

Diffusion of Two Associated Solvents in Various Compositions Through a Swelling Polymer Material, EVAc

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Received 27 October 2005; accepted 23 March 2006

DOI 10.1002/app.24622

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The particular sorption by a swelling polymer with the transfer of hydrocarbons was studied in order to evaluate some barrier properties of this material. The transfer of two types of solvents through two varieties of ethylene vinyl acetate was investigated: absorption of pure toluene and pure *n*-hexane and absorption of a toluene/hexane mixture in various compositions. A comparison between the two processes showed that these transfers were very different and depended on two factors: vinyl acetate content and

composition of the mixture. The kinetics of absorption were calculated for various compositions. The profiles of concentration as well as the kinetics of swelling were evaluated using a numerical model deduced from the general theory of radial diffusion of a substance with change in dimensions. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 2099–2106, 2007

Key words: swelling; mixture solvents; polymer; diffusion

INTRODUCTION

The solution and transport behavior of low-molecular-weight substances in polymeric materials is a topic of interest for many fields of science and technology. The importance and relevance of such behavior has become more apparent in recent years with the accelerating development of separation membrane systems and highly impermeable or selectively permeable packaging or barrier films and the overall increase in the use of polymeric materials for diverse applications with the consequent exposure to various environmental agents.¹ Polymers are permeable. This may seem to be a disadvantage, in that polymeric containers may allow loss or contamination of their contents and aggressive substances such as water will diffuse into polymeric structures such as adhesive joints or fiber-reinforced composites and cause weakening. However, in some cases permeability is an advantage. One particular area where this is so is the use of polymers in drug delivery systems. These polymers have since been augmented by the introduction of materials such as ethylene vinyl acetate copolymer (EVAc) for intrauterine devices and various hydrogels, which may be used to construct devices that release larger molecules

in a controlled manner.² Following the transfer of a diffusing substance through polymer materials, a change in the dimensions of the materials is often observed. The extent of this change depends on the amount of the liquid absorbed. This generally appears with nonporous polymers such as rubbers or elastomeric materials³ that can absorb a volume of liquid representing up to 200%–300% of the volume of the polymer free from liquid.

There have been many interesting studies of the interdiffusion of two components, liquid or gas, in which volume changes on mixing do or do not occur. The particular sorption by a swelling sheet when only the thickness varies with the transfer of liquid was studied by considering the flux of liquid through sections with respect to the mass of the substance of the sheet.⁴ Two dimensionless numbers, known as Deborah's number and the swelling interface number, were thus introduced as criteria for prediction of diffusional solute.⁵ The kinetics and degree of equilibrium of swelling were studied with different solvents of interpenetrating polymer networks. In this complex system, the number of phases present was found to play a key role, among other factors.⁶ The kinetics of swelling of spherical acrylamide gels were determined and studied by considering shear modulus.⁷ Few studies have investigated the kinetics of swelling following the diffusion of a liquid through a polymer.⁸ A good knowledge of the process of the transport of liquids controlled by diffusion in which there

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is a subsequent change in the dimensions of the solid is of high interest because of the wide use of polymers, especially for the swelling of biocompatible polymers in oral dosage forms.⁹

The main purpose of the present study was to precisely determine the behavior of EVAc polymers in a toluene/hexane mixture in various compositions ranging from 0% to 100% in order to evaluate the barrier properties of these materials. Their capacity for absorption and their solubility are related to the effect of the composition on volume expansion. The kinetics of swelling as well as the diffusivity were determined and studied using a numerical model deduced from the general theory of radial diffusion of a substance with change in dimensions.¹⁰⁻¹²

THEORETICAL

Mathematical treatment

The process of radial diffusion through a sphere with a consequent change in dimensions can be expressed mathematically by eqs. (1) and (2):

$$\frac{\partial u}{\partial r} = \frac{u^2}{r^2} \left[1 - \frac{C(u,t)}{d} \right]^{-1} \quad (1)$$

$$\frac{\partial}{\partial t} \left[C \left(1 - \frac{C}{d} \right)^{-1} \right] = \frac{1}{u^2} \cdot \frac{\partial}{\partial u} \left[\frac{r^4}{u^2} \cdot D \cdot \left(1 - \frac{C}{d} \right) \cdot \frac{\partial C}{\partial u} \right] \quad (2)$$

These relations represent the general form of the diffusion.¹²

When the amount of diffusing substance is very small and not followed by a subsequent change in dimensions of the solid, that is, when the volume of liquid transferred can be neglected, then $(1 - C/d) \rightarrow 1$ and the radial abscissa $r \rightarrow u$; thus, eqs. (1) and (2) reduce to the second Fick's equation for radial diffusion in a sphere:^{13,14}

$$\frac{\partial C}{\partial t} = \frac{1}{r^2} \cdot \frac{\partial}{\partial r} \left[r^2 \cdot D \cdot \frac{\partial C}{\partial r} \right] \quad (3)$$

where D is the diffusivity, C is the concentration of the liquid, and R is the radius of the spherical surface considered.

When the diffusivity is constant, a solution can be obtained from eq. (3):¹⁴

$$\frac{M_t}{M_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{n^2 \pi^2}{R^2} \cdot Dt\right) \quad (4)$$

where M_t and M_∞ are the amounts of matter transferred at time t and at equilibrium, respectively; n is an integer; and R is the radius of the spherical beads.

Another solution can be obtained¹⁴ in terms of errors functions from eq. (5):

$$\frac{M_t}{M_\infty} = \frac{6}{R} \sqrt{\frac{Dt}{\pi}} - \frac{3Dt}{R^2} \quad (5)$$

When $t \rightarrow 0$, the second term on the right-hand side of eq. (5) becomes smaller than the first term, leading to eq. (6).

Diffusivity is calculated from the slope of the straight line obtained by plotting the amount of liquid absorbed as a function of the square root of time, shown in eq. (6):

$$\frac{M_t}{M_\infty} = \frac{6}{R} \left[\frac{Dt}{\pi} \right]^{0.5} \quad \text{when} \quad \frac{M_t}{M_\infty}$$

Resulting from the penetration of liquid through the polymer beads, volume expansion can be expressed by eq. (7), as indicated previously:^{13,14}

$$\frac{V(u,t)}{V(u,0)} = \frac{\Delta(r^3)}{\Delta(u^3)} = \left[1 - \frac{C(u,t)}{d} \right]^{-1} \quad (7)$$

where $C(u,t)$ is the concentration of liquid at the radial abscissa, $r(u,t)$, and time t ; and d is the density of the liquid (g/cm^3).

Numerical treatment

A numerical model derived from the general theory of radial diffusion with a change in dimensions and constant concentration on the surface is used for the calculation of the new parameters.¹⁰⁻¹² The main results with the equations follow.

The sphere free of liquids is divided into N spherical membranes of a constant thickness, Δu , with $\Delta u = R/N$, and the radial abscissa of each spherical surface, u , is associated with integer j : $u = j\Delta u$ with $0 \leq j \leq N$.

- *Within sphere* ($1 \leq j \leq N - 1$) The new amount of liquid evaluated in a spherical membrane for an elapsed time, Δt , is:

$$BN_j = VN_j(CN_j) = B_j + 4\pi(G_{j+0.5} - G_{j-0.5})\Delta t \quad (8)$$

with function G :

$$G_{j+0.5} = r_{j+0.5}^2 \cdot D_{j+0.5} \cdot \frac{C_{j+1} - C_j}{r_{j+1} - r_j} \quad (9)$$

and the new concentration at time $t + \Delta t$ was:

$$CN_j = BN_j \cdot \left[4\pi \left(\frac{R}{N} \right)^3 \cdot \left(j^2 + \frac{1}{12} \right) + \frac{BN_j}{d} \right]^{-1} \quad (10)$$

- *Center of sphere* ($j = 0$) The new amount of liquid after the elapsed time, Δt , is:

$$BN_0 = VN_0(CN_0) = B_0 + 4\pi(G_{0.5})\Delta t, \quad (11)$$

and the new concentration is:

$$CN_0 = BN_0 \cdot \left[\frac{4\pi}{3} \left(\frac{R}{2N} \right)^3 + \frac{BN_0}{d} \right]^{-1}. \quad (12)$$

- *Surface of sphere* ($j = N$) During the absorption stage, the concentration on the surface is constant and equals the equilibrium concentration:

$$C_N = CEA \quad (13)$$

- *Amount of liquid in the sphere* The amount of diffusing substance in the sphere at time t is expressed in terms of the concentration of the substance at this time:

$$\begin{aligned} \frac{M'_t}{4\pi} \left(\frac{N}{R} \right)^3 &= \frac{C_0}{24} \left(1 - \frac{C_0}{d} \right)^{-1} \\ &+ \sum_{j=1}^{N-1} \left(j^2 + \frac{1}{12} \right) \cdot C_j \left(1 - \frac{C_j}{d} \right)^{-1} \\ &+ \frac{N^3 - (N - 0.5)^3}{3} C'_N \left(1 - \frac{C'_N}{d} \right)^{-1} \end{aligned} \quad (14)$$

where the concentration, C' , at position $N-0.25$ can be given by linear interpolation:

$$C'_N = \frac{1}{4}(3C_N + C_{N-1}) \quad (15)$$

EXPERIMENTAL

Materials

Two types of spherical beads made of ethylene vinyl acetate copolymer (EVAc) containing different vinyl acetate (VAc) contents, 14 and 28 wt %, were obtained from Elf-Atochem la défense (Paris, France).

Test conditions

Experiments were carried out in a closed flask with a stirring control rate. In the first step the beads were soaked in pure solvents—toluene and *n*-hexane—and in the second step they were soaked in toluene/hexane mixtures of various compositions, with toluene content ranging from 0 to 100 vol %, and were kept at 25°C. Liquid samples were taken after certain intervals for analysis (UV measurements), and the beads were weighed (using a balance accurate to 10^{-5} g). Volume

expansion was determined by a lens. The various compositions of the mixture were obtained, taking into account Scott and Flory's hypothesis (single-liquid approximation) that mixture composition is the same in the two phases and when a mixture (toluene–hexane) is considered one solvent.¹⁵ Thus, the volume of the mixture was expressed by $v_{\text{mixt}} = x_1v_1 + x_2v_2$ and the density of the mixture by $d_{\text{mixt}} = [(\%_1)v_1 + (\%_2)v_2]/(\%_1 + \%_2)$, where v_{mixt} is the volume of the mixture, d_{mixt} is the density of the mixture, x_i is the molar fraction of i , and v_i is the molar volume of i . Toluene concentrations of 0%, 20%, 40%, 50%, 60%, 80%, and 100% were used in the present investigation.

After presaturation with the toluene/hexane mixture, the beads were then immersed in a pure solvent, *n*-hexane, and UV measurement of the release of toluene that followed was performed with a UV 1100-Hitachi at 265 nm.

GPC was performed on a fraction of the mixture solvents released to verify that the toluene/hexane mixture was absorbed at the same proportion by the polymers beads.

RESULTS AND DISCUSSION

This study investigated sorption of toluene by two EVAc beads with different compositions and the effect of VAc content on the rate of absorption; profiles of concentrations of toluene that dissolved through EVAc beads with changes in dimensions; and the kinetics of swelling of toluene/hexane mixtures of various compositions by 14.40 EVAc and by 28.40 EVAc and compared the 14.40 and 28.40 beads for transfer of the mixture.

Absorption of toluene solvent by two varieties of EVAc beads

The stage of absorption was determined by immersing the two varieties of EVAc beads in pure toluene so that the external concentration was uniform, constant, and equal to the density of the liquid. Thus, the liquid concentration on the surface reached the value at equilibrium as soon as the process started. The spherical-shaped EVAc beads containing different VAc contents were tested for this process (Table I). An increase in volume expansion of the 28.40 EVAc beads followed

TABLE I
Characteristic Parameters of 28.40 and 14.40 EVAc Beads Soaked in Pure Toluene

	14.40 EVAc Beads	28.40 EVAc Beads
VAc (%)	14	28
D (cm ² /s) absorption $\times 10^7$	9.0	90
Volume expansion factor	1.2	1.33
M_∞ (%) absorption	72	128

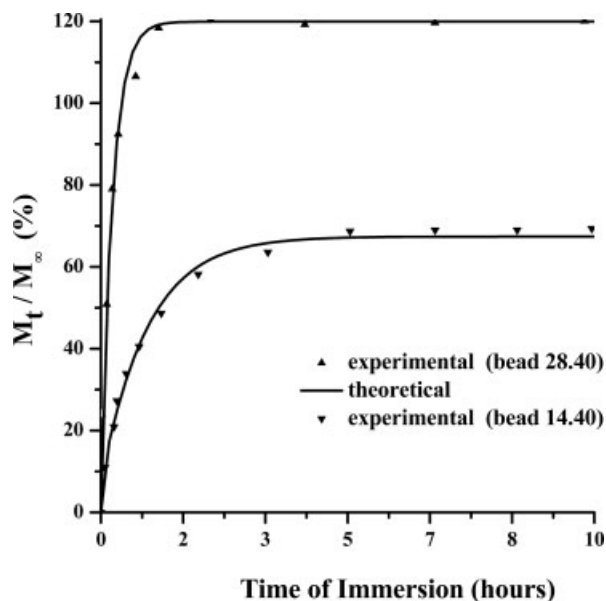


Figure 1 Kinetics of absorption of solvent toluene by two EVAc beads, 14.40 and 28.40.

by a nonsoluble gel was observed at the end of the step. The kinetics obtained by weighing the beads after various intervals is illustrated in Figure 1. Diffusivity, D , volume expansion factor, VEF, and rate of sorption, M_t/M_0 , are listed in Table I.

The following conclusions are worth noting:

1. In both cases, the absorption stage was reached (Fig. 1); nevertheless equilibrium was reached more quickly with a higher VAc content (28%).
2. The rate of absorption as well as the volume expansion of the EVAc beads largely depended on the VAc content, as shown in Figure 2 and

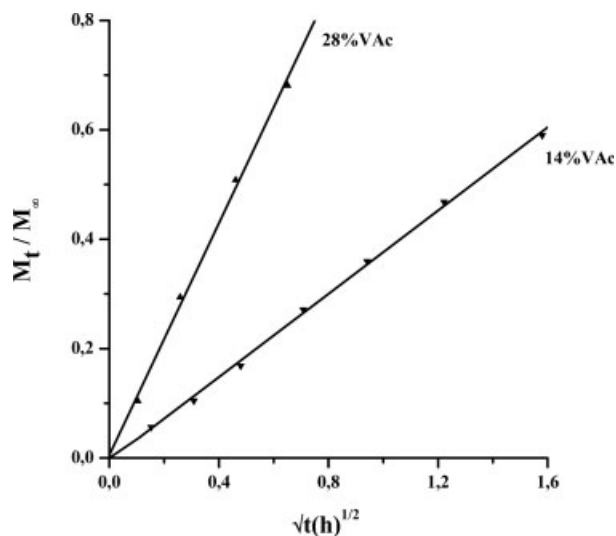


Figure 2 Determination of diffusivity of toluene solvent during the absorption stage.

Table I. The ratio of the absorption capacities for toluene was nearly twice as large with 28.40 beads than with 14.40 beads.

3. The plot of the amount of toluene absorbed versus $(\text{time})^{1/2}$ produced straight lines (Fig. 2). These processes can then be described by transient diffusion. Moreover, the diffusivity obtained from the slopes of these lines and from the amount of toluene absorbed at equilibrium by using eq. (6) depended on VAc content. Diffusivity was about 10 times larger with the beads that had a higher VAc content (Table I).
4. These results showed that VAc content was a determinant factor and that a concentration of 28% must be considered the limit in order to avoid different aspects of solubility.¹⁶

Profiles of concentration of toluene with change in dimension

Profiles of concentration of toluene that had moved through the polymers beads are shown in Figures 3 and 4 for the absorption stage. With the plots, obtained by computation of the toluene concentration at various intervals using the numerical model,¹⁰⁻¹² the progress of the liquid through the polymers beads can be easily followed. The concentration at time t , C_t , is expressed as a fraction of the maximum concentration, when the solid is saturated with the liquid, C_∞ . Changes in dimensions clearly appeared with an increase in the radius of the spherical beads.

In both cases, equilibrium was reached at the end of the absorption stage; nevertheless, the time required for this stage is rather short for the beads that had the

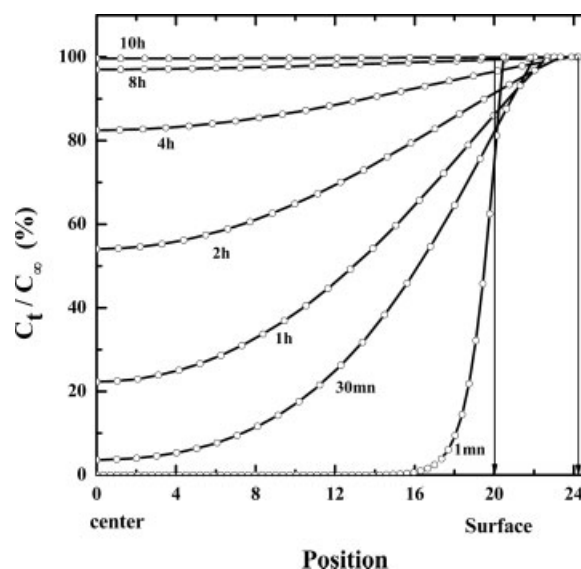


Figure 3 Profiles of concentration of pure toluene through EVAc bead 14.40 during absorption at various times.

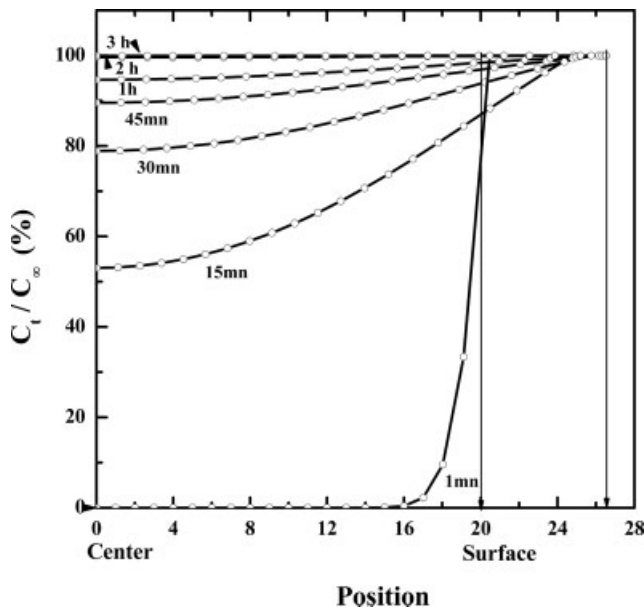


Figure 4 Profiles of concentration of pure toluene through EVAc bead 28.40 during absorption at various times.

higher VAc content. Figures 3 and 4 show that an increase in the radius of the spherical beads was observed. Thus, the higher the VAc content, the greater was the change in the dimensions. Moreover, as shown in Figures 3 and 4, the concentration of toluene reached equilibrium as soon as the process started because of the very high coefficient of mass transfer; the dimensionless number $h.R/D$ was larger than 100, as noted in ref. 17.

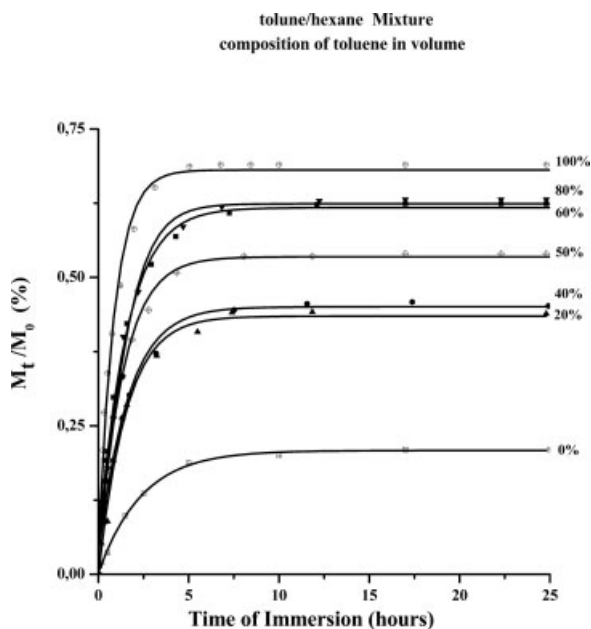


Figure 5 Kinetics of absorption of toluene/hexane binary solvent by EVAc bead 14.40.

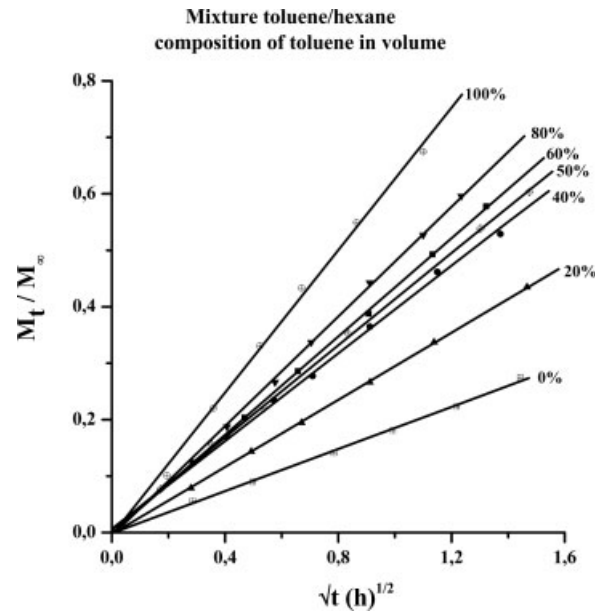


Figure 6 Determination of diffusivity of the toluene/solvent mixture during the absorption stage.

Kinetics of sorption process of the toluene/hexane mixture in various compositions by 14.40 EVAc beads

Toluene solvent was associated with *n*-hexane in various compositions ranging 0% to 100% to constitute a toluene/hexane mixture. No solubility was observed overall. The kinetics of matter transferred during these processes are shown in Figures 5 and 6.

In all cases, equilibrium was reached at the end of the absorption stage (Fig. 5). The amount of matter absorbed at equilibrium depended on the composition. For example, for the mixture with 50% toluene, the polymer beads absorbed about 50% of the equilibrium sorption (Table II). The absorbed liquids were transferred with a high matter transfer coefficient at the surface, as shown in Figure 5 (the tangent at the origin of time being vertical). This process can be described by transient diffusion, as shown by the straight line obtained when plotting the amount of matter transferred versus $t^{1/2}$ (Fig. 6). Moreover, diffusivity increased with mixtures whose composition had greater toluene concentration (Table II). Swelling was subsequently observed through the polymer beads regardless of the composition of the mixture (Table II).

An attempt was made to determine the diffusivity of each solvent in the mixture. Unfortunately, this process did not give the value of diffusivity because one peak appeared on the spectra of the fraction released by the beads. This result confirmed that this fraction was absorbed in the same proportion. Thus, the diffusivity evaluated was surely that of the mixture.

TABLE II
Characteristic Parameters of Diffusional Phenomenon through 14.40 EVAc Beads

	Mixture composition (% toluene)						
	0	20	40	50	60	80	100
D (cm ² /s) $\times 10^7$ absorption	5	5.5	5.75	7.5	7.75	7.85	90
M_∞ (%) absorption	20	44	45.7	53.9	62.3	63.5	128
h (cm/s)	very high	very high	very high	very high	very high	very high	very high
Volume expansion factor	1.08	1.13	1.134	1.15	1.162	1.163	1.33

Kinetics of absorption of toluene/hexane mixture in various compositions by 28.40 EVAc

The process of absorption of toluene/hexane mixtures containing various toluene concentrations ranging from 0 to 100% was studied, and the different kinetics of absorption are plotted in Figure 7 (the kinetics of the pure solvents hexane and toluene are not represented because of their lower rate of absorption).

In all cases, equilibrium was reached at the end of the absorption stage, which occurred after 5 h of immersion. Equilibrium was followed by gel formation and dissolution (Fig. 7). The amount of matter absorbed at equilibrium increased with the rate of toluene in the mixture, with the maximum reached at 80% (Fig. 8). The kinetics of swelling shown in Figure 7 demonstrate that the mixtures were transferred with a very low matter transfer coefficient at the surface, with the tangent at time zero being oblique, as shown in Figure 8. In the particular case shown in Figure 8, the sorption curves are sigmoid in shape with a single inflexion point at about 50% equilibrium sorption. Such curves represent one of three basic categories of diffusional behavior, known as diffusional case II, which occurs when sorption processes are strongly dependent on swelling kinetics.¹⁸ So it was difficult to

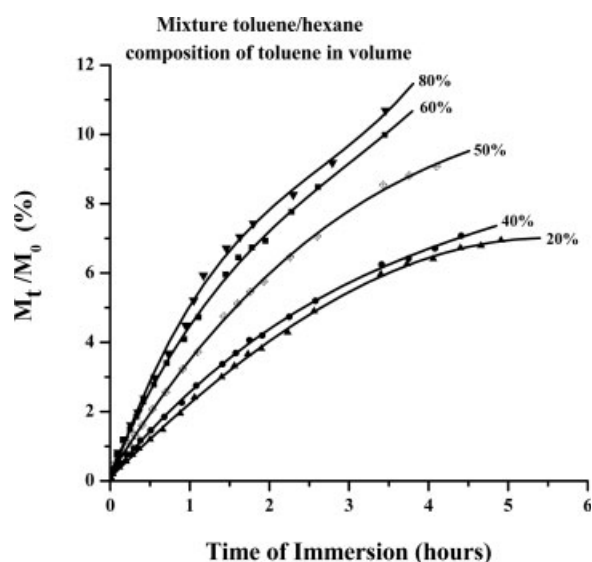


Figure 7 Kinetics of absorption of toluene/hexane binary solvent by EVAc bead 28.40.

calculate diffusivity with a higher accuracy. The volume expansion factor values were higher and nearly constant (Table III), that is, there was greater swelling, and the beads could absorb a volume of liquid of up to 1000% of that when they were empty.

In the literature many models have been proposed to describe some features related to this anomalous behavior.¹⁹

Comparative study

There were big differences between the two types of EVAc beads in the transfer of the toluene/hexane mixtures.

1. With the 14.40 EVAc beads, the process was simple and classical. It can be described by transient diffusivity. The liquids were transferred with a high matter transfer coefficient at the surface of the spherical beads; moreover, the beads remained spherical during all of the absorption stage.

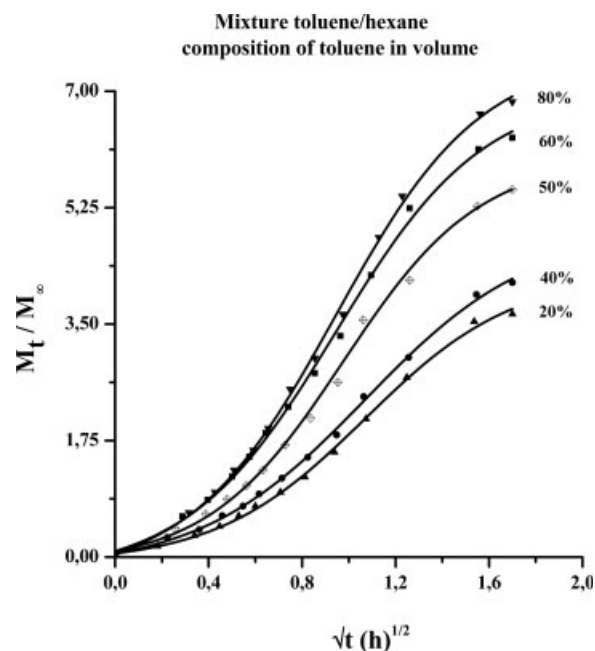


Figure 8 Variation in the amount of toluene/hexane transferred in the absorption stage by EVAc bead 28.40 versus the square root of time (M_0 is the weight of the empty bead).

TABLE III
Characteristic Parameters of the Mass Transfer of Toluene/Hexane through EVAc 28.40 Beads

	Mixture composition (% toluene)						
	0	20	40	50	60	80	100
M_{∞} (%) absorption	64.5	695	708	908	999	1060	128
h (cm/s)	very low	very low	very low	very low	very low		very low
Volume expansion factor	1.1	2.15	2.15	2.29	2.34	2.35	1.33

2. With the 28.40 EVAc beads, the process was more complex: with the pure liquid toluene, the amount of matter transferred was able to reach as much as 100% or more of the volume of the polymer. Nevertheless, with the toluene/hexane mixture, the results were very different. It was observed that a large amount of matter transferred and that the high swelling increased with an increase in the percentage of toluene. Also, the coefficient of mass transfer on the surface of the polymer was very low. Moreover, in all cases equilibrium was interrupted by gel formation and dissolution.

These results suggest that the changes in size observed with the 28.40 beads were probably influenced by two factors: (1) a strong swelling agent, the toluene/hexane mixture, and (2) highly reactive groups—the hydrophilic polar acetate of the VAc content of the polymer and the polar methyl group of toluene. The toluene/hexane mixture was a better solvent for the macromolecular chain of the polymer than was the pure solvent alone. In fact, the interdiffusion of these two liquids led to a stronger solvent that could be considered a unique solvent if the interactions between the two solvents remained lower (single-liquid approximation) according to Scott and Flory's hypothesis.¹³

The power of a mixture solvent is a result of the solubility parameter (δ) and the chemical structure of the backbone of polymer. The first parameter depends largely on the length of the hydrocarbon chain and on the aromatic cycle of the toluene.²⁰ That is why it can be easily deduced that the percent increase in toluene produced more swelling with 28.40 beads than with 14.40 beads. This difference in swelling led to a difference in the free volume of the random structure of the polymer chains, enabling more liquid to be absorbed. Moreover, the polarity led to an interaction and the preferential repartition of solvents around the polymer.

Approach of absorption mechanism

The main penetration mechanism, diffusion, may be considered mechanistically as transport of toluene molecules through holes in the polymer structure. The ease of transport mobility depends on the size

of these holes, which in turn depends on the free volume, which is the difference between the specific volume of the polymer and the actual volume of its molecules.

The greater volume of liquid absorbed by the 28.40 EVAc beads, representing up to 1000% of the volume of the polymer free from liquid, caused some damage such as deterioration of the mechanical properties and swelling, implying the combined action of the permeability of the materials and the solubility of the solvents. These effects resulted from chemical interactions between the penetrating solvent (toluene) and one of the constituent materials of the polymer (vinyl acetate content, VAc). Chemical interactions also included a strong attack at the fiber-matrix interface. The penetration of liquid then caused disorder in the distribution of the macromolecular chains of network polymer, so that the concentration of toluene was not uniform within the polymer. This prevented liquids from diffusing to the radius because there was no more isotropy. In this case, it was more complex to determine the diffusivity, as it depended on several parameters such as concentration, shape, and anisotropy.

In contrary of the effect observed with 14.40 EVAc beads, in which the weakness of the interactions of the VAc-solvent system did not lead to anisotropy of spherical bead, which conserved its shape during all of the process, the liquid concentration was uniform and the radial diffusion process took place.

The interaction mechanism occurred as follows. The chains of EVAc macromolecules presented hydrogen bonds (H and C=O). The diffusion of toluene, considered a good solvent because of its higher solubility parameter, $\delta = 8.94$, presented an active center very rich with π electrons, with an additive repulsive effect of methyl that broke these hydrogen bonds to reconstitute other hydrogen bonds between chains and the active center, thus enhancing the free volume (interchain distance more important) and allowing the important diffusion of toluene. This important diffusion can lead to dissolution of the system.

The intensity of the interactions are responsible for the formation of the complex of inserted toluene (chain-solvent-chain), consequently producing diversely accentuated swelling. It is also probable that the surface charges of EVAc are positive, thus creating electrostatic forces with the negative centers of

toluene, in opposition to the positively charged *n*-hexane. This was confirmed by the immersion of 33% EVAc beads, which completely disintegrated.

CONCLUSIONS

This study was concerned with aspects of the solubility and diffusion of two penetrant liquids in effectively nonporous polymeric materials. Two varieties of EVAc polymer beads with different VAc contents were used, and the transfer of two types of matter were considered: the absorption of toluene and *n*-hexane separately and the absorption of a toluene/hexane mixture in various compositions. The results showed that these transfers were very different. With the pure solvents the process was simple and classical and could be described by transient diffusivity, whereas with the mixture solvent, the process was complex, as it led to high swelling, showing an anomalous diffusion (not of the classical type). The overall transport process in EVAc polymer therefore depends on two major factors that, in turn, are governed by a wide variety of factors related to composition, VAc content, and experimental conditions. An attempt to correlate the rate of absorption with the composition of binary mixture solvents was also done. The mathematical model based on a numerical method with finite difference was successfully tested, and the basic parameters were determined with accuracy.

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