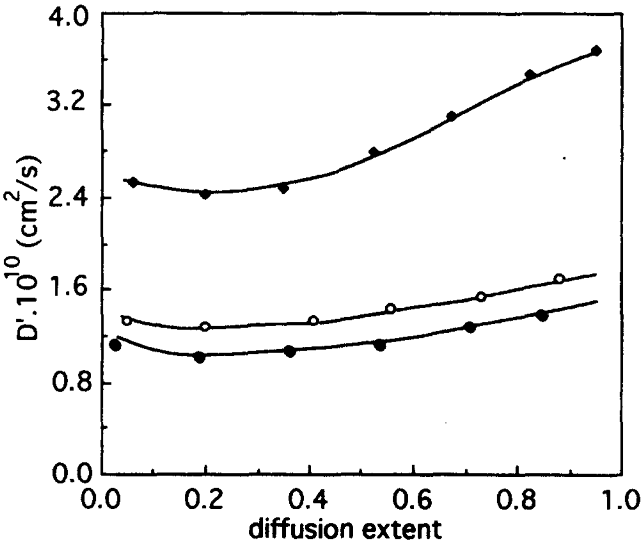

Figure 10 Plot of D' vs. diffusion extent α for the systems of heptane with various cellulose esters at 40°C: (●) CA; (○) CAP and; (◆) CB

structural changes, and therefore the curves of $D'(\alpha)$ must also reflect structure changes in the systems, e.g. by different shapes of these curves. This depends not only on the nature of the interactions but also on the molecular structure of the system, with the exception of the case in which no internal state variation occurs during diffusion. Differences in the behaviour of the same membrane (cellulose triacetate) in solvents of a different nature (ethanol and heptane) can be clearly seen in *Figures 1* and *2*. *Figures 6–12* show the different patterns that were obtained when the nature of the membrane, that of the liquid solvent and the temperature were changed. We shall discuss in the following the correlations between the shapes of the curves (i.e. concave, convex or flat) and the possible interactions within the respective polymer systems.

First, it is noted that concave curves were obtained for methanol, ethanol, or propanol with different cellulose ester membranes (see *Figures 2*, *6*, *7*, *9*, *11* and *12*). With heptane as the solvent, they can be either convex (see *Figures 1*, *8* and *10*) or flat (see *Figure 8*), depending on the nature of the membrane and the temperature.

In the first type of system the solvents are all alcohols, i.e. permeants which can interact with the cellulose esters by hydrogen bonding. The concave form corresponds to a negative value of the coefficient q, i.e. to an exothermic phenomenon. From a physical point of view, this is consistent with a strong (exothermic) hydrogen bonding. (Typically, the enthalpy of a hydrogen bond is $\approx -7\,\text{kcal mol}^{-1}$.)

The second type of system involves the non-polar solvent, heptane, in which the probable interactions would be weak and dipole induced. The swelling by this solvent would correspond to an endothermic process, due to the strain and configurational changes that are induced by this swelling. The convex form of the D' *versus* α curves for this permeant is entirely compatible with this physico-chemical analysis.

Figures 6 and *9* show the influence of temperature in the permeation of ethanol through cellulose triacetate (CTA) (*Figure 6*) and cellulose acetate (CA) (*Figure 9*). It can be observed that the higher the temperature the larger

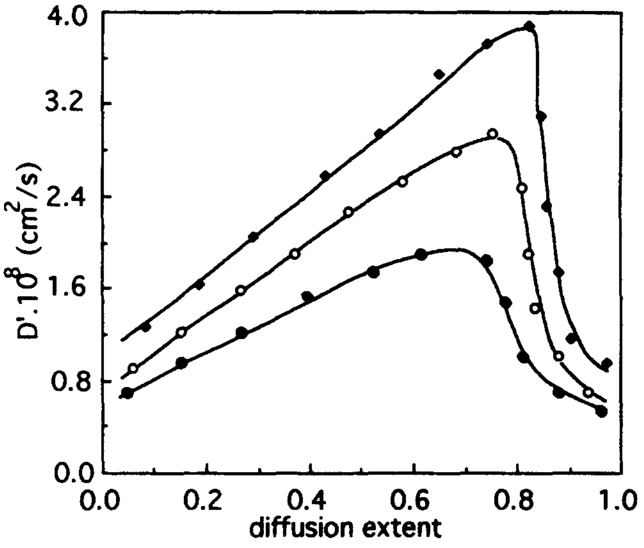

Figure 11 Plot of D' vs. diffusion extent α for the MeOH/CTA system at different temperatures: (●) 30°C; (○) 40°C and; (◆) 50°C

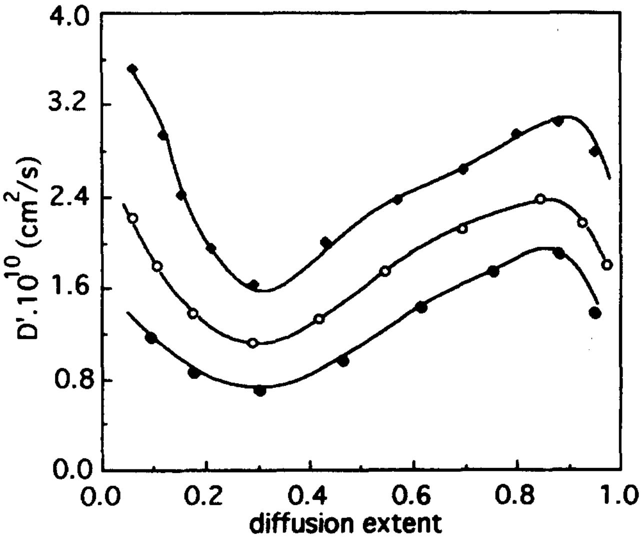

Figure 12 Plot of D' vs. diffusion extent α for the 1-PrOH/CTA system at different temperatures : (●) 30°C; (○) 40°C and; (◆) 50°C

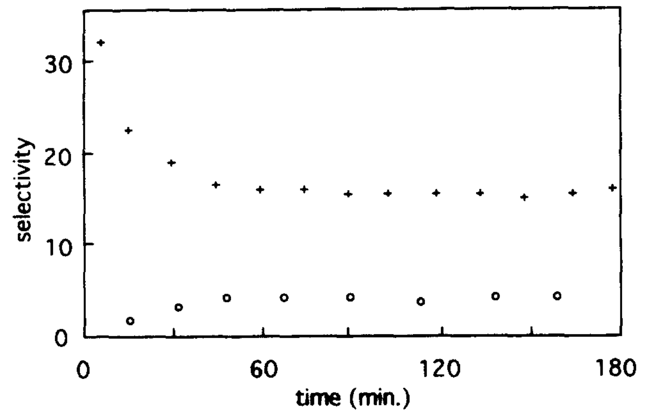

Figure 13 Pervaporation selectivity of the CTA membrane at 40°C, measured for 50:50 wt% mixtures of: (○) MeOH and EtOH and; (+) MeOH and 1-PrOH

the diffusion coefficient, and also the larger the magnitude of the changes due to solvent penetration.

Similar behaviour was observed for other systems (see *Figure 7*). The increase in the diffusion coefficient with the temperature is quite usual (increase in the energy of penetrant molecules). The higher magnitude of the changes probably comes from the higher diffusivity.

It appears from examination of the curves that have been obtained with the same solvent (ethanol), but with different cellulose esters, that the diffusion coefficient (and the magnitude of the changes) increases from CA to CTA and then to cellulose butyrate (CB) (see *Figure 7*) indicating stronger interactions of the CB and CTA polymers with the solvent. When the behaviour of the same membrane (CTA) in the permeation of different alcohols (methanol, ethanol and propanol) was investigated (see *Figures 9*, *11* and *12*), different conclusions could be drawn. For MeOH (which is the smallest molecule), the polymer–solvent interactions are strongest and they therefore dominate the other phenomena (showing a sharp maximum). For PrOH, the organic 'tail' is the longest and the swelling due to hydrophobic interactions is seen first (convex at low α), whereas the effect of hydrogen bonding (or polar interactions) appearing later (concave at high α). The case of ethanol is intermediate between the two other cases, as might be expected.

For the binary mixture of methanol and ethanol in the CTA membrane, from the results above one can expect that the dipole interactions between the polar OH groups of MeOH and EtOH and the polar CO groups of CTA prevail in the swelling. This causes a 'negative' effect on the diffusion flux of the slow component (EtOH). A low swelling, however, may cause positive effects on the fast component (MeOH). Therefore, in this case membrane diffusion selectivity increases during the transient stage of diffusion. For the binary mixture of methanol and propanol in the CTA membrane, from the above results one can expect the swelling processes to prevail over the dipole interactions. This may cause large positive effects on the diffusion flux of the slow component (PrOH), and leads to a decrease in the membrane diffusion selectivity during the transient stage of diffusion. If the change in membrane solubility selectivity is small then one can expect that the membrane selectivity of the mixture of methanol and propanol decreases in the transient stage, while for the mixture of methanol and ethanol it increases. Indeed, one can see in *Figure 13* that the CTA membrane loses its separation ability for the PrOH/MeOH mixture in pervaporation, as a result of swelling (about one half of its initial value). Similarly, from the results above one can expect that the selectivity of the CB membrane for the mixture of methanol and propanol also decreases in the transient stage of diffusion, but to a larger degree than that of the CTA membrane.

However, it should be mentioned that the above is only one way of interpreting the experimental results; if the change in membrane solubility selectivity is large, this interpretation would be incorrect. Therefore, in order to obtain a better understanding of the results one must also study component solubilities in the membrane materials. It can be expected that a combined analysis of sorption and permeation results will result in a better understanding of the transport processes in polymers, especially those under non-steady transport conditions.

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APPENDIX

Thermodynamics

In rational thermodynamics the general Gibb's equation (i.e. the second law of thermodynamics) for a heterogeneous mixture of solid and liquid (or gas) is given by:

$$\mathrm{d}F = -S\,\mathrm{d}T + \boldsymbol{K}\,\mathrm{d}\boldsymbol{B} + g\,\mathrm{d}\rho + A\,\mathrm{d}\beta \tag{A1}$$

where F and S are, respectively, the total free energy and entropy density of the mixture (per unit volume of system), T is the absolute temperature, $\boldsymbol{K}$ is the chemical potential tensor of elastic deformation, $\boldsymbol{B}$ is the elastic deformation tensor of the polymer network, g is the chemical potential of the penetrant, ρ is the partial concentration (mass density) of the penetrant, β is an internal state variable, and A is the affinity of the internal state change. The general axioms and principles of rational thermodynamics, and the difference between rational thermodynamics and the well-known irreversible thermodynamics can be found in the literature[1–3].

More explicitly, $\boldsymbol{K}$ is the energy corresponding to elastic deformations of the polymer network. It is defined by

$$\boldsymbol{K}=\frac{\partial F}{\partial \boldsymbol{B}} \tag{A2}$$

while g is the energy corresponding to concentration change and is defined by

$$g=\frac{\partial F}{\partial \rho} \tag{A3}$$

This wnergy g is related to the conventional chemical potential μ[18] by

$$\mu=Mg \tag{A4}$$

where M is the molecular weight of the penetrant.

A is the energy required for a molecular internal state change and is defined by

$$A=\frac{\partial F}{\partial \beta} \tag{A5}$$

By internal state changes, we mean all changes occurring in the polymer material, such as changes in the configuration of the polymer segments, formation of new superstructures in the polymer network (such as crystalline regions, aggregates of groups or inter- and intra-chain crosslinks due to dipolar, electrostatic or hydrogen bonding, entanglements of chains, etc.), and formation of complex species with solvent molecules between certain polymer sites, including species involving several solvent molecules with multiple 'physical bonds' (i.e. interactions). For an event which actually occurs, β is always positive. (The process has two possibilities, i.e. it either occurs or not, under given conditions.) Some conclusions can be drawn from an examination of the practical derivatives of the variables in equation (A2).

For an isolated system, $\mathrm{d}F=0$. From equation (A1) one can obtain the following Maxwell's equations.

Elastic deformation:

$$\left(\frac{\partial S}{\partial \boldsymbol{B}}\right)_{T,\rho,\beta}=\left(\frac{\partial \boldsymbol{K}}{\partial T}\right)_{\boldsymbol{B},\rho,\beta} \tag{A6}$$

From this equation one can see that if the elastic entropy increases and the elastic deformation process requires some energy from the system, then $\partial B_{ij}>0$ and $\partial B_{ii}>0$. This means that in isolated systems, the elastic deformation is swelling (expansion). The opposite situation (a decrease in the elastic entropy) corresponds to a 'de-swelling'.

Mixing process:

$$\left(\frac{\partial S}{\partial \rho}\right)_{T,\boldsymbol{B},\beta}=\left(\frac{\partial g}{\partial T}\right)_{\rho,\boldsymbol{B},\beta} \tag{A7}$$

This equation indicates that if the mixing entropy increases, then the penetrant tends to spread over the whole system. (Penetrant concentration tends to be uniform in the polymer matrix.)

Configuration change in swelling:

$$\left(\frac{\partial S}{\partial \beta}\right)_{T,\boldsymbol{B},\rho}=\left(\frac{\partial A}{\partial T}\right)_{\beta,\boldsymbol{B},\rho} \tag{A8}$$

From this equation one can see that if the configuration entropy increases, then the internal state energy of the polymer molecules also increases. This is understandable, because a change from a more ordered structure (e.g. due to an enthalpy minimized structure, obtained in a solvent-cast film by slow evaporation) to a less organized one due to swelling, would lead to a change in segmental bond angles and segmental bond lengths. One should bear in mind that this is an energy state of the polymer molecules, but not of the system. Of course, for a mixture in which there is no elastic deformation and no configuration change then only the mixing entropy increases.

Creation of some chemical species (by weak molecular interaction):

$$\left(\frac{\partial \Delta G}{\partial \beta}\right)_{n,T,\boldsymbol{B}}=\left(\frac{\partial A}{\partial n}\right)_{\beta,T,\boldsymbol{B}} \tag{A9}$$

where n is the number of moles of penetrant in the system. For the example of the combination of two species by physico-chemical interactions, i.e. $\mathrm{S}+\mathrm{P}\rightarrow\mathrm{SP}$, where S is the penetrant (solvent), P is the polymer and SP is the resulting chemical species, ΔG is the Gibb's energy change in the system due to the interactions, i.e. $\Delta G=\mu_{\mathrm{SP}}-\mu_{\mathrm{S}}-\mu_{\mathrm{P}}$. The necessary condition for an interaction to proceed is $\Delta G<0$[11,18]. Equation (A9) indicates that for $A<0$, the interaction creating a chemical species releases energy.