INTRODUCTION

Significant improvements in the performance of polymeric membranes for gas separation have occurred for the last two decades, and the basic understanding of the relationships between the structure, permeability and selectivity of polymer membranes has been greatly advanced. Both because of the polymer technology involved and for scientific reasons, there is an increasing interest in efficient measuring methods for characterization of the diffusion behavior of solvents in polymer matrices. However, the segmental flexibility of polymeric membranes often limits their ability to discriminate similar-sized penetrates, and they often lose performance stability at high temperatures. Several studies on the permeation and similar-sized penetrates, and they often lose performance stability of solvents in polymer matrices. However, the segmental flexibility of polymeric membranes often limits their ability to discriminate similar-sized penetrates, and they often lose performance stability at high temperatures. Because of the polymer technology involved and for scientific reasons, there is an increasing interest in efficient measuring methods for characterizing the diffusion behavior of solvents in polymer matrices. However, the segmental flexibility of polymeric membranes often limits their ability to discriminate similar-sized penetrates, and they often lose performance stability at high temperatures.

The information on organic vapor permeability through polymer films is essential for various kinds of applications, such as for the development of packaging materials, for the improvement of membranes for vapor separation processes, solvent devolatilization, residual monomers stripping, polymer synthesis, drying of paints and coating processes. Various techniques and approaches are reported to measure diffusion coefficient values. The techniques used include gravimetric sorption, isostatic permeation procedure, piezoelectric sorption, nuclear magnetic resonance, flame ionization detection, light scattering and inverse gas chromatography. The differential method, the integral method and the sorption method are the three general approaches to determine diffusion coefficients of gases or vapor in polymer membranes. Among these, the integral (time lag) method, conceived by Daynes, is the most commonly used, and this observes time lag as a function of diffusion coefficient. Since most of the conventional methods to determine the diffusion coefficient rely on bulk equilibration, the processes are slow and less accepted. In this context, a method based on Quantum Resistive Sensors (QRS) has great significance. QRS is nothing but composites containing conductive nano fillers. In this study, we used Carbon Nanotubes (CNT) as filler due to its availability and several reported works. Basically, the sensing mechanism involved in QRS is based on resistance change via Quantum tunnelling or hopping of electrons in the conducting polymer CNT nanocomposite. The conduction through polymer CNT nanocomposite is entirely different from the CNT alone, where the pi electrons of sp² hybridized carbon atoms make it highly conducting. In polymer nanocomposites, the conductivity depends on the amount of filler particles, their geometry and the architecture of the formed conductive network within the matrix, particularly if the particles have a very high aspect ratio and high surface area.
The method proposed here is proved to be reliable, simple and cheaper. Moreover, less quantity of materials required (even a few milliliters) for the analysis makes this technique extensively accepted. The time lag approach is effectively combined with the QRS technique in this work. We analysed the diffusion process of volatile organic solvents (VOCs) through poly (lactic acid) and poly (isobutylene-co-isoprene) membranes. The analytical determination of the diffusion coefficient was pursued for all systems effectively combining the "time-lag" method based on coupled Fourier transform infrared (FT-IR) and QRS sensor technique. The diffusion coefficients obtained from this method are compared with other methods. Since the diffusion coefficient values significantly vary with the polarity and purity of the solvents used, the technique developed can also be applied for detecting the purity parameters in this study.

**EXPERIMENTAL**

**Materials**

Poly (isobutylene-isoprene) was purchased from Exxon Company, Multiwalled CNT N-7000, from Nanocyl (Belgium). The materials were dried under vacuum at 60 °C temperature for 24 h prior to composite preparation. PLA from Ingeo™ Biopolymer 7001D, Poly Carbonate from Lexan 141 R/GE Plastics and Chitosan, Poly caprolactone (M<sub>n</sub> 14,000), all the other chemicals as well as all the solvents are obtained from Aldrich, France and used as received.

**Preparation of the polymer films**

Poly(isobutylene-co-isoprene) film has been prepared by adding curing agents such as stearic acid at 1.7 wt%, zinc oxide (activator) at 4.4 wt%, MBTS (2-bisbenzothiazole-2, 2'-disulfide) at 0.4 wt%, tetramethylthiuram disulfide at 0.9 wt% and sulfur (elemental sulfur S8) at 1.3 wt%, by mixing in an internal brabender mixer at 20 rpm, at 50 °C for 30 min. It is then compression molded at 160 °C for the respective cure times determined. For making PLA films, calendaring process is used, and homogeneous films are prepared at 170 °C.

**Fabrication of vapor sensors**

Two types of sensors, one detecting the organic vapors (CNT, poly (carbonate) (PC)-CNT and poly (c-caprolactone) (PCL)-CNT) and the other detecting water vapors (chitosan-CNT) are prepared. Fabrication of vapor sensors was performed in two steps. First, 100 mg of PC and PCL were separately dissolved in chloroform under constant stirring and a solution of chitosan (Chit) in 1% acetic acid, all at 50 °C temperature. After obtaining a clear solution, the desired amount of Multi Walled CNT (in vol. %) was dispersed under sonication for 1 h at 50 °C and kept degassing for 30 min to achieve homogeneous CNT, PC-CNT, PCL-CNT and Chit-CNT dispersions. In the second step, QRS transducer films were processed by spray deposition layer-by-layer technique onto inter-digitated electrodes. The layer-by-layer spraying of QRS solution is done with a homemade device allowing a precise control of nozzle scanning speed (V<sub>n</sub> =10 cm.s<sup>-1</sup>), solution flow rate (index 2), stream pressure (ps = 0.20 MPa) and target to nozzle distance (d<sub>n</sub>, = 8 cm). During solvent evaporation, QRS micro beads of 50–100 nm can weld to form hierarchical 3D networks by percolation. After fabrication, vapor sensors were conditioned overnight at 30 °C in controlled atmosphere. Type of sensors, number of layers on sensor and their mean initial resistance (R<sub>0</sub>) are shown in Table 1.

<table>
<thead>
<tr>
<th>Sensor</th>
<th>No. of layers on electrode</th>
<th>Initial resistance (av.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNT</td>
<td>4</td>
<td>58 ± 5 kΩ</td>
</tr>
<tr>
<td>PC-CNT</td>
<td>8</td>
<td>5.2 ± 1.2 kΩ</td>
</tr>
<tr>
<td>PCL-CNT</td>
<td>12</td>
<td>65 ± 10 kΩ</td>
</tr>
<tr>
<td>Chit-CNT</td>
<td>12</td>
<td>2.1 ± 0.2 kΩ</td>
</tr>
</tbody>
</table>

**Sorption studies**

The circular samples of poly (isobutylene-co-isoprene) composites from compression molded tensile sheets (2 × 2 × 0.2 cm<sup>3</sup>) were immersed in diffusion bottles containing the solvent toluene and were kept at constant temperature in a thermostatically controlled oven. Using an electronic balance (reproducibility within 10<sup>-4</sup> g) the weights of the swollen samples were periodically determined, until equilibrium swelling was reached. Since the weighing was done within 40 s, the error associated with the evaporation of the solvents is negligible. To provide volume dependencies of the mass transfer process, four volume levels were evaluated: 0.3, 1, 5 and 10 ml. The solubility coefficients for polymer films were determined gravimetrically at 25 °C over a range of permeant vapor concentrations. Under these experimental conditions, equilibrium sorption times of less than 30 h were observed.

The swelling data is used to calculate diffusion coefficient (D), which is a measure of the ability of vapor molecules to move into the polymer. The diffusion coefficient (D) is calculated using the data fitting eqn (1) for sorption of a penetrant by a polymer film, as described by Crank:

\[ D = \pi \left( \frac{4 \theta t}{Q_\infty} \right)^2 \]  

Where \(i\) is the thickness of the dry sample, and \(\theta\) is the slope of the initial linear portion of the curve of \(Q\), versus \(\sqrt{t}\); and \(Q_\infty\) is the mole percent uptake of the solvent at infinity. The value of \(Q_\infty\) can be obtained from the following eqn (2).

\[ Q_t = \frac{M_t}{M_r} \times \frac{100}{M_i} \]  

Where \(M_t\) is the mass of the solvent up taken at time interval \(t\), \(M_r\) is the relative molar mass of the solvent and \(M_i\) is the mass of the dry sample. For each experimental run, sorption of solvent by the rubber sample was monitored for an additional 24 to 48 h after reaching steady state.

**DETERMINATION OF DIFFUSION COEFFICIENT BY FT-IR SPECTROSCOPY AND QRS SENSOR USING TIME LAG METHOD**

**Experimental setup**

Figure 1 shows the experimental setup for the simultaneous determination of diffusion coefficient by suitably coupling the Bruker Vertex FT-IR spectrometer and the QRS sensor. The vapor...
sensing characteristics of the QR sensor were investigated by recording their chemo-electrical properties using a Keithley 6517A electrometer connected to a homemade device. The polymer film acts as a membrane to separate the source of vapor from a solvent chamber and QR sensor chamber. The polymer film separates the two chambers; one of which is filled with defined solvent to get saturated vapor pressure, and a quasi-constant pressure difference is applied to both sides of the membrane. The QRS placed in the second chamber gives change in relative resistance (\( A_R \)) versus time signals corresponding to the vapors getting in to the chamber after diffusing through the polymer film. During the experiment, the pressure inside the solvent chamber is nearly equal to the vapor pressure of analysed solvent inside the chamber, and that of QR sensor chamber is equal to atmospheric pressure. The device works at controlled room temperature 25 °C. The instrument records the relative resistance changes of the QRS when solvent enter from solvent chamber to sensor chamber.

During the experiment, the solvent vapor enters in to the chamber and Fourier transform infrared (FTIR) gives corresponding signals. In the FTIR, KBr is used as the blank. The time taken for the diffusant to penetrate the film with a constant thickness from FTIR is a measure of its mobility and allows calculating the diffusion coefficient. The time-dependent change of concentration of the diffusant in the sensor chamber was determined by using the ratio of absorbance signal intensity of the aromatic C–C group at 1506 cm\(^{-1}\) (characteristic peak of the diffusant toluene) and constant signal intensity of blank (1350 cm\(^{-1}\)). The electrical response of the sensor was also determined at the same time. For the reproducibility of the results, measurements were repeated thrice for each composite sample. Following the time lag method, the time \( t_{lag} \) from eqn (10) is measured. Depending upon the concentration of the vapor, the area of the curve varies. More clearly, the area under a characteristic signal of the diffusant increases with time when diffusant enter in to sensor chamber from solvent chamber through polymer (PLA) film.

**Preparation of the calibration curves of sensors**

Prior to the study, calibration curves of sensors were plotted as \( A_R \) versus concentration of the solvent vapor in ppm. This is done by controlling the organic vapor concentration and the flow rate of background gases following Kumar et al.\(^{[28]}\) method. The resistance relative amplitude or relative differential resistance responses (\( A_R \)) is according to eqn (5).

**RESULTS AND DISCUSSION**

**Calibration curve - Correlation between electrical responses and solvent volume fraction**

In order to characterize the conducting network architecture, the determination of current transport mechanisms operating in QRS is essential and is regarded as the first step. This can be done by plotting the current/voltage (I/V) curves.\(^{[39]}\) Fitting curves with the fundamental eqn (3) allows to determine the deviation of conduction from linearity and thus to evaluate the proportion of Ohmic and tunnel contribution.\(^{[40]}\)

\[
I = A.V^n
\]  

(3)

The value of \( n \) determines the type of conduction. If the value is close to 1, the conduction is mainly ohmic whereas larger values correspond to a tunnelling-dominated phenomenon. Since there is always an insulating polymer thin film present between two conducting fillers,\(^{[41]}\) the major component in QRS conduction is suggested to be the tunnel resistivity \( \rho_T \) expressed by eqn (4).

\[
\rho_T = e^\left(\frac{\pi m}{2h^2}\sqrt{\frac{2mV_c}{(h/2e)^2}}\right)
\]  

(4)

Where \( m \) is the electron rest mass, \( h \) is Planck's constant; \( V_c \) is the height of the barrier and \( w \) its width.

From eqn (4), it is clear that with the increase in voltage, electrons gain energy to cross the insulating barrier and thus give an additional contribution to conduction. Temperature also influences the conduction mechanism. The analysis of composites at different temperatures indicates a decrease in the power law exponent at high voltages with an increase in temperature. This clearly explains an increase in conductivity at higher temperatures, so that in the limit case, the characteristic I–V curves approach Ohmic conduction.\(^{[42,43]}\)

In the case of sensing applications, it is preferable to keep the transducer conductivity in Ohmic mode so that any perturbation of electrons circulation will generate a detectable tunnel flow.
The electrical resistance of filler-loaded polymer composite usually increases when it is exposed to vapors because of the breakage of conductive pathways due to swelling of the polymer and thereby increasing the filler/filler average gap. This damages the interconnected filler network in the composites and eventually results in the positive vapor coefficient (PVC) effect. Singh et al. [44] studied the swelling behavior of polymer matrix when exposed to saturated water vapor and observed that the solvent molecules enter into the nanoporous structure of the polymer and diffuse into all accessible volumes. If the polymer is soluble in the solvent, there is a strong attractive interaction between the polymer and the solvent which results in a net repulsive interaction between the polymer segments. Due to this reason, as soon as the coiled polymer chains “see” the solvent molecules, they start to swell. When these swollen polymer chains reaches a thermodynamic equilibrium with the solvent, the sorption process attains saturation. The stabilization of QRS electrical signal, corresponding to its thermodynamic equilibrium, is characterized by a plateau region after sufficient exposure to vapors. The swelling of polymer matrix causes the separation of the conductive particles and thus the concomitant diminution of the composite conductivity. [35] This process of partial disconnection of interconnected network can be observed as an enhancement in the resistivity of QRS. The amplitude of PVC is expressed as the variation in resistance of QRS relative to its initial resistance, as shown by eqn (5):

$$A_R = \frac{R - R_0}{R_0}$$  \hspace{1cm} (5)

where $R$ and $R_0$ are the QRS resistance in the presence of vapor and its initial resistance (in the dried state) in inert atmosphere, respectively. The magnitude of sensitivity of a QR sensor depends on many factors such as nature of the polymer matrix, filler concentration, initial resistance, vapor molecule characteristics, solubility parameter, etc. Among all these factors, the chemical nature of polymer matrices is the most important parameter that can determine $A_R$.

The correlation of VOC content with electrical response changes of three sensors (PC-CNT, PCL-CNT and CNT) with different organic vapors of toluene and ethanol is shown in Fig. 2(c,d) and also for Chit-CNT for water vapor in Fig. 2(a). Figure 2(b) summarizes the electrical responses of Chit-CNT sensors when exposed to different volumes of water vapor with on and off switching, and is related to Fig. 2(a). A linear calibration curve was obtained between the $A_R$ and its relative vapor concentrations (ppm). The limit of detection (LOD) and limit of quantification (LOQ = 3 LOD) of VOC sensors was calculated (about 10 ppm) from the calibration curve. It is clear that measurable resistance changes could be obtained at lower concentration levels of organic vapors. The linear part (assumed) of the relation between concentration and electrode response was evaluated by a regression technique and can be explained by eqn (6).

$$A_R = \frac{b_L(f'' - f)Q}{1 + b_Lf} + k_H + (f - f''), f''$$  \hspace{1cm} (6)

where $b_L$ is the Langmuir affinity constant, $f''$ is the vapor fraction over which Langmuir’s diffusion is replaced by Henry’s diffusion, $f$.
During the second step, the weight of the sample increases, as the model.

Diffusion coefficients from sorption technique

The amount of diffusing substance across a polymer liquid interface is monitored as a function of time by the equilibrium swelling method. The mole percentage of vapor uptake as a function of time for poly (isobutylene-co-isoprene) at 25 °C is illustrated in Fig. 3(a). The curves show two steps (Fig. 3(a)) in accordance with the slope of the linear parts. The final value is reached by an asymptotical approach. The three different steps involved in the reception of the vapor can be interpreted in the following way:

- At first, molecules diffuse into the polymer matrix; this is absolutely solvent free. In this step, the diffusion coefficient is independent of solvent (toluene) concentration in the compound.
- During the second step, the weight of the sample increases, because of the expansion of the chains of polymer matrix and based on reception of solvent. The surface area of the sample also increases.
- The third is the asymptotical approach, in which a swelling equilibrium is reached, which is defined by the chemical and physical crosslink density and solubility.

The diffusion coefficient is determined by calculating the slope (linear regression) using eqn (1). The value of the diffusion coefficient obtained is summarized in Table 2.

The device employed (Fig. 1) consists of two chambers separated by the film to be tested. The first chamber is “sensor chamber” having QRS sensor, and the second chamber is “vapor chamber” containing solvent inside, the tested polymer separated from the two chambers. The process of vapor diffusion through polymer membranes is referred to the transference of vapor molecules such as dissolved, low-molecular weight substances, up to a state of equilibrium, i.e. a concentration balance constituting its driving force. The integral (time lag) method is used to calculate diffusion coefficient using Fick’s law from the following.

The basis for the mathematical description of diffusion processes is Fick’s law, which explains an analogy between heat flux and mass flux in a polymer, based on free chain mobility. The transfer of a substance through a polymer matrix is thus proportional to the concentration gradient within a volume unit which can be represented as eqn (7).

\[ F = -D \frac{\partial c}{\partial x} \]  

(7)

Where \( F \) is the transfer rate (mass flux) per unit of volume and cross-sectional area, \( c \) is the concentration of the substance.

Figure 3. a) Sorption curve of IIR in toluene at room temperature (3 samples) b) Intensity (notation I) of relative solvent and Relative resistance (notation R) of QRS sensor signal in dependency on time (time lag method) for PLA film.
being diffused (diffusate), \( x \) is the distance of diffusion perpendicular to the cross section and \( D \) is the diffusion coefficient.

The diffusion coefficient \( D \) is a substance-specific variable that can be regarded as a constant at low concentrations, while a concentration dependency prevails at higher concentrations. With respect to eqn (8), Fick’s second law generally applies for one-dimensional diffusion in isotropic substances, e.g. in the direction of the \( x \) axis:

\[
\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad (8)
\]

Where \( t \) is time, and \( x \) is vertical distance from the membrane surface using the boundary conditions, \( c = c_1 \) at \( x = 0 \) and \( c = c_2 \) at \( x = l \).

Final simplified form of the expression relating to the total solute transferred with time can be summarized as eqn (9):

\[
Q(t) = \frac{AD\Delta c}{l} \left[ t - \frac{l^2}{6D} \right] \quad (9)
\]

where \( Q(t) \) is the total amount of solute transferred through a membrane of area \( A \) at time \( t \), and \( D \) is the effective diffusion coefficient. A graph of \( Q \) versus \( t \) approaches a straight line which intercepts the axis at \( t_{\text{lag}} = \frac{l^2}{6D} \). The intercept of the linear part of the curve is referred to as the lag time.

Diffusion coefficients are calculated from the intercept time and the membrane thickness (\( l \)) using eqn (10)

\[
D = \frac{l^2}{6t_{\text{lag}}} \quad (10)
\]

While using polymer film VOC vapor takes some time (time lag) to diffuse from vapor chamber to sensor chamber as shown in Fig. 4(b). Using time lag from eqn (10), we determine diffusion coefficient of vapor through polymer membrane.

### Diffusion coefficients from coupled FT-IR spectroscopy with QRS technique

The attenuated total reflectance FTIR spectroscopy is used for evaluation of additive diffusivity in polymer films or analysis of polymer surfaces. Using micro-interferometry, Gardiner showed a considerable change in diffusion coefficient with curative concentration, and he demonstrated that the sulfur diffusion between different polymers like NR, SBR and IIR is quite similar to diffusion in the homopolymer. FT-IR spectra of PLA film with vapor at different times using the experimental setup (Fig. 1) illustrated are shown in Fig. 3(b). The spectrum of pure solvent, toluene (standard), shows the characteristic signal of the aromatic C–C group in the region of 1506 cm\(^{-1}\). As the diffusion process progresses, there is an increase in solvent content in sensor chamber (Fig. 1), which causes the increase in signal intensity at 1506 cm\(^{-1}\). For all the arrangements studied, the behavior was similar. These findings indicate that an increase in the signal intensity in the region of a wavenumber of 1506 cm\(^{-1}\) depends on diffusion time.

As it can be seen in Fig. 3(a), there is an initial increase, but eventually a linear relationship develops. This plot has an

### Table 2. Diffusion coefficients \( D \) of toluene through PLA and poly(isobutylene-co-isoprene) films calculated by different techniques

<table>
<thead>
<tr>
<th>S.No</th>
<th>Polymer</th>
<th>Method</th>
<th>Medium</th>
<th>Diffusion coefficient (cm(^2).s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PLA</td>
<td>FTIR experiments</td>
<td>Vapor</td>
<td>1.24 E–9 ± 0.3E–9</td>
</tr>
<tr>
<td>2</td>
<td>PLA</td>
<td>QRS sensor experiment</td>
<td>Vapor</td>
<td>1.26 E–9 ± 0.4 E–9</td>
</tr>
<tr>
<td>4</td>
<td>IIR</td>
<td>QRS sensor experiment</td>
<td>Solvent</td>
<td>5.2 E–7 ± 0.4 E–7</td>
</tr>
<tr>
<td>5</td>
<td>IIR</td>
<td>Swelling experiments</td>
<td>Solvent</td>
<td>2 E–7 ± 0.2 E–7</td>
</tr>
<tr>
<td>6</td>
<td>IIR</td>
<td>Literature ([37])</td>
<td>Solvent</td>
<td>1.8 E–7</td>
</tr>
</tbody>
</table>

### Figure 4. a) Correlation between \( \chi \) (PLA-penetrant interaction parameter) and diffusion coefficients of volatile organic solvents (1 cm\(^3\)) through PLA. b) QRS sensor signals without polymer and with polymer film for toluene diffusivity.
intercept on the time axis known as the time lag. This is related to the diffusion coefficient that can be calculated by eqn (10). The diffusion coefficients of poly (lactic acid) and poly (isobutylene-co-isoprene) composites from different techniques are compared in Table 2.

### Diffusion coefficient by solubility parameter approach

The diffusion coefficient describes the kinetic aspect of the transport, which can also be explained through solubility increase mechanism based on the interaction between the penetrants and the polymer. In this comparison, 2-butanone, toluene, carbon tetrachloride and tetrahydrofuran are regarded as good solvents for PLA due to the similarity of solubility parameters and the occurrence of polymer swelling, whereas n-hexane, ethanol, methanol and water are considered as poor solvents. To better understand the PLA–VOC vapor interaction, we have used the sorption data to calculate the Flory–Huggins interaction parameter \( \chi \) of the system. This parameter estimates the interaction energy between the penetrant VOC species and the polymer segments. The interaction parameter can be calculated from eqn (11):

\[
\chi = \beta + \frac{V_1}{RT} (\delta_1 - \delta_2)^2
\]

Where \( \beta \) is a constant equal to 0.34, \( V_1 \) is the molar volume of the penetrant, \( \delta_1 \) and \( \delta_2 \) are the solubility parameters of the penetrant and the polymer, respectively. For calculation of \( \chi \), the mean value of 20.1 was selected as the solubility parameter value for poly (lactic acid). The results for the calculated interaction parameter, \( \chi \) values of PLA membrane with different VOC solvents are also included in Table 3. Since an increase in the mean values of solubility parameter causes \( \chi \) value to get decreased, the possible change occurring in solubility parameters is nullified. Theoretically, for a given polymer to be dissolved in a solvent, \( \chi \) should be less than 0.5, but here it is experimentally found that none of the solvents used are good for PLA dissolution. The diffusion coefficient values also support this observation.

### Comparison of the diffusion coefficient from sorption, FT-IR and QRS techniques

As indicated, the objective of this study was to investigate the correlation between the diffusion coefficient values obtained from sorption, FT-IR and QR sensor experiments. Diffusion coefficient values of PLA and IIR films over the considered vapor activity range, obtained from the different procedures, are compared in Table 2. Reasonably good agreement was obtained between the diffusion coefficient values determined by all procedures. Small deviation between the two sets of diffusion coefficient values may be due to the inherently different methods by which the respective \( D \) values are determined. In the QRS method, solvent diffuses from one side of the film, but in the case of sorption method, solvent flows in all directions. This basic difference is considered while comparing the values.

Finally, the QRS method is successfully implemented to determine the purity of solvents. This is done by measuring the diffusion coefficients for various compositions of the selected impure solvent, toluene, with benzene as the impurity. A plot of relative diffusion coefficient \( (D/D_0) \) against the percentage of purity is illustrated in Fig. 5. It is clear from the figure that the relative diffusion coefficient of toluene through PLA film is decreasing when purity of solvent is increased. In the presence of impurities, the number of solvent molecules passing through the polymer phase varies. This causes variation in the rate of diffusion and obviously in the diffusion coefficient. This variation can be positive or negative depending on the type of solvent molecules, type of impurities and nature of the polymer film. By plotting calibration curves, the percentage of purity can be calculated. This technique can be used as a purity test capable of distinguishing between the organic impurities present in commonly used organic solvents.

![Figure 5](image_url)  
**Figure 5.** Variation of diffusion coefficient ratio \( (D/D_0) \) pure diffusion coefficient/impure diffusion coefficient of toluene through PLA membrane (with benzene as the added impurity).

### Table 3. Diffusion coefficient \( (\text{cm}^2/\text{s}) \) different organic solvents through PLA film and their characteristics in vapor medium

<table>
<thead>
<tr>
<th>S.No</th>
<th>Material</th>
<th>Sol. Param. ( \delta ) (MPa(^{0.5}))</th>
<th>( \chi ) of PLA-penetrant inter. Param.</th>
<th>Molar volume (\text{cm}^3.\text{mol}^{-1})</th>
<th>Boiling point (°C)</th>
<th>Diffusion coefficient ( (\text{cm}^2.\text{s}^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Poly(lactic acid)</td>
<td>19.2–21.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.26E–9 ± 8E–11</td>
</tr>
<tr>
<td>2</td>
<td>Toluene</td>
<td>18.2</td>
<td>0.4945</td>
<td>106.8</td>
<td>110.6</td>
<td>8.61E–10 ± 1E–10</td>
</tr>
<tr>
<td>3</td>
<td>Carbon tetrachloride</td>
<td>17.6</td>
<td>0.5833</td>
<td>97.10</td>
<td>76.72</td>
<td>4.09E–9 ± 1E–10</td>
</tr>
<tr>
<td>4</td>
<td>Tetrahydrofuran</td>
<td>19.4</td>
<td>0.3560</td>
<td>81.7</td>
<td>66.0</td>
<td>3.29E–9 ± 1.5E–10</td>
</tr>
<tr>
<td>5</td>
<td>2-Butanone</td>
<td>19.0</td>
<td>0.3834</td>
<td>89.5</td>
<td>80</td>
<td></td>
</tr>
</tbody>
</table>
CONCLUSIONS

The diffusion coefficient value for various solvents is a powerful tool to analyse the various properties of polymer membranes. We demonstrated a novel, convenient and simple method for the determination of diffusion coefficients by effectively combining the QRS technique with the conventional time lag method. The developed new instrumental setup is proved to be superior for the analyses and economical due to the low cost of the QRS used. A very detailed theoretical study has been carried out on the mechanism involved in the QRS technique as well as on the time lag method involved in the diffusion mechanism. Comparison of the diffusion coefficient values determined by the sorption and infrared spectroscopy analysis showed acceptable agreement for the polymer/penetrant systems with those evaluated by QRS method. To the best of our knowledge, this kind of experimental setup is for the first time ever reported.

Diffusion characteristics of poly (lactic acid) films were studied using different solvents of varying solubility parameters, and the values obtained are used for finding out the diffusion rates and purity of solvents. In summary, we believe that this low-cost method has remarkable importance to find diffusion coefficient of the organic vapors with good reproducibility. We successfully implemented the QRS technique to find out the effect of two-dimensional plate-like fillers such as clay and graphene on the barrier properties of polymer films. These results are the subject of another study.

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