

# Studies on the Diffusion Characteristics of Some Aromatic Solvents into Polypropylene Film

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**ABSTRACT:** The sorption properties of the solvents benzene, toluene, and xylene into polypropylene films at 40, 60, and 80°C have been investigated. The diffusivity and permeability of the solvents into polypropylene films were found to increase in the order of solvent, benzene, toluene, and xylene at the different temperatures studied. The properties were also found to be temperature dependent. The solubility of the solvents into polypropylene films was found to be highest in toluene, followed by xylene, and least

in benzene. However, a general increase in solubility with temperature was observed for all the solvents studied. The calculated values of activation energy of diffusion did not show any relationship with solvent properties. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 1985–1989, 2006

**Key words:** diffusion; activation energy; polypropylene; films

## INTRODUCTION

The diffusion of organic molecules through polymeric films has continued to receive adequate attention in the scientific literature. The interest provoked by these studies emanate mainly from the fact that knowledge gained are utilized in the concentration of sea water and treatment of effluent water,<sup>1</sup> microelectronics,<sup>2</sup> controlled drug release,<sup>3,4</sup> food packaging,<sup>5,6</sup> and separation science.<sup>7–9</sup> The understanding of the diffusion of solvents through polymeric films also helps polymer scientists in the selection of polymer materials and processing considerations to minimize sorption level in potential barrier polymers.

If the transport of organic molecules through a polymer in a polymer-solvent system is controlled by the rate of diffusion of the penetrant, the process is referred to as Fickian or Case 1 transport. Sorption data for much of the uptake process in Fickian systems can be expressed by the relationship,

$$M_t = Kt^n \quad (1)$$

where  $M_t$  is the mass of penetrant transported at time  $t$ , and  $K$  and  $n$  are system parameters. When the Fickian transport is obeyed,  $K$  in eq. (1) can be expressed as,

$$K = 4(D/\pi l^2)^{0.5} \quad (2)$$

where  $D$  is the diffusion coefficient and  $l$  is the thickness of polymer film. For most purposes, diffusion in rubbery polymers typically follows Fickian law.<sup>10</sup> On the other hand, diffusion in glassy polymers are non-Fickian or anomalous especially when the weight uptake of the solvents is high.<sup>11</sup> When the anomalies are caused by slow diffusion process when compared with the rate of polymer relaxation, the non-Fickian behavior is referred to as Case II transport.

Diffusion and solvent uptake are the limiting factors affecting polymer end-use applications because these processes might change the mechanical properties and sometimes cause destruction in polymer properties. An understanding of the solvent uptake in polymers requires a thorough knowledge of the following sorption parameters: the diffusion coefficient ( $D$ ), solubility ( $S$ ), and permeability ( $P$ ) of the solvents. The permeability coefficient is given by the expression<sup>12</sup>

$$P = D \times S \quad (3)$$

Factors that affect the diffusion processes in polymers have been identified and they include followings: the degree of solvent-polymer interactions and solvent properties such as hydrogen bonding, polarity, solubility parameter, solvent size and shape, among others.

Because of polypropylenes outstanding properties, it is used for an unusually wide range of applications, some of which bring it into contact with various solvents. Numerous sorption studies have been investigated using different solvents for solvent uptake in polypropylene films. Thus, Michaels et al.<sup>13</sup> reported

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that liquid flux rates through polypropylene films were faster for solvents with small absolute difference between solubility parameters of polymers and solvent, and *vice versa*. Uzoma and Isa<sup>14,15</sup> reported that the absorption of organic solvents into polypropylene films was governed by molecular size, polarity, and interaction constant of polypropylene-solvent systems. Uzoma and Ibrahim<sup>16</sup> studied the sorption and energetic properties of methyl acetate, ethyl acetate, trichloromethane, tetrachloromethane, and chlorobenzene into polypropylene film at 28, 40, 60°C. They found that the diffusivities, solubilities, and permeabilities were generally lower for polar esters, compared with the chlorosolvents, and that all properties increased with increase in temperature. Also reported were the swelling equilibrium and diffusion kinetics of the solvents *n*-hexane, toluene, and carbon tetrachloride into polypropylene films at 27°C. The sorption properties of the solvents acetone, benzene chloride, and dioxane into polypropylene films at 25°C have been reported.<sup>17</sup>

Aminabhavi and Phayde<sup>18</sup> reported on the sorption, desorption, resorption, and redesorption of carbon tetrachloride, chloroform, methylene dichloride, 1,1,2,2-tetrachloromethane, bromoform, tetrachloroethylene, 1,1,1-trichloroethane, and trichloroethylene into polymeric blend of ethylene-propylene random copolymers and isotactic polypropylene at the temperature intervals of 25–70°C. They found that at higher temperature, an increase in solvent diffusion and relaxation rate of the polymer accompanied by an increase in the polymer free volume resulted in a high equilibrium uptake, and that the smallest solvent among the series of liquids investigated exhibited higher diffusivity coefficient. Moaddeb and Koros<sup>19</sup> studied the kinetics and equilibria of sorption and desorption of *D*-limonene in three polypropylene films at 30°C (unoriented polypropylene, uniaxially oriented polypropylene, and biaxially oriented polypropylene) and found that the kinetics of sorption of a saturated vapor of limonene exhibited an increasing tendency toward Fickian transport as the degree of orientation of polypropylene film increased.

In the present study, we report the sorption characteristics of the aromatic solvents benzene, toluene, and xylene into polypropylene films at 40, 60, and 80°C. To our knowledge, the effects on the diffusion of the homology of the aromatic solvents benzene, toluene, and xylene into polypropylene films have not been reported. The present study affords a very good example of how the gradual changes in solvent properties (molecular weight, polarity, molar volume, etc.) affect the diffusion of solvents into polymeric films. The effects of temperature on the solvent diffusion parameters are also reported.

TABLE I  
Properties of Solvents Used

Solvent	Density (g cm <sup>-3</sup> )	Molecular mass volume ( $M_v$ ) (g/mol)	Dipole moment (D)	Solubility parameter (Mpa) <sup>1/2</sup>
Benzene	0.8790	78.12	0	18.7
Toluene	0.8661	92.14	0.36	18.3
Xylene	0.8650	106.17	0.70	18.2

## EXPERIMENTAL

### Materials

The polypropylene films used in this study was obtained from the Plastic Technology Development Centre (PTDC), Eleme Petrochemical Company Limited (EPCL), Rivers State, Nigeria. The polypropylene film was processed by the chill roll/water quench cast process in which the polypropylene melt was extruded from a slot die and cooled. The process involved the use of high extrusion temperatures (180–245°C). The polypropylene film has a melt flow index of 3.0 dg/min and specific gravity 0.9. The approximate thickness is about 0.33 mm. The analytical grade solvents used were benzene, toluene, and xylene (all of BDH Chemicals, Poole, England).

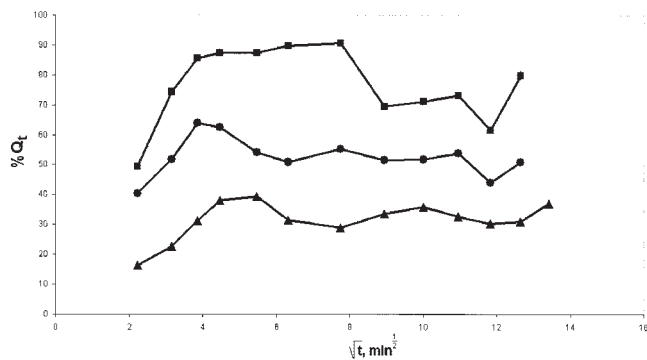
### Procedure for sorption experiment

Polypropylene film sample (0.10 g) was approximately weighed and put into a sample bottle with a cover. Benzene or toluene or xylene (20 mL) was poured into the sample bottle. The thermostatic water bath was equilibrated at the temperatures of 40 or 60 or 80°C for the sorption experiment. After equilibration at the required temperature of investigation, the sample bottle containing the film was put into the equilibrated water bath and allowed to equilibrate for the time required. At the expiration of the required time, each film was removed from the bottle using a forcep. The solvents adhering on the surface of the polypropylene films were removed by carefully pressing the films in between filter paper wraps. Care was taken to ensure that the solvents absorbed by the film were not removed during the process of wiping, using the filter paper. The wet film was weighed ( $W_o$ ) and the difference between the dry film ( $W$ ) and wet film was obtained ( $\Delta W$ ).

All the weighings were done using Sartorius Analytical Balance, Model A 200 S with a weighing accuracy of  $\pm 0.1$  mg.

## RESULTS AND DISCUSSION

The properties of the solvents (benzene, toluene, and xylene) used are presented in Table I. The sorption



**Figure 1** Percentage swollen quotient sorbed ( $\%Q_t$ ) into polypropylene film in xylene at different temperatures: ( $\blacktriangle$ ) 40, ( $\bullet$ ) 60, and ( $\blacksquare$ ) 80°C.

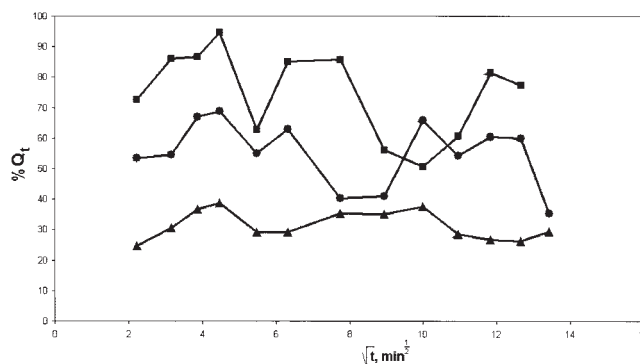
data of the solvents into polypropylene films at the different temperatures studied (40, 60, and 80°C) showed that the uptake of solvents into polypropylene films reached maximum values within 20–30 min depending on the solvent in question at all the temperatures studied. However, for xylene in polypropylene film, the uptake of solvents reached a maximum value within 15 min at 40°C and 80 min at 60 and 80°C, respectively. From the data obtained, it is evident that equilibrium solvent absorption was not obtained in contrast to what is generally reported of solvent absorption into polymers.<sup>14,15,18</sup> After the attainment of maximum absorption of solvents, a rise and fall pattern of the mass of solvent absorbed was obtained throughout the duration of the experiment. The decrease in the mass of solvent absorbed could be attributed to a leaching-out effect.<sup>18</sup>

The solvent uptake data expressed as the percentage quotient were obtained using eq. (4) for all the solvents studied at the different temperatures investigated. The percent swollen quotient ( $\%Q_t$ ) is given by the expression<sup>20</sup>

$$\%Q_t = \Delta W/W_o \times 100/\sigma_s \quad (4)$$

where  $\Delta w$  = change in weight of film (g),  $W_o$  = initial weight of film (g), and  $\sigma_s$  = density of solvent ( $\text{g}/\text{cm}^3$ ).

The percentage swollen quotient ( $\%Q_t$ ) at any particular temperature was plotted against square root of time and are shown in Figures 1–3. From these figures, the percent swollen quotient of solvents sorbed at any particular temperature ( $\%Q_t$ ) reached a maximum value and then falls, followed by a rise and fall pattern for the duration of the experiment. The observed rise and fall pattern in the  $\%Q_t$  of solvents sorbed by polypropylene may also be dependent on the structure of polypropylene. Future work may account for more details. It is important to note that the time interval during the wiping of adhering solvent did not generally exceed 30 s so that errors due to solvent

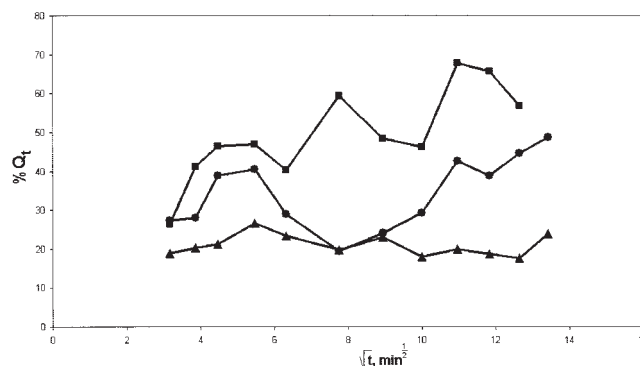


**Figure 2** Percentage swollen quotient sorbed ( $\%Q_t$ ) into polypropylene film in toluene at different temperatures: ( $\blacktriangle$ ) 40, ( $\bullet$ ) 60, and ( $\blacksquare$ ) 80°C.

evaporation other than that from the surface are considered insignificant. Also, the uncertainties in the determination of the mass of the swollen polymer that may arise from the “blotting” procedure (since the blotting may sometimes “blot-out-less” or “blot-out-more than” the solvent adhering on the surface of the polymer sample depending on the pressure applied) was taken care of with the skill acquired by repeated determinations.

Equilibrium sorption was not observed as was pointed out earlier from these figures. Several studies have indicated that the weight gain curves for polymers immersed in different solvents show a decrease after reaching a maximum.<sup>21–24</sup>

The diffusion coefficient ( $D$ ) was obtained from the linear of the curves of Figures 1–3, using the least square method and are given in Table II. The diffusion coefficients of the solvents were observed to increase with increase in temperature. This is in general agreement with the findings of Uzomah and Ibrahim,<sup>16</sup> who reported that this parameter of sorption increases with increase in temperature. The temperature effect is because the diffusing molecules are facilitated by the



**Figure 3** Percentage swollen quotient sorbed ( $\%Q_t$ ) into polypropylene film in benzene at different temperatures: ( $\blacktriangle$ ) 40, ( $\bullet$ ) 60, and ( $\blacksquare$ ) 80°C.

TABLE II  
Values of Diffusion Coefficient ( $D \times 10^6, \text{cm}^2 \text{s}^{-1}$ )

Solvent	Temperature ( $^{\circ}\text{C}$ )		
	40	60	80
Benzene	18.33	36.67	50.00
Toluene	35.00	43.33	88.33
Xylene	53.33	56.67	90.00

higher thermal energies at the increased temperature.<sup>13</sup> The diffusion coefficient ( $D$ ) was also found to increase from benzene to xylene, which means that diffusion of solvents into polymers is affected by molar mass of the solvent. Thus, the bigger the molar mass of the solvent, the higher the value of  $D$  and *vice versa*. The higher diffusion coefficient observed for xylene could be due to the similarity of its solubility parameter with that of polypropylene ( $\delta = 18.1 \text{ Mpa}$ ). The solubility parameter, which is a measure of intermolecular attraction, is a very important factor that affects solubility of polymers in solvents. Thus, polymers and solvents absorb or dissolve if they have similar solubility parameter values.

The values of the solubility of the solvents into polypropylene films were estimated from the maximum solvent sorbed per unit mass of the film and are given in Table III. For any particular solvent studied, the solubility was found to increase with an increase in sorption temperature. This finding is in agreement with the works of Michaels et al.,<sup>13</sup> and Uzoma and Isa.<sup>14,15</sup> From Table III, it was observed that solubility increases from benzene to toluene. A lower solubility was, however, found for the solvent benzene. Thus, the solubility of the aromatic solvents into polypropylene film is solvent dependent.

The permeability of the solvent molecules into polypropylene films was calculated using eq. (3). The values of the permeability of the solvents benzene, toluene, and xylene into polypropylene films at the temperature studied are presented in Table IV. From Table IV, it is clear that the permeability of the aromatic solvents into polypropylene film increases with increase in temperature as higher temperatures will tend to fluidize or make more flexible the polymer chains to facilitate solvent permeability. The permeability was also observed to increase with increase in

TABLE III  
Values of Solubility (g) of Solvents into Polypropylene Film

Solvent	Temperature ( $^{\circ}\text{C}$ )		
	40	60	80
Benzene	0.2346	0.3549	0.4114
Toluene	0.3370	0.5960	0.8175
Xylene	0.3280	0.5517	0.7562

TABLE IV  
Values of Permeability ( $P \times 10^6, \text{g cm}^2 \text{s}^{-1}$ ) of Solvents into Polypropylene Film

Solvent	Temperature ( $^{\circ}\text{C}$ )		
	40	60	80
Benzene	4.30	13.02	20.50
Toluene	11.80	25.83	39.56
Xylene	17.50	31.33	68.00

molecular weight, molecular mass volume, and dipole moment of the aromatic solvents. However, the permeability of the solvents into polypropylene films decreased with increasing values of the density and solubility parameters of the solvents.

### Energies of absorption

To obtain the activation energy of absorption of the aromatic solvents into polypropylene films, the data on diffusion coefficient ( $D$ ) have been treated by the Arrhenius type expression

$$D = D_0 \exp(-E_D/RT)$$

where  $E_D$  is the activation energy of diffusion, which is a function of the intra- and interchain forces that must be overcome to create the space for a diffusional jump of the penetrant molecule,  $D_0$  is a pre-exponential factor, and  $RT$  has the conventional usual meaning. Plots of  $\log D$  against  $1/T$  for the aromatic solvents were made and the calculated activated energy of diffusion are shown in Table V. From Table V, it is evident that there is no relationship between the activation energy of diffusion into polypropylene films and the solvent properties. Generally, the activation energy of diffusion ( $E_D$ ) will be greater, the larger the size of the solvent molecule and *vice versa*. From Table V, the order in the value of  $E_D$  into polypropylene films obtained is toluene > benzene > xylene. The obtained  $E_D$  values did not show any regular trend with solvent size; the molar mass volume of the solvents is in the order: xylene > toluene > benzene. Thus, the activation energy of diffusion into polypropylene films may depend on the structure of the solvents.

TABLE V  
Values of Activation Energies of Diffusion ( $E_D$ ) of Solvents into Polypropylene Film

Solvent	Activation energies ( $E_D$ )/(KJ mol $^{-1}$ )
Benzene	15.96
Toluene	23.93
Xylene	1.58

### CONCLUSIONS

The sorption properties of the solvents benzene, toluene, and xylene into polypropylene films have been investigated. The diffusivity, solubility, and permeability of the solvents into polypropylene films were found to increase with increase in temperature. The solubilities of the solvents were observed to depend on the nature of solvent. The calculated values of activation energy of diffusion did not show any relationship with solvent properties.

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