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# Application of positron annihilation: Study of pervaporation dense membranes

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## Abstract

Separation of liquid mixtures, particularly azeotropic mixtures, is being tried out by pervaporation process, which utilizes dense membranes. Such membranes, although are of non-porous type, still requires determination of free volume sizes which is crucial to the understanding of the process. Positron annihilation technique has been developed into a powerful characterization tool for the study of free volume and free volume fraction in polymers. In the present work, an attempt has been made to estimate the free volume sizes of commercial and laboratory made pervaporation membranes with the application of positron annihilation lifetime spectroscopy. The positron lifetime spectra were analyzed, assuming 3 or 4 exponential components. Long-lived components (lifetimes: in the range of 1.4–3 ns) were found, which were attributed to *ortho*-positronium (*o*-Ps) pick-off annihilations in free volumes. Accordingly, free volume size determinations were carried out, considering shapes for free volumes as spherical as well as cylindrical. Further, utilizing such free volume data, results of hydrazine hydrate separation by pervaporation were interpreted leading to a better understanding of the process.

*Keywords:* Positron annihilation; Pervaporation; Free volume

## 1. Introduction

Pervaporation is relatively a new membrane separation process, particularly applied to separate homogeneous liquid mixtures of azeotropic type. The separation is carried out using dense polymeric films. The feed solutions, to be separated, is contacted on one side of the membrane and the permeating flux, in the vapour form, is obtained on the other side of the membrane by applying a pressure lower than the saturated vapour pressure. The mass transport mechanism through the membrane is considered complex because of the high interaction between the liquid feed components and the membrane, resulting into high swelling of the membrane. Free volume, existing in the membrane, plays an important role in pervaporation process. Free volumes can be in the form of static holes (unfilled spaces) or created and destroyed as a result of molecular motions (dynamic free volumes), in the macromolecular network, or in the form of connected free volumes, known as pores. Principally, there are two mechanistic models to describe the mass transport: (i) solution–diffusion model and (ii) pore flow model. The solution–diffusion model is widely accepted; particularly, because of its simplicity. According to this model, pervaporation permeability is simply the product of solubility and diffusivity. Free volume theory of diffusion when extended to polymeric systems [1,2] suggests diffusivity (of a component within the membrane) being a strong function of concentration of permeating component. Yeom and Huang [3] developed a model to predict pervaporation performance of membranes, based on the free volume theory. An empirical relation connecting free volume and glass transition temperature was used to estimate the free volume fraction of the dry membrane. However, as the determination of glass transition temperatures of cross-linked and composite commercial membranes is difficult, this model may not be very useful for wider applications. In this context, a direct determination of the free volume parameters may greatly help in understanding the complex processes that are involved during pervaporation process. Further, in their model [3], the free volume fraction of wet membrane was assumed to be the sum of free volume of the polymer and the increase in free volume due to the plasticizing action of the permeating components. The latter contribution

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was estimated from the increase in specific free volume with increase in temperature, which may be considered for increase in free volume for any membrane–permeate combination. However, the mechanism leading to expansion in free volume is related to plasticizing action and it is also known that not all permeating components plasticize with membrane [4]. In these situations, the vital input parameter may be grossly incorrect. Thus, the model can be utilized only if the free volume size of the wet membrane is available from more direct and reliable measurements.

According to solution–diffusion model, the zero flux condition during pervaporation may be achieved at a downstream pressure equal to the saturation pressure of the permeating component [5]. However, our recent experiments on single component permeation through commercial membranes [6] and work done by Vallieres, et al. [7] showed the importance of air leaks in pervaporation experiments. Quantitative estimation of air leaks showed the occurrence of zero flux condition well below the saturation vapour pressure during pervaporation. It was inferred that this might be due to depression of equilibrium vapour pressure within the membrane. Such depression of equilibrium vapour pressure may be estimated by Kelvin's equation [8], if we assume cylindrical pores to exist and know the effective radius of such pores.

Thus measurement of free volume size assumes an important role for understanding pervaporation process. However, free volumes of a dense membrane are generally in the size range of 1–6 Å; a direct determination of this size range is not straightforward. Positron annihilation technique [9] has developed into a powerful characterization tool for the study of free volume sizes and free volume fraction in polymeric materials. By measuring the lifetimes of the positrons, it may be possible to get fairly accurate estimates of the free volume of angstrom (2–10 Å) range. When positrons are implanted into a polymeric material, some of them interact with the electron clouds in the material to annihilate and give two gamma rays of energy 511 keV each. However, a fraction of positrons combine with the electrons to form a hydrogen-like quasi-stable atom, known as positronium and denoted as Ps. Depending upon the spin alignment, positronium could be in the form of *para*-positronium (*p*-Ps) or *ortho*-positronium (*o*-Ps). The positronium atom preferentially gets localized within the free volume cavities and annihilate after an average time characteristic for the shape and size of the free volume. The term 'free volume', in this paper, as in many papers in the field of positronium chemistry [10], refers to regions of low electron density in which Ps is trapped and subsequently annihilates. However, the term 'free volume' in polymer science refers more specifically to the excess free space due to molecular dynamics and thermal agitation of the constituents of the medium [11].

Positron annihilation lifetime spectra are analyzed in terms of three lifetime components, viz.: *para*-positronium (*p*-Ps) annihilation, $\tau_1$; free positron and positron-molecular species annihilation, $\tau_2$; and *o*-Ps annihilation, $\tau_3$. While $\tau_1$ and $\tau_2$ are of the order of few 100 ps, $\tau_3$ is of the order of nanoseconds. Each lifetime has an intensity $I$, corresponding to the fraction of annihilations taking place with the respective lifetimes. The parameters $\tau_3$, $I_3$ corresponding to the decay of *o*-Ps provide the size-specific information for free volumes and pores.

Free volume radius $r$ is obtained by first considering *o*-Ps trapped into a spherical volume with radius $r_0$, providing infinite potential barrier. The Schrödinger equation is solved to obtain the positronium wave function for the centre of mass motion of *o*-Ps in the ground state. The *o*-Ps pick-off annihilation rate is then calculated through a semi-empirical approach, by assuming a homogeneous electron layer with a thickness of $\Delta r = r_0 - r = 0.166$ nm adjacent to the wall and calculating the overlap of positronium wave function with the electron layer. Accordingly, the following expression may be obtained, which relates *o*-Ps pick-off lifetime, $\tau_3$ and free volume radius, $r$ [12–14].

$$\tau_3 = \frac{1}{2}\left[1 - \frac{r}{r_0} + \left(\frac{1}{2\pi}\right)\sin\left(\frac{2\pi r}{r_0}\right)\right]^{-1} \tag{1}$$

This equation can also be used for cylindrical free volume (pore) with the value of $\Delta r$ set at 0.196 nm [15]. In this case, for the same lifetime value, one gets a higher value for the radius as compared to the spherical case.

Further, the fractional free volume $f$ may be estimated from the following empirical relation [16].

$$f = CV_F I_3 \tag{2}$$

where, $V_F$ is free volume and the scaling factor; $C$ is obtained from variation of free volume with temperature. However, in the absence of such data, it may be typically assigned a value of 1.0 [17], in which case the values of $f$ obtained are proportional to the actual free volume fraction.

It is to be noted that the validity of such a relation is debated [18]. The intensity $I_3$ is strongly influenced by various factors essentially referring to the availability of open volume, i.e. free volume holes or nanovoids [19], and to radiation chemistry processes at the end of the positron track that leads to Ps formation [20]. Thus, the chemical nature of the environment, such as the presence of chemically active moieties able to inhibit Ps formation through electron capture, may have important consequences. These factors have to be taken into account while interpreting the intensity data by using Eq. (2). However, in the absence of such active groups [21], as in the present case, one may expect the proportionality of $I_3$ to the concentration of Ps traps to be valid [19].

In the present work, we report the measurement of free volume size and their fraction in the total volume of the material for a number of dry membranes as well as for wet membranes (obtained in real experimental situation).

## 2. Experimental

### 2.1. Materials

Analytical grade toluene (Ranbaxy, India), acetone (Ranbaxy, India), formamide (Loba-Chemie, India), ethyl cellulose (ethoxy content 48–49.5%: Loba-Chemie, India), cellulose acetate (Jams Chemicals, Bombay), benzyl *iso*-cyanate (laboratory prepared) and acrylonitrile styrene butadiene (Strasis & Co, USA) were used to cast the membranes. Ethanol (Hychem, England), hydrazine hydrate (Qualigens, India) and double distilled water were used for soaking and pervaporation purpose. The commercial composite membrane PERVAP® was obtained from Sulzer Chemtech, Germany. The membrane consists of a very thin (0.5–2 μm) separating layer on top of a porous support (70–100 μm), which in turn is on top of a polymer fleece (non-woven fabric of thickness 100 μm). Another composite membrane HR-98-PP was obtained from Danish Separation Systems, Denmark.

### 2.2. Membrane preparation

Ethyl cellulose (EC) polymer (10 g) was dissolved in toluene (90 g). The solution was centrifuged (REMI—model: R 24) at 10,000 rpm for 15 min for the removal of un-dissolved polymer and dust particles. The supernatant homogeneous solution was transferred to a conical flask (air tight) and kept for overnight for the removal of entrapped air bubbles. The casting of membrane was carried out on a modified thin film applicator (ACME, India) using a glass plate. After around 24 h of solvent evaporation at room temperature, the membrane together with the base glass plate was placed in vacuum oven for another 4 h for the removal of residual traces of solvent. Finally, the membrane was peeled off the glass plate.

Similar procedure was followed for casting of acrylonitrile butadiene styrene (ABS) membrane; for the purpose, 16 wt% of the polymer was taken using toluene as solvent. Hydrophobic modified ethyl cellulose membrane (ECNCO) was prepared by reacting ethyl cellulose with isocyanate; for the purpose 4 mL of benzyl isocyanate was added to 100 mL of 10% polymeric solution. Cellulose acetate (CA) membrane was prepared by taking 17 wt% cellulose acetate in 68% acetone and 15% formamide.

### 2.3. Sorption studies

Pre-weighed dry membranes were taken in a conical flask containing water or ethanol for sorption purpose. The flask was kept on shaking bath (model SW-23, Julabo, Germany) under 200 rpm for a longer period (6–7 days) at room temperature. The membranes in conical flasks were taken out at regular intervals and were wiped with tissue paper for the removal of the adhering liquid. Accordingly, the wet weight of the membrane was measured. The procedure was repeated until consecutive readings of weights of wet membranes were equal. The difference of weights was presented, with respect to dry weight of membranes, as percentage of sorption.

### 2.4. Positron annihilation lifetime (PAL) measurements

The PAL measurements were carried out using a fast-fast system having a resolution of 300 ps (FWHM for the $^{60}$Co prompt $\gamma$-rays, under $^{22}$Na window settings). The positron source was prepared by depositing around two micro-Curie aqueous $^{22}$NaCl on a thin aluminium foil (thickness ~ 12 μm), and was covered with an identical foil. The source was sandwiched between 13 layers (on each side) of the polymeric membrane, which were stacked together. The separating layer portion (membrane) was peeled out from the 'woven fabric' for commercial membranes for positron study. However, for laboratory made membranes, samples (membranes) were prepared with sufficient thickness to absorb 99.9% of the positrons. The source-sample sandwich was placed in between the two NE111 scintillators, coupled with RCA 8575 tubes. The anode signals were processed in ORTEC constant fraction differential discriminators; whereas, an ORTEC time-to-pulse height converter (TPHC) generated the lifetime distribution spectra which were recorded in a multi-channel analyser. All the measurements were made at room temperature (24 °C). Approximately, one million counts were collected at each spectrum and for each sample four spectra were measured. The lifetime data were analysed using PATFIT-88 programs [22]. Source correction was done for all spectra. In the case of measurements on water-soaked and ethanol-soaked samples, the soaked membranes were sealed inside a commercial polymer cover. The polymer cover was tested for its non-permeability of water and ethanol with satisfaction (0.1% loss for both the components). Corrections of positron spectra were made for any annihilation that could take place within the cover material.

### 2.5. Pervaporation

Batch experiments in a laboratory made pervaporation cell [23] were carried out with hydrazine hydrate (64% by weight of hydrazine) at 50 °C and 0.1 mm Hg. Permeate was analysed for concentration of hydrazine by gas chromatography [24]. The separation factor $\alpha_{\mathrm{W,H,O}}$ (water-to-hydrazine) is defined as:

$$\alpha_{\mathrm{W,H,O}} = \frac{y/(1-y)}{x/(1-x)} \tag{3}$$

where, $y$ and $x$ are the mass fractions of water in permeate and feed, respectively. W, H and O refer to water, hydrazine and overall.

## 3. Results and discussion

The positron lifetime spectroscopy data were analysed, in general, by fitting three lifetime components. Scanning electron microscopy picture of the porous layer in the case of commercial membrane showed (Fig. 1) pore size range of 1–10 μm. The positron annihilation lifetime in such large pores may be of the order of several tens of nanoseconds, which may not affect the spectrum, as recorded. Accordingly, the contribution of the porous layer for the positron annihilation lifetime spectrum (under dry state of membrane) was neglected. A typical positron lifetime spectrum (a sum of decaying exponentials corresponding to the number of positron

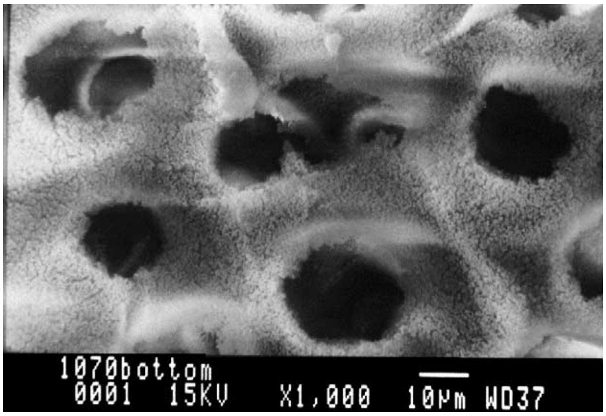

Fig. 1. Scanning electron microscope picture of porous layer of PERVAP® 1070.

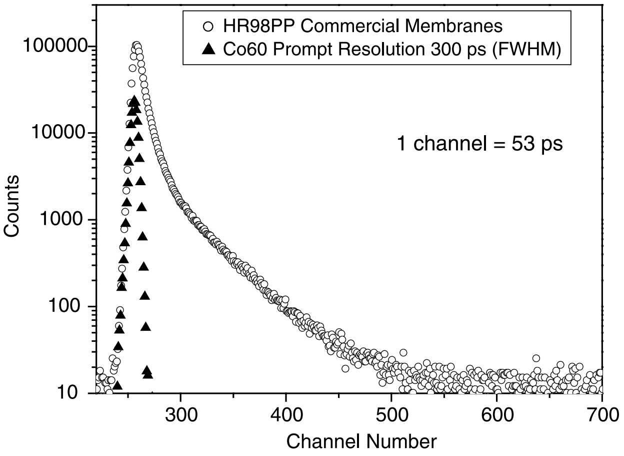

Fig. 2. A typical positron lifetime spectrums for HR-98-PP membrane.

states in the material convoluted with instrumental resolution function) for the membrane HR-98-PP is shown in Fig. 2.

### 3.1. Positron annihilation measurements

#### 3.1.1. Commercial membranes: dry state

The base polymer and the cross-linking level for commercial membranes [25] are given in Table 1. The positron lifetime parameters and the calculated free volume parameters for commercial membranes are also presented in Table 2.

Table 1
Base polymers and cross-linking level for commercial membranes (PERVAP® is a registered trademark of Sulzer Chemtech, Germany)

| Membrane | Base polymer | Cross-linking level | Reference |
|---|---|---|---|
| HR98PP | Polypropylene | – | As specified by the manufacturer |
| PERVAP 1060 | PDMS | Not available | [25] |
| PERVAP 1070 | PDMS + silicalite zeolite | Not available | [25] |
| PERVAP 2201 | PVA | High | [25] |
| PERVAP 2210 | PVA | Low | [25] |
| PERVAP 2256 | PVA | Not available | [25] |

The HR-98-PP membrane for which the base material is polypropylene, the free volume radius obtained from our measurements is 0.281 nm. This value is in excellent agreement with an obtained value from a mathematical model by Rosa and de Pinho [26]. Further, positron annihilations also provide the value of intensity $I_3$ as 15.2%, which is incidentally the largest value, obtained for commercial membranes (Table 2). This value reflects interesting fact that high free volume, available for such commercial membrane, are meant to be applied for reverse osmosis operation which is indeed the case for this HR-98-PP membrane.

PDMS polymer is the base material for both PERVAP 1060 and PERVAP 1070. Further, as per the information gathered from the manufacturer, an extra component in the form of silicalite zeolite is also present in PERVAP 1070. Accordingly, the positron lifetime spectrum corresponding to the latter had to be fitted with four lifetime components; whereas, the usual three components were sufficient for PERVAP 1060. The lifetime $\tau_3$ was observed to be almost same ($\sim$2.3 ns) for both the membranes, reflecting same size of voids in the base material. However, the presence of zeolites for PERVAP 1070 was reflected by the lifetime measurement [9], employing an extra component $\tau_4$ (4.53 ns). Vankelecom et al. [27] have found that only compounds with molecular size below 0.55 nm may permeate through silicalite zeolite. This implies the size of pores being around 0.55 nm and our measured value of the radius of free volume (assuming cylindrical pores) was found to be 0.52 nm.

The component values of $\tau_3$ are found to be slightly at variance (Table 2) for PERVAP 2201, 2256 and 2210. This is because of varied preparation techniques of these membranes; in spite of having same base material (PVA). PERVAP 2256 required addition of a fourth component ($\tau_4 = 6.19$ ns) with a small intensity value (1.1%) to obtain improved fit. Requirement of $\tau_4$ suggests the presence of extra component on base PVA; as this membrane is meant for organic–organic separation [28]. Comparing PVA based membranes (2201, 2256 and 2210) to PDMS based membranes (1060, 1070) and polypropylene based membrane (HR98PP), it was observed that the fraction of free volume of PVA based membranes are consistently smaller than others. This is expected as the base polymer PVA has glassy structure compared to rubbery structure of PDMS. The free volumes are known to be larger for rubbery structures [29]. Such measurements of free volume fractions may help to model [3] for efficient design of pervaporation process.

#### 3.1.2. Commercial membranes: wet state

As mentioned earlier, free volume may change from the dry state to the wet state of a membrane due to swelling. Therefore, accurate estimation of free volume of membrane under wet state assumes importance as it eventually relates diffusivity of species within the membrane; commonly obtained through empirical relations. Further, it was thought to examine the reversibility or irreversibility of swelling effect, due to sorption, on the free volume of the membrane. Therefore, in

Table 2
Free volume parameters of commercial membranes

| Membrane | State | $\tau_3$ (ns) | $I_3$ (%) | $r$ (nm) | $V_{\mathrm{f}}$ (nm$^3$) | $F$ | $r$ (nm), cylinder |
|---|---|---|---|---|---|---|---|
| HR98PP | Dry | $1.96 \pm 0.01$ | $15.2 \pm 0.2$ | 0.281 | 0.093 | 0.014 | 0.324 |
| PERVAP 1060 | Dry | $2.30 \pm 0.02$ | $9.4 \pm 0.2$ | 0.311 | 0.126 | 0.012 | 0.359 |
| PERVAP 1070 | Dry | $2.32 \pm 0.28$ | $10.6 \pm 1.5$ | 0.312 | 0.128 | 0.014 | 0.36 |
| | | $\tau_4$: $4.53 \pm 0.48$ | $I_4$: $5.1 \pm 2.0$ | 0.451 | 0.385 | 0.020 | 0.52 |
| PERVAP 2201 | Dry | $1.64 \pm 0.04$ | $8.3 \pm 0.4$ | 0.249 | 0.065 | 0.005 | 0.288 |
| PERVAP 2256 | Dry | $1.73 \pm 0.06$ | $8.8 \pm 0.2$ | 0.259 | 0.073 | 0.006 | 0.298 |
| | | $6.19 \pm 0.36$ | $1.1 \pm 0.1$ | 0.526 | 0.608 | 0.007 | 0.606 |
| PERVAP 2210 | Dry | $1.46 \pm 0.02$ | $9.3 \pm 0.3$ | 0.229 | 0.050 | 0.005 | 0.264 |
| PERVAP 2210 | Water soaked | $1.52 \pm 0.03$ | $14.6 \pm 0.6$ | 0.236 | 0.055 | 0.008 | 0.272 |
| PERVAP 2210 | Water soaked and dried | $1.48 \pm 0.02$ | $9.3 \pm 0.2$ | 0.231 | 0.052 | 0.005 | 0.267 |
| PERVAP 2210 | Ethanol Soaked | $1.26 \pm 0.40$ | $4.6 \pm 1.4$ | 0.204 | 0.036 | 0.002 | 0.235 |
| | | $\tau_4$: $3.30 \pm 0.11$ | $I_4$: $8.8 \pm 0.8$ | – | – | – | – |

this paper positron lifetime measurements were carried out for sorbed (water soaked and ethanol soaked) and air dried water soaked (prior to) membrane (PERVAP 2210). The results are reported in Table 2.

The following general observations may now be mentioned (as reported in literature) for information purpose only in order to enhance the clarity of understanding while interpreting results of wet membranes. In polymers, positronium atoms are formed in the free volumes [30]. It is known that only about 28% [31] of the positrons, entering into bulk water, are able to form *o*-Ps. Whereas, 22% of positrons enter into ethanol bulk to form *o*-Ps [32]. The probability of positronium formation in the free volumes containing water or ethanol may be smaller compared to empty free volumes. Thus, a decrease in $I_3$ is expected in the case of sorbed (soaked) membranes, in the absence of plasticization.

*3.1.2.1. Water soaked membranes.* Water soaked membrane (wet state) shows a positron lifetime of 1.52 ns, which is slightly greater than that, was observed under dry state. The intensity, $I_3$ is increased from 9.1 to 14.6%. Water occupying larger size pores ($\sim 10$ μm) in the porous support may also contribute to positron lifetime spectrum. The lifetime of positronium in bulk water is known to be 1.81 ns [31] and the lifetime for dry state membrane (2210) is 1.46 ns. This small difference of lifetime may be insufficient for four-component fit. Therefore, the lifetime 1.52 ns (measured for the water-soaked membrane) may represent a weighted average of the two. The contribution from water may also be responsible for the increase in $I_3$; at least partially. The other contribution may come from the interaction of water with the skin layer. PERVAP 2210 is highly selective for water as the solubility is around 193 g of water in 100 g of polymer; if the skin layer is assumed to be of PVA. The molecules efficiently dissolve where they contact the membrane and plasticization occurs. Plasticization can expand the existing free volumes and it can also create newer free volumes. This may enhance the lifetime as well as the intensity. However, quantitative estimation is difficult because of the presence of water in the porous support as well as due to the change in the positronium formation probability, once the free volumes are filled with water.

*3.1.2.2. Water soaked and dried membranes.* The lifetime $\tau_3$ and its intensity $I_3$ are almost same for both dry as well as for dried water sorbed membrane (PERVAP 2210). Therefore, it is obvious that there is no change in the free volume or in other words the free volume is reversible by nature if a dry membrane undergoes consecutive paths of sorption followed by drying. However, an interesting observation was noticed with regard to sorption (amount) of water for PERVAP 2210 under two different conditions: (i) sorption for a fresh dry membrane and (ii) sorption of air-dried water sorbed (prior to) membrane. The results are reported in Table 3. In the first case, sorption is more than 300%; whereas, for the second case, sorption was only 125% (by weight). Therefore, it is evident that fresh polymer initially gives much higher sorption than with its repeated use for sorption. It is known that the porous support is of poly acrylonitrile material [25], which may not be much affected by water; hence, the difference in the water sorption between the two cases appears to reflect the changes in the sorption property of the skin layer. Further, the fact that the positron annihilation lifetime does not show any change, it may be understood by noting that the sorption is a thermodynamic phenomenon which depends on the surface characteristics of the membrane; whereas, the positron annihilation lifetime measurements in the present study provide free volume properties of the bulk of the membrane (depth-averaged information).

*3.1.2.3. Ethanol soaked membrane.* Free volume measurements were also done through sorption of ethanol on PERVAP 2210 membrane. Earlier studies [33] have showed that 2210 membrane is highly selective for water compared to ethanol. Pervaporation studies were conducted for ethanol–water

Table 3
Sorption of water in PERVAP 2210

| Type | Dry weight (g) | Equilibrium weight of wet membrane (g) | % Absorption |
|---|---|---|---|
| Fresh | 0.0340 | 0.1363 | 300.9 |
| Soaked and dried | 0.0340 | 0.0765 | 125.0 |

system [33] with a feed of 10% of water; the permeating solution of which contained more than 90% of water. This shows that ethanol is much less soluble in PERVAP 2210 membrane. Thus, the value of positron lifetime $\tau_3$ and intensity $I_3$ of ethanol sorbed (soaked) membrane may be expected to be nearly same as that for dry membrane. However, this is not the case, as is seen from Table 2.

A four-component fit was needed with an intense component having 3.30 ns, which is a high value. Incidentally, the positron lifetime for bulk ethanol is also known to be 3.30 ns [32]. This high value is expected, as the presence of ethanol in the larger pores of the porous support (~10 μm) contributes significantly. Further, unlike the case with water-sorbed membrane, the lifetime for ethanol is much different from that of dry membrane. Therefore, a four component fit resolved well for such a large lifetime difference (3.3–1.46 ns) between ethanol sorbed and dry membrane conditions. The value of $\tau_3$ (1.26 ns) corresponds to the free volume of the polymer itself. This value is smaller than 1.46 ns found for the case of the dry membrane. Correspondingly, the free volume radius is also smaller, as seen by the positrons. This reduction in $\tau_3$ may be attributed to the fact that larger size free volumes are being filled with ethanol because lower probability of positronium formation may contribute less lifetime spectrum.

### 3.1.3. Laboratory cast membranes: dry state

The free volume parameters for four laboratory-prepared homogeneous membranes (EC, ECNCO, CA and ABS) were measured (through positron lifetimes) and are reported in Table 4. The free volume radii and the fractional free volume are observed to be larger than those for the commercial membranes. This may be due to the fact that laboratory prepared membranes were untreated; i.e. there was no cross-linking, either by chemical addition or by heat treatment. Lower free volume radii may be directly related to the high selectivity of the commercial membranes for specific cases.

Generally, the estimated pore size of pervaporation membranes is a little more than a nanometer [34]. The present measurements, which are far more direct in nature, show that for all the membranes studied the pores are smaller than one nanometer in size. The pore sizes are found in the range of 0.2–0.6 nm.

Ambient temperature variation (on casting of membrane) leads to variation in the permeability; hence, effect of such ambient temperature variation can be observed on free volume. Ethyl cellulose membranes were prepared at 30 °C (EC) and also at 25 °C (EC1). As seen from Table 4, EC1 has lower free volume fraction compared to EC. It may be due to the fact that at lower temperature the rate of evaporation of solvent is less and the polymer molecules get more time to rearrange themselves. This provides compact structure of the membrane and hence a lower free volume may lead to lower pervaporation flux.

### 3.1.4. Laboratory cast membranes: wet state

To study the characteristics of wet membranes in terms of positron lifetimes, the EC membrane was sorbed (soaked) with water and the CA membrane with ethanol. These represent combinations when the solubility of the liquid in the membrane is small. Sorption studies made on these membranes showed that only 4 g of water dissolves in 100 g of EC and 27 g of ethanol dissolves in 100 g of CA. In water soaked EC, the positron lifetime was decreased from 2.63 to 2.26 ns; whereas, in ethanol soaked CA it increased from 2.16 to 2.91 ns. It may be mentioned that the lifetime of positronium decay in water (1.81 ns) is smaller than that of dry EC; whereas, the lifetime in ethanol (3.30 ns) is larger than that in dry CA. In the case of laboratory prepared membranes, there is no porous support and the change in lifetime or the intensity reflects the changes occurred in the membrane in far more direct manner.

The decrease of lifetime for the water soaked EC membrane may be indicating the lack of plasticization of the membrane. Whereas, the increase in lifetime for the case of ethanol soaked CA membrane may also be interpreted in terms of plasticization of the membrane due to filling of free volumes by the sorbate and the consequent expansion of free volume. However, such a hypothesis may be ruled out, as ethanol is less soluble in CA membrane. At this point, similar conclusion may also be made for ethanol soaked PERVAP 2210 membrane (Section 3.1.2.3).

The intensity $I_3$ decreases for both (soaked EC and CA) cases compared to corresponding dry states. This is due to presence of sorbate in the cavities, which reduces the intensity $I_3$. The reduction of $I_3$ in the case of ethanol-soaked CA is more than that in the case of water-soaked EC. This may be related to the higher solubility of ethanol in CA restricting the positronium formation more effectively. These observations show that there may be a relation between the reduction in intensity $I_3$ and solubility of the component in the membrane. Interestingly, our observations (shown in Table 4) satisfy the equation derived by MacQueen et al. [35] for the weight gain of

Table 4
Free volume parameters of laboratory cast membranes

| Membrane | State | $\tau_3$ (ns) | $I_3$ (%) | $r$ (nm) | $V_f$ (nm$^3$) | $F$ | $r$ (nm), cylinder |
|---|---|---|---|---|---|---|---|
| EC | Dry | 2.63 ± 0.01 | 26.0 ± 0.2 | 0.337 | 0.160 | 0.042 | 0.385 |
| EC1 | Dry | 2.55 ± 0.02 | 22.5 ± 0.3 | 0.331 | 0.151 | 0.034 | 0.381 |
| ECNCO | Dry | 2.26 ± 0.01 | 17.5 ± 0.2 | 0.308 | 0.121 | 0.021 | 0.355 |
| ABS | Dry | 2.37 ± 0.02 | 21.1 ± 0.3 | 0.317 | 0.133 | 0.028 | 0.365 |
| CA | Dry | 2.16 ± 0.02 | 18.8 ± 0.3 | 0.300 | 0.112 | 0.021 | 0.345 |
| CA | Ethanol-soaked | 2.91 ± 0.05 | 7.5 ± 0.2 | 0.357 | 0.190 | 0.014 | 0.411 |
| EC | Water-soaked | 2.26 ± 0.02 | 17.7 ± 0.2 | 0.308 | 0.121 | 0.021 | 0.355 |

Table 5
Pervaporation of hydrazine–water (concentration of hydrazine: 64%; $T=50$ °C; downstream pressure: $p=0.1$ mm Hg; batch mode)

| Membrane[a] | Flux (g/m$^2$h) | Selectivity |
|---|---|---|
| EC | 9.65 | 1.72 |
| ECNCO1-1.0 | 9.35 | 1.87 |
| ABS | 7.81 | 5.07 |

[a] Thickness of the membrane is 50 μm.

the membranes due to sorbate; in terms of the free volume parameters. However, it should be mentioned here that the relation between the *o*-Ps lifetime in the free volumes containing the sorbate and their size is not straightforward.

### *3.2. Pervaporation*

In order to observe the relationship between the pervaporation flux and free volume of the membrane, data on hydrazine–water separation were utilised [36]. Both hydrazine and water are highly polar liquids. The separation of this system requires high-energy consumption through conventional separation processes [37]. Pervaporation may be an alternative technology. Pervaporation of hydrazine hydrate were carried out using EC, ECNCO and ABS. The results are shown in Table 5. The pervaporation flux through the EC membrane is somewhat larger compared to ECNCO and ABS. Qualitatively, this can be understood from the higher free volume in the case of EC than the other two membranes (refer Table 4). However, in the case of ECNCO, the flux was found to be more, despite free volume being lower compared to ABS. As discussed earlier, there is no plasticization of the membranes due to the feed components. Therefore, higher flux through ECNCO compared to ABS films may be because of different values of $C$ in Eq. (2); but was assumed here to be the same. Further, the difference in the free volume radius of ECNCO and ABS is not much and even a small difference in $C$ could affect the result.

## 4. Conclusions

Application of positron annihilation lifetime spectroscopy technique provides the estimate of free volume size and may establish the existence of sub-nanometer size pores in pervaporation membranes. The free volume parameters, estimated for commercial membranes, may be considered to be reflective and therefore, may be useful for the purpose of transport modelling. The laboratory cast membranes showed higher values of free volume parameters than those for commercial membranes. Influence of membrane preparation conditions, like solvent evaporation temperature on the free volume fraction was studied.

Positron measurements were also made on wet state membranes. Qualitatively, a decrease in the positron lifetime in the soaked state may indicate lack of plasticization of the membrane due to the sorbate. However, quantitative estimation of free volume fractions for wet membranes, if further pursued, may help to better understand the actual phenomena behind pervaporation process.

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