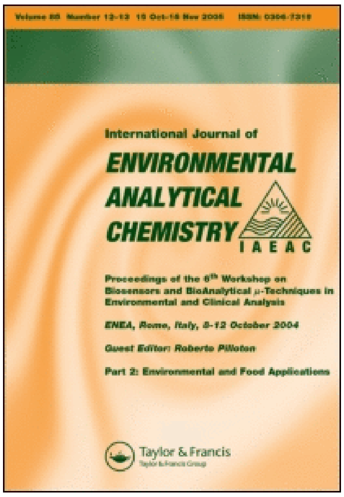

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A comparison of polymeric materials as pre-concentrating media for use with ATR/FTIR sensing

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A comparison of polymeric materials as pre-concentrating media for use with ATR/FTIR sensing

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Polymer-modified ATR-FTIR spectroscopy was investigated to determine its potential suitability for use as an analytical methodology for process stream analysis. The process stream under investigation contains toluene, tetrahydrofuran, ethanol, and acetonitrile in an aqueous matrix. Four polymers, Teflon® AF2400, poly(acrylonitrile-co-butadiene) (PAB), polydimethylsiloxane (PDMS), and poly(styrene-co-butadiene) (PSB), were chosen for study based on partition coefficients measured using a novel automated GC technique. Polymer suitability as pre-concentration media was assessed utilizing analyte/polymer diffusion coefficient data, equilibrium absorbance values, water ingress, and polymer plasticization. PAB displayed the fastest sensing times and enhanced sensitivities. Teflon® AF2400 demonstrated a low water absorption and a low degree of plasticization. Other factors affecting the diffusion rate of analytes were also investigated including molecular size, shape and analyte concentration. This research demonstrated that the choice of pre-concentrating medium is not a trivial issue, being dictated by a combination of sensitivity constraints as well as polymer robustness in real sample matrices.

Keywords: ATR-FTIR spectroscopy; Polymer films; Diffusion; Solvent sensing

1. Introduction

There has been extensive research into the permeation of organic solvents into polymeric materials [1–7]. Such materials are of interest in a number of industrial applications, including controlled-release drugs [8], barrier materials [2, 9], and pre-concentrating media for sensors [3, 5–7, 10–17]. The use of mid-IR polymer clad

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attenuated total reflectance (ATR) as a sensing method is well established [3, 5, 13, 18–21].

In polymer-coated ATR methodologies, analytes are extracted from solution into a hydrophobic membrane. The membrane is in intimate contact with a core material of higher refractive index through which mid-IR radiation is internally reflected. An appropriate contact angle with the wave-guide (denser medium) results in an exponentially decaying standing evanescent wave into the (less dense) surrounding medium, in this case the polymer. The polymer cladding is coated onto the surface of the wave-guide at a thickness of approximately three times the depth of penetration (d_p). The magnitude of d_p is dependent on the refractive index of the surrounding medium (n_s), the wave-guide (n_c), and the wavelength of light absorbed (λ) [22]. At three times d_p, the evanescent field has decayed to 5% of its original magnitude, which in this instance is considered the entire sensing region [22]. The analyte, which is commonly in aqueous solution, is concentrated within the information depth through diffusion into the hydrophobic layer. The attenuated radiation is measured, and a spectrum of the material within the evanescent field is plotted. In this work, the polymers are coated on to a ZnSe crystal, which has six internal reflections (11 in total) at the crystal surface intimate with the polymer. The use of optical fibres in which many more internal reflections are possible can result in sensitivity increases of orders of magnitude over ATR systems [6, 16].

Numerous polymers have been examined in order to determine those with the most favourable properties for both the study of diffusion and their value as pre-concentration media for evanescent wave sensors [3, 5, 12, 23]. Polymers are chosen for pre-concentration on the basis of their physical properties and the physical properties of the compounds to be detected. One of the goals of this research is to find an appropriate system for the on-line mid-IR sensing of residual solvents in an industrial process stream originating at a pharmaceutical production process. The solvents utilized during the pharmaceutical synthesis were acetonitrile, ethanol, THF and toluene. Their polarities are 5.8, 5.2, 4.0 and 2.4, respectively [24]. There is a large variation in the polarities and sizes of these analytes, which increases the importance of, and creates unique difficulties in polymer choice. In many applications of polymer-modified ATR & FEW (Fibre optic Evanescent Wave) spectroscopy, the impact of water ingress, polymer plasticization by analytes, and the resulting impact on analyte diffusion are not addressed. This overall robustness issue is a key analytical consideration in the future development of this technology.

Membranes, which allow elevated rates of diffusion as well as absorption of enhanced concentrations of analyte, are most useful from a sensing point of view. The sensitivity is dependent on the analyte concentration within the polymer, which depends primarily on the partition coefficient for the diffusant between the matrix solvent and the polymer [5, 20]. One of the aims of this research was to assess whether partition coefficients calculated using a novel automated GC technique could be used as the sole means of pre-concentrating medium selection.

The main objectives of this research were:

- to demonstrate the suitability of polymer-modified ATR-FTIR spectroscopy for analysis of an industrial process stream of varying polarity;
- to investigate the effect of varying analyte concentrations on the diffusion coefficient (D) and the equilibrium absorbance value (A_∞) in each polymer;

- to compare/select the most suitable polymer as a pre-concentrating medium based on sensing time (related to D), sensitivity (related to A_∞), water ingress and analyte plasticization;
- to establish the effect of size and shape of the analyte on the diffusion rate characterized by D;
- to investigate whether the partition coefficient of a particular analyte is a suitable parameter for polymer selection.

2. Experimental

Polymers which have been successfully used for pre-concentration in conjunction with mid IR techniques including Teflon® AF1600 [25] and EP_{co} [26] did not show absorption of the higher polarity solvents, which is illustrated by log K values equal to 0 for both chloroform and butyronitrile. From the remaining six polymers, Teflon® AF2400, PAB, PDMS and PSB were selected above poly(butadiene) (36% cis, 55% trans, 9% vinyl) (PB(c&t)) and polyisobutylene (PIB) due to their superior partition coefficients (table 1). The partition coefficients of a wide variety of analytes between their aqueous solutions and various polymers were calculated utilizing a novel automated GC methodology described by Jakusch [27].

A BIO-RAD Excalibur series 3000 FTIR spectrometer equipped with a cryogenic mercury cadmium telluride (MCT) detector was used for measurements. The waveguide was a trapezoidal ZnSe crystal (MacroOptica Ltd, Moscow, Russia) with dimensions of 72 mm × 10 mm × 6 mm and a 45° angle of incidence giving six reflections in contact with the sample.

The polymers were coated using a Chemat Technology KW-4A spin coater and their membrane thickness calculated using a gravimetric technique (equation 1) [18]:

$$L = \frac{m}{\rho A}, \tag{1}$$

where the membrane thickness (L) is dependent on film mass (m), polymer density (ρ), and the coated surface area (A). The coating procedure plus curing conditions for each of the polymers is as follows.

Teflon® AF2400 was obtained in solution from Dupont Fluoroproducts, Wilmington, DE (1% solids in fluorinert FC-75 perfluorinated solvent). A 5.1 μm film was coated onto the crystal. The AF2400 was cured at 25°C for 10 min, 112°C for 10 min, 245°C for 5 min, and 330°C for 10 min.

Table 1. Partition coefficient (log K) values for selected analytes into eight polymers[a].

Analyte	Teflon® AF1600	Teflon® AF2400	EP_{co}	PAB	PB(c&t)	PDMS	PIB	PSB
Toluene	2.38	2.42	2.46	2.71	2.14	2.25	2.30	2.71
Chloroform	0	1.41	0	1.96	0	0.88	1.26	1.74
Butyronitrile	0	0	0	0	1.72	0.97	0	0

[a] The polarity of chloroform is approximately that of THF with butyronitrile intermediate between ethanol and acetonitrile.

Poly(acrylonitrile-co-butadiene) (PAB) was obtained as a solid (30–32 wt% acrylonitrile) from Aldrich, MI (3 g was dissolved in 200 cm^3 2 : 1 butanone : toluene by refluxing for 3.5 h). A 7.7 µm film was coated to the crystal, and this was cured at 120°C for 2 h.

Poly(styrene-co-butadiene) (PSB) was obtained as a solid (45 wt% styrene) from Aldrich, MI (3 g was dissolved in 200 cm^3 toluene by refluxing for 3.5 h). A 7.4 µm film was coated to the crystal and cured at 120°C for 2 h.

Polydimethylsiloxane (PDMS) was obtained as Sylgard® 184 silicone elastomer and Sylgard® 184 curing agent. A 20 and 2 g quantity, respectively, were added and made up to 100 cm^3 with chloroform. In this case, the polymer solution was drop-coated to leave a 7.0 µm film and cured at 230°C for 2 h.

Each coated crystal was fitted into a Specac Thermostabilized Top Plate stainless steel temperature controlled ATR flow cell (110 µL). Analyte solutions were pumped over the surface of each polymer at 5 mL/min using a Shimadzu LC-10ATvp solvent delivery system. Analyte solutions were temperature-controlled during analysis using a Grant W20 thermostabilized water bath. When preparing solutions, all analytes were measured directly into low-headspace volumetric glassware and dissolved with sonication prior to use. Fresh solutions were prepared for each run. All experiments were carried out in triplicate, and all solutions were sealed during analysis.

The size and shape of analytes were characterized using ChemWindow® Spectroscopy 6.0 by calculating an averaged minimal cross-section [28]. The molecular radius is measured in the x, y, and z dimensions and used to calculate the volume of the molecule. The cube root of the volume presents the averaged minimal cross-section of the molecule. In this work, conformational changes were considered negligible, as penetrants have either small or rigid structures.

3. Results and discussion

The four polymers studied in this work (Teflon® AF2400, PAB, PDMS, and PSB) were selected based on the high partition coefficients calculated for the analytes (or those of similar polarity) using a novel automated GC methodology [29]. Not all of the solvents of interest were analysed by this GC technique. The partition coefficients originate from an investigation carried out prior to the commencement of this work and hence the process stream composition. Consequently, the partition coefficients for analytes, which reflected the approximate polarity range of the process stream components under investigation, were utilized and are illustrated in table 1. The polarities of toluene, chloroform, and butyronitrile are 2.4, 4.1, and 5.4, respectively [24], with THF (4.0) having a polarity similar to chloroform and butyronitrile intermediate between ethanol (5.2) and acetonitrile (5.8).

Following coating of the polymers onto ZnSe crystals, the diffusion of toluene, THF, ethanol, and acetonitrile was monitored (table 2). As previously mentioned, the choice of the polymers was based on the partition coefficients observed for the analytes of interest into these particular polymers. Ethylbenzene and three xylene isomers were also monitored into AF2400 to investigate the impact of the additional methyl group on D. THF, ethanol, and acetonitrile diffusion were monitored into PAB, PDMS, and PSB, at 2% concentrations. As a result of low partition coefficients, ethanol and acetonitrile were monitored into Teflon® AF2400 from 5%

Table 2. Diffusion coefficient (D) and diffusion velocity (D/L) values (triplicate runs with 95% confidence intervals) calculated for each polymer/analyte[a].

Compound	Conc.	Polymer	λ (cm^{-1})	$D \times 10^{10}$ (cm^2/s)	$D/L \times 10^{15}$ (cm/s)	$1/V^{1/3}$
Toluene	100 μL/L	Teflon	3033	18.23 ± 1.38	35.30 ± 2.29	0.282
THF	2% (v/v)	Teflon	916	41.35 ± 2.99	80.92 ± 5.86	0.359
Ethanol	5% (v/v)	Teflon	1045	24.43 ± 1.42	47.82 ± 2.76	0.382
Toluene	200 μL/L	PDMS	1497	9.34 ± 0.60	12.87 ± 0.57	0.282
THF	2% (v/v)	PDMS	2881	29.17 ± 2.67	41.54 ± 8.31	0.359
Ethanol	2% (v/v)	PDMS	2981	70.30 ± 0.17	100.43 ± 2.57	0.382
Acetonitrile	2% (v/v)	PDMS	2259	91.38 ± 8.70	130.54 ± 0.12	0.464
Toluene	100 μL/L	PAB	1495	28.97 ± 1.59	37.62 ± 2.44	0.282
THF	2% (v/v)	PAB	1065	137.77 ± 1.76	178.23 ± 2.29	0.359
Ethanol	2% (v/v)	PAB	1066	72.36 ± 1.42	93.60 ± 1.84	0.382
Acetonitrile	2% (v/v)	PAB	2251	156.65 ± 7.51	203.44 ± 9.74	0.464
Toluene	200 μL/L	PSB	1495	4.64 ± 0.55	6.27 ± 0.76	0.282
THF	2% (v/v)	PSB	1729	69.41 ± 10.68	93.80 ± 14.40	0.359
Ethanol	2% (v/v)	PSB	1069	36.44 ± 1.48	49.24 ± 2.00	0.382
Acetonitrile	2% (v/v)	PSB	2259	82.56 ± 22.41	111.57 ± 30.28	0.464

[a] $1/V^{1/3}$ reflects the average minimal cross-section for each of the diffusing species.

aqueous solutions (table 2). Acetonitrile demonstrated no pre-concentration within Teflon® AF2400 at this concentration.

Each polymer was coated to approximately three times the depth of penetration (4.4, 5.1, 6.6, and 6.4 μm for Teflon® AF2400, PDMS, PAB, and PSB, respectively). As a function of the polymer refractive index, this value varies between polymers. Equally, D is a function of the polymer thickness (equation (3)) and has been shown to vary linearly with thickness [30]. For a given polymer/penetrant system obeying Fick's law with all other conditions fixed, a thickness-independent value is calculable for the comparison of diffusion rates between polymers of varying thickness. D is divided by the membrane thickness (5.1, 7.0, 7.7, and 7.4 μm for Teflon® AF2400, PDMS, PAB, and PSB, respectively) to give an average diffusant diffusion velocity illustrated in table 2.

3.1 *Effect of analyte size on sensor response*

A number of authors [3, 4, 28, 31–34] have shown that D varies inversely with solvent size. Clément *et al.* have shown a linear correlation between average minimal cross-section (the larger the value of $1/V^{1/3}$, the lower the average minimal cross-section) and D within a homologous series [28]. Table 2 demonstrates this trend within each of the polymers with the exception of ethanol into Teflon® AF2400, PAB, and PSB. This would be expected due to intermolecular hydrogen bonding causing an apparent increase in molecular cross-section possibly resulting from clustering of molecules. Clustering was also observed by Sammon *et al.* for diffusion of water [21, 35]. Ethanol into PDMS, however, does not follow this trend and follows the relationship between minimal cross-section and D. Apart from Teflon® AF2400 (5% aqueous solution showed no response), acetonitrile is the fastest diffusing component into each polymer and toluene the slowest, where acetonitrile has the smallest minimal cross-section, and toluene has the largest. This demonstrates the inverse relationship between solvent size and diffusion rate. One would thus assume that ethanol should demonstrate the second greatest rate of diffusion into Teflon® AF2400, PAB, and PSB. This is, however, not the case as THF acts as the second-fastest diffusing species. This occurs a result of

Table 3. Diffusion coefficient (D) and equilibrium absorbance values (A_∞)[a].

Compound	λ (cm)	$D \times 10^{10}$ (cm^2/s)	A_∞	$1/V^{1/3}$
Toluene	3033	18.23 ± 1.38	0.0013 ± 0.0001	0.282
1,4-Xylene	795	8.30 ± 0.82	0.0705 ± 0.0004	0.270
1,2-Xylene	768	8.02 ± 1.10	0.0439 ± 0.0014	0.277
1,3-Xylene	741	8.16 ± 0.47	0.0588 ± 0.0007	0.259
Ethylbenzene	2973	7.61 ± 0.11	0.0046 ± 0.0000	0.236

[a] Values (triplicate runs with 95% confidence intervals) for penetrants in Teflon® AF2400 were calculated for each polymer/analyte system at 100 μL/L analyte concentration.

hydrogen bonding between ethanol molecules causing an apparent increase in its molecular diameter.

Table 3 demonstrates that the addition of a methyl group to toluene with respect to diffusion into Teflon® AF2400 causes a decrease in D. The location of the methyl group is an important factor. In ethylbenzene, the additional methyl group is not in the plane of the molecule. Molecules preferentially move in a direction which minimizes the displacement of the polymer chains [33]. The out-of-plane methyl group shall hence cause increased resistance during transport through the polymer. For the xylene isomers, the rate of diffusion has decreased with respect to toluene but not to the same extent as ethylbenzene. The methyl group is attached to an sp^2 carbon and so shall be in the plane of the molecule, causing less resistance while displacing polymer chains, accounting for the observed xylene diffusion coefficient rates.

3.2 *Effect of solvent concentration on sensor response*

Standard calibration data for toluene into the four polymers are summarized in table 4. The system displayed a good correlation between analyte concentration and A_∞ for Teflon® AF2400, PAB, and PSB showing the quantitative nature of this sensing methodology. However, as a consequence of higher spectral noise observed for toluene diffusion into PDMS, a lower r^2 value is obtained. PAB followed by Teflon® AF2400 demonstrated the greatest sensitivities illustrated by lower limits of detection (table 5), with PDMS and PSB displaying a poorer sensitivity for toluene.

The relationship between D and toluene concentration was monitored for each polymer. No explicit trends were witnessed between the toluene concentration and rate of diffusion into each of the membranes. Plots of Long's model (equation (2)) [36] did not display a definitive change in diffusion rate. Concentration-dependent diffusion is not observed for toluene within the concentration ranges studied:

$$D = D_0 e^{(\gamma C)}, \tag{2}$$

where D_0 = diffusion coefficient at infinite dilution, γ = plasticization coefficient, and C = analyte concentration.

It is unusual that D does not display concentration dependency. This may occur according to Crank in dilute solutions where dependency is slight, and D may be considered constant [37]. However, investigating an increased concentration range may reveal concentration-dependent toluene diffusion into these polymers.

Table 4. Standard calibration data for toluene diffusion into the four polymers[a].

Polymer	Range (μL/L)	Slope × 10^5 (μL/L)	r^2	LOD (μL/L)
Teflon®	70–160	1.379	0.995	27
PDMS	125–200	2.086	0.981	114
PAB	100–175	8.918	0.995	10
PSB	200–275	5.582	0.994	91

[a]Each concentration was run in triplicate, and the 95% confidence interval for each was less than 5%.

Table 5. T_{90} and A_∞ values for the four polymers[a].

Compound	Polymer	Concentration	λ (cm^{-1})	A_∞	t_{90} (s)
Toluene	Teflon	100 μL/L	3033	0.0013 ± 0.0001	151
Toluene	PDMS	200 μL/L	1497	0.0034 ± 0.0002	494
Toluene	PAB	100 μL/L	1495	0.0089 ± 0.0003	153
Toluene	PSB	200 μL/L	1495	0.0111 ± 0.0001	1180
THF	Teflon	2%	916	0.0039 ± 0.0002	62
THF	PDMS	2%	905	0.0056 ± 0.0002	151
THF	PAB	2%	907	0.0127 ± 0.0003	46
THF	PSB	2%	902	0.0126 ± 0.0004	72
Ethanol	Teflon	5%	1045	0.0084 ± 0.0004	134
Ethanol	PDMS	2%	2981	0.0042 ± 0.0002	82
Ethanol	PAB	2%	1066	0.0127 ± 0.0003	85
Ethanol	PSB	2%	1069	0.0454 ± 0.0001	69
Acetonitrile	PDMS	2%	2259	0.0025 ± 0.0002	82
Acetonitrile	PAB	2%	2251	0.0049 ± 0.0003	42
Acetonitrile	PSB	2%	2259	0.0041 ± 0.0001	68

[a]Error bar data are based on 95% confidence intervals from triplicate analyses.

In this case, it was not possible due to limited water solubility of the analyte but could be investigated in a less polar matrix.

3.3 *Comparison of polymers*

3.3.1 Diffusion into the polymers. Table 2 reveals that of the four polymers, coated to approximately three times the depth of penetration, PAB has the greatest D/L values for each solvent. This trend was not followed for ethanol, as the D/L value is larger into PDMS. This is as a result of greater clustering of ethanol within PAB than PDMS. The solvents have a large polarity range, which would suggest that the larger D values are not attributable to solvent affinity for the polymer alone. The polymer micro-organization (molecular weight, morphology, crystallinity, glass transition temperature, void distribution, etc.) [35] defines the free volume size and distribution which may be responsible for the greater ease of transport [38] through PAB. From the other three polymers, Teflon® AF2400 has the largest D/L values for the larger, less polar toluene. This confirms that the rate of transport is dependent on the chemical structure of the polymer [39], which will characterize the affinity of analyte for the polymer as well as penetrant size and polymer micro-structure.

3.3.2 Nature of the polymer. When calculating the diffusion coefficient (D), it is assumed that the movement of the penetrant follows Fick's second law, which relates the concentration gradient to the flux. This differential is solved using the appropriate boundary conditions to give the following equation [40]:

$$\frac{c}{c_L} = 1 - \frac{4}{\pi}\sum_{n=o}^{\infty}\frac{(-1)^n}{2n-1}\exp\left[\left[\frac{-D(2n+1)^2\pi^2 t}{4L^2}\right]\cos\left[\left[\frac{(2n+1)\pi x}{2L}\right]. \right.\right. \tag{3}$$

Equation (3) is modified for use in ATR-FTIR through combination with the general expression for absorbance in ATR-FTIR spectroscopy followed by integration yielding equation (4) [40]:

$$\frac{A_t}{A_\infty} = \frac{8\gamma}{\pi[1-e^{-2\gamma L}]}\sum_{n=0}^{\infty}\left[\frac{e^{(-D(2n+1)^2\pi^2 t/4L^2)}\left[((2n+1)\pi/2L)e^{-2\gamma L} + (-1)^n(2\gamma)\right]}{(2n+1)\left(4\gamma^2 + ((2n+1)\pi/2L)^2\right)}\right], \tag{4}$$

where, at time (t), the absorbance (A_t) may be related to the inverse of d_{p} (γ), polymer thickness (L), penetrant solution concentration (c), penetrant concentration at the polymer/crystal interface (c_{L}), and distance from the crystal surface (x).

In figures 1a–2a, averaged data sets for penetrants into each polymer are compared with model-generated diffusion curves derived from equation (4). The diffusion of toluene into Teflon® AF2400 illustrated in figure 1a demonstrates a good fit to the theoretical Fickian diffusion profile. All analytes previously monitored [34, 41] into Teflon® AF2400 as well as those in tables 2 and 3 were found to be Fickian in nature. Diffusion of toluene into PAB also displays a Fickian profile seen in figure 1b. The diffusion of toluene into PDMS (figure 1c) and PSB (figure 2a) conversely shows inferior fits to the theoretical curve.

It is clear from figures 1c and 2a that the correlation between the experimental data and the theoretical profile is poor and that the diffusion of toluene into PDMS and PSB does not appear to be Fickian in nature. In PDMS, the deviation of the experimental data from the model is random and is simply a case of elevated noise levels. It is proposed that the lack of Fickian character of the diffusion into PSB is a result of plasticization or swelling of the membrane resulting in alteration of the diffusion profile. The swelling process causes the interface between the polymer and the liquid to move, causing serious complications in the analysis of the process [42] as D is a function of L (equations (3) and (4)). If the membrane swells during the diffusion process the free volume will increase, causing a rise in A_∞. Experimental data for the first 15 min of toluene diffusion into PSB (figure 2b) were plotted and compared with the theoretical profile using a predictive model [43]. An excellent fit for this plot is demonstrated in figure 2b. The calculation of A_∞ from a full data set resulted in an absorbance value of 0.0132; however, predicting A_∞ from a reduced data set (which would exclude plasticization at longer run times) resulted in an absorbance of 0.0098. This 35% increase in the penetrant concentration within the polymer supports this plasticization hypothesis. As a result, D values calculated using a full data set are expected to be in error due to plasticization. The averaged D value estimated for the full data set was $3.76 \times 10^{-10}\,\mathrm{cm^2\,s^{-1}}$, while with the predictive approach from the reduced set, a more accurate value of $5.15 \times 10^{-10}\,\mathrm{cm^2\,s^{-1}}$ was obtained. Figure 2b demonstrates that diffusion into PSB is Fickian at early stages, when the polymer swelling is minimal. The movement of the boundary layer and the increase in free volume during diffusion

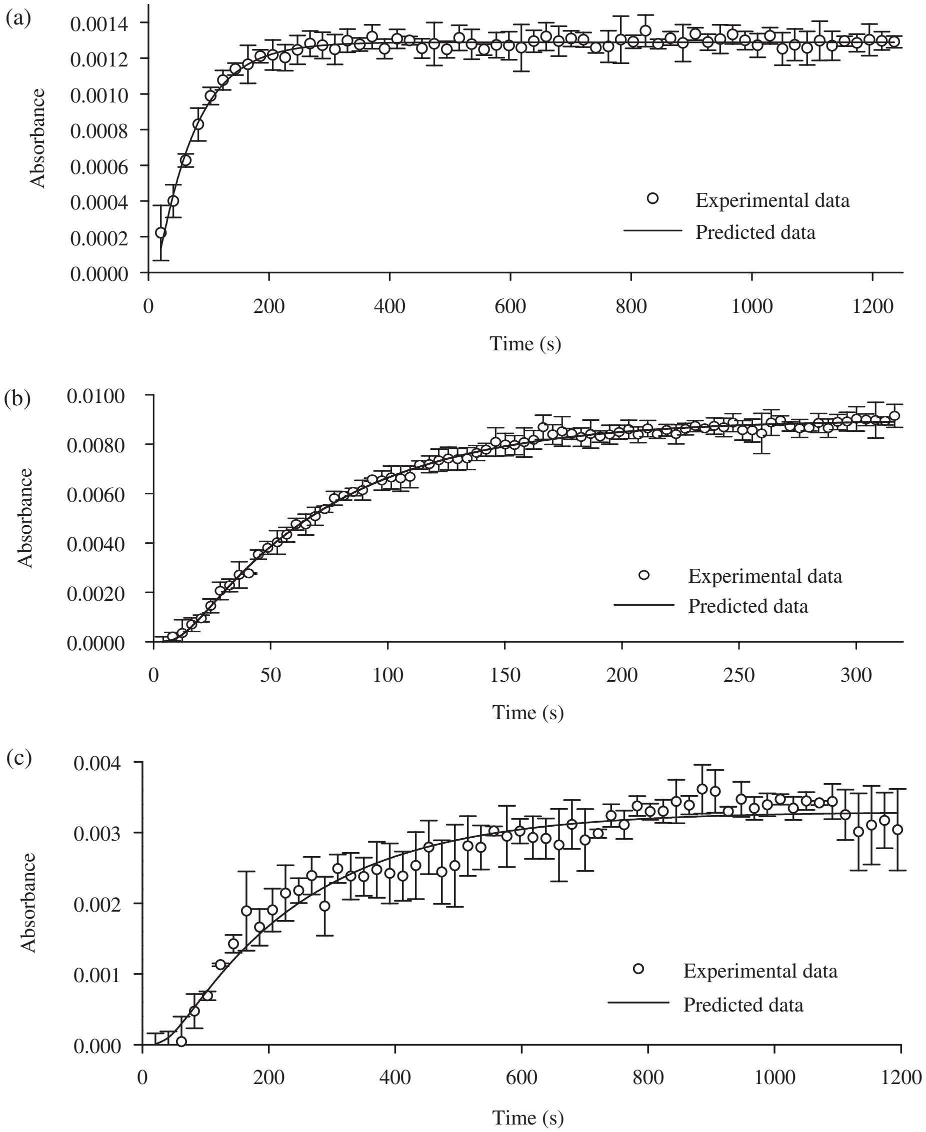

Figure 1. 100 µL/L toluene diffusion into polymer films at 25°C. Error bars were calculated based on triplicate runs with 95% confidence intervals. (a) Teflon® AF2400. (b) PAB. (c) PDMS.

are also evident by the appearance of negative polymer bands at elevated diffusion times. As the analyte concentration does not reach equilibrium while swelling of the polymer occurs, A_∞ was not reached. The experimental data therefore no longer fit the model and cause the apparent non-Fickian behaviour in PSB. The predictive model was originally designed as a technique for reducing sensing times through the prediction of A_∞ at pre-equilibrium times. For polymers, which demonstrate high pre-concentration of analytes and undergo swelling/plasticization, this predictive approach may be used as a method for calculating D and A_∞ values prior to the onset of non-Fickian behaviour.

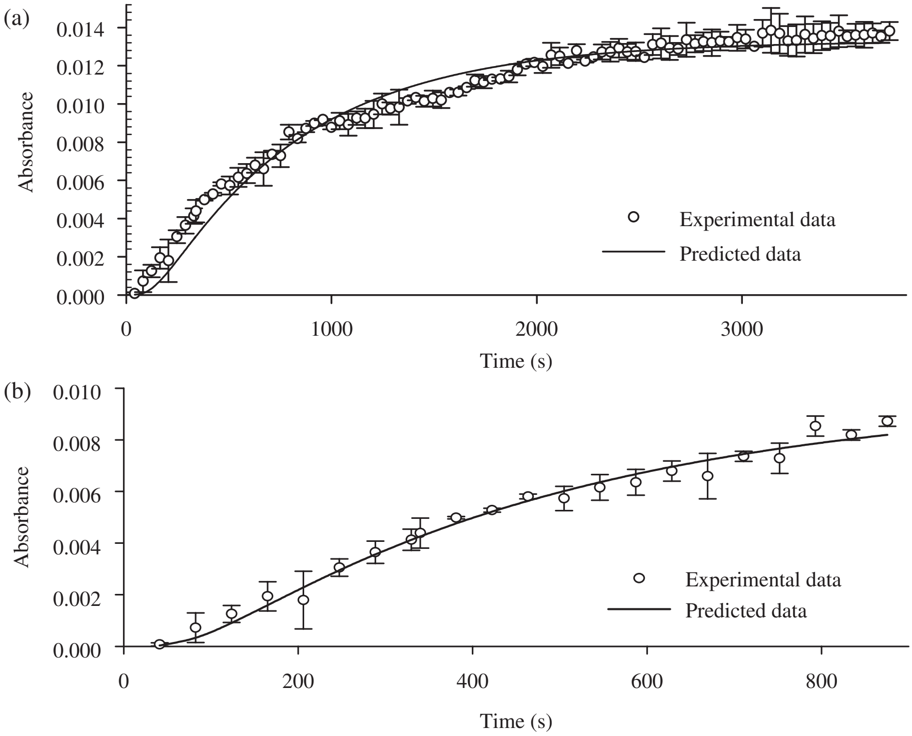

Figure 2. Toluene diffusion into PSB film at 25°C. Error bars were calculated based on triplicate runs with 95% confidence intervals. (a) Diffusion of 275 µL/L into PSB over 3600 s. (b) Diffusion of 275 µL/L into PAB over 900 s (predictive model) [43].

As many process/waste streams are aqueous-based, it is important to look at the influence of water on any cladding medium. Therefore, the penetration of water was monitored (OH stretch 3200–3500 cm) into each of the polymers. In each case, a polymer band was also monitored as a means of investigating solvent plasticization of the polymer. As the polymer swelled or plasticized, the amount of polymer within the evanescent field decreased, causing negative polymer band generation, the intensity of which was proportional to the degree of swelling or plasticization. PSB (figure 3a) experienced the greatest degree of swelling with large negative polymer bands present after saturation. These result data support the diffusion data presented in figure 2a and b. PDMS (figure 3b) and PAB (figure 3c) also plasticized but not to the same extent. Teflon® AF2400 (figure 3d) appears to display no swelling; this is demonstrated by no decrease in the polymer band intensity during water diffusion into the polymer.

3.3.3 Sensing viewpoint. The rate of diffusion of target analytes into polymer films as described by D has a profound dependency on membrane thickness [30, 44, 45]. T_{90} (the time taken for a penetrant to reach 90% of A_∞) is frequently used as a simple mechanism to compare polymers regarding the timescale of pre-concentration.

From a sensing viewpoint, table 5 reveals that PAB had superior pre-concentration times over a wide polarity range of solvents. PAB would be a good pre-concentrating

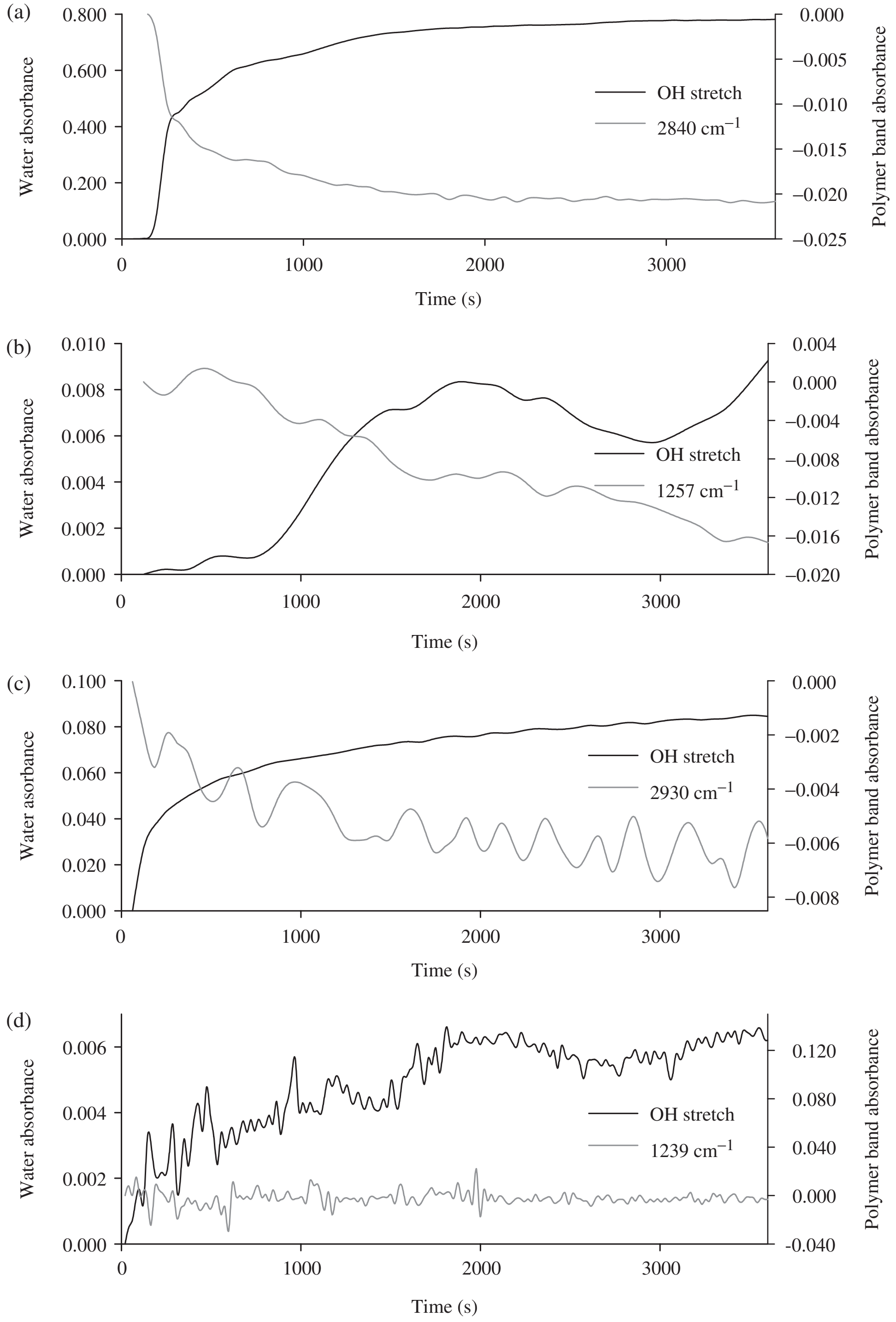

Figure 3. Diffusion of water (OH stretch) into cladding materials and the corresponding variation of their absorption bands. (a) PSB (2840 cm^{-1}). (b) PDMS (1257 cm^{-1}). (c) PAB (2930 cm^{-1}). (d) Teflon® AF2400 (1239 cm^{-1}).

Table 6. Comparison of log K, D/L, A_∞ and LOD values for toluene diffusion into four polymers, for the purpose of cladding choice for polymer modified ATR/FEW spectroscopic sensing.

	A_∞	T_{90} (s)	$D/L \times 10^{15}$ (cm/s)	$\log K$	LOD (μL/L)
Teflon®	0.0013 ± 0.0001	151	35.30 ± 2.29	2.42	27
PDMS	0.0034 ± 0.0002	494	12.87 ± 0.57	2.25	114
PAB	0.0089 ± 0.0003	153	37.62 ± 2.44	2.71	10
PSB	0.0111 ± 0.0001	1180	6.27 ± 0.76	2.71	91

medium for a waste stream, which has a broad range of solvents where the level of each was to be monitored. Teflon® AF2400 alternatively displayed rapid t_{90} values for less polar penetrants, while more polar solvents hardly diffuse into the membrane. This is demonstrated by the elevated analyte concentrations needed for detection (tables 2 and 5). Teflon® AF2400 would be suitably utilized for enrichment and monitoring of lipophilic components in a waste stream with a complex polar matrix. Both the PDMS and the PSB show an affinity for the more polar solvents. This can cause difficulties due to plasticization by water, which is least problematic in the case of Teflon® AF2400.

Each analyte was monitored at a characteristic absorbance wavelength (λ) illustrated in tables 2 and 5. Monitoring of the same absorbance bands for an analyte into each polymer was not possible as a result of noise or polymer absorption. A_∞ is not comparable between bands or analytes as a result of the variation of molar absorptivity. In this work, polymers may be compared in blocks of three, where A_∞ for each analyte was measured using the same absorbance band into three of the four polymers. PDMS, PAB, and PSB are compared for toluene and acetonitrile (table 5). For both of these analytes, PAB has the largest equilibrium concentration followed by PSB, with PDMS having absorbed the smallest quantity of each solvent. Teflon® AF2400, PAB, and PSB are compared for THF and ethanol (table 5). Both PAB and PSB absorbed an equal amount of THF, with ethanol pre-concentrating the least in AF2400. PSB absorbed over three times the quantity of ethanol absorbed by PAB; again, Teflon® AF2400 absorbed the least. From this, PAB and PSB demonstrate the largest pre-concentration of each analyte due to higher free volumes. However, PAB demonstrates a greater affinity over the polarity range studied, with the exception of ethanol, for which it is the only analyte not displaying the largest D/L, t_{90}, and A_∞ values. Acetonitrile demonstrates a greater pre-concentration through increased affinity as a result of interaction of the nitrile groups within the polymer. Evidence of this is the red shift of the nitrile stretching band from 2259 to 2251 cm^{-1}, which does not occur in PDMS and PSB (table 5). PSB demonstrates a greater affinity for the more polar analytes. Both PDMS and Teflon AF2400 show less analyte pre-concentration and are presumed to have lower free volumes. Teflon® AF2400 shows the definite trend of increasing analyte affinity with decreasing polarity, where the more polar analytes are absorbed to a far lesser extent as a result of its non-polar nature.

3.4 *Partition coefficient and polymer selection*

Log K, t_{90}, D/L, A_∞, and LOD values are illustrated in table 6. A comparison of these data is made with the purpose of ascertaining whether partition coefficient ($\log K$)

values alone are an adequate means of polymer selection for use in ATR/FEW clad spectroscopic sensing.

The partition coefficient for toluene between water/PAB and water/PSB is equivalent (table 6). If the choice of polymer were based solely on log K values, it would appear that toluene pre-concentration demonstrated by PAB and PSB would be identical. Table 6, however, illustrates a significant variation in the pre-concentration characteristics between PAB and PSB. Both t_{90} and D/L values show an approximate sevenfold increase in diffusion rate from PSB to PAB. Toluene A_∞ values demonstrate a 25% higher concentration within PAB relative to PSB. However, due to greater spectral noise within PSB, a ninefold greater LOD than PAB was observed.

The difference between the partition coefficients measured for PSB and Teflon® AF2400 demonstrated in table 6 is significant. If comparing their pre-concentrating capability based on log K, the assumption would be made that PSB is a superior pre-concentrating medium. Table 6, however, illustrates a significantly lower LOD for Teflon® AF2400, albeit the substantially larger log K value. The Teflon® AF2400 also displays an enhanced rate of diffusion of toluene over PSB.

Consequentially, table 6 demonstrates that a simple partition coefficient is not sufficient to characterize a polymer/analyte system. Important polymer characteristics, which define the rate of diffusion, polymer plasticization, etc., are ignored. The partition coefficient will give a good indication of the analyte concentration, which a polymer shall absorb, but shall not be definitive, as illustrated by the A_∞ difference between PAB and PSB. Finally, the partition coefficient provides no suggestion as to spectral noise idiosyncratic to a polymer.

4. Conclusion

A comparison of a number of polymeric materials as pre-concentrating media for use with ATR/FTIR sensing was made in this article. It is evident from the work carried out that polymer modified ATR/FTIR spectroscopy is a suitable methodology for the analysis and quantification of analytes in such an industrial process stream. Of the four polymers investigated, Teflon® AF2400 and PAB demonstrated the highest degree of suitability for use as pre-concentrating media.

PAB gave rise to the shortest sensing times, as described by the largest D/L and the shortest t_{90} values for the range of solvents studied as a result of its relatively large free volume. PAB also displayed the largest pre-concentration demonstrated by the largest A_∞ values (with the exception of the ethanol/PSB system) and greatest sensitivity illustrated by the lowest toluene LOD value.

Teflon® AF2400 displayed increased sensing times relative to the other polymers for the less polar analytes and displayed little or no pre-concentration of the more polar analytes. Teflon® AF2400 also demonstrated the least ingress of water in a comparison of the four polymers and was the only polymer that displayed no swelling/plasticization. To individually monitor toluene in the process stream, Teflon® AF2400 would be the most suitable polymer. PAB, however, would be more suitable if it was necessary to monitor all four solvents in the process stream.

The size of a diffusing molecule or its molecular diameter is demonstrated to inversely affect the rate of diffusion. However, it has also been shown that size is not the only factor affecting *D*, where functionality and bulkiness may cause a significant variation in its rate of diffusion into a polymer.

From this work, it may also be concluded that the partition coefficient of an analyte is a good indicator for polymer selection. However, it is not definitive, as it will only indicate to what extent the polymer pre-concentrates, but will not reveal the rate of pre-concentration or the extent of plasticization. Plasticization may be overcome by the use of predictive modelling in conjunction with absorbance data obtained at the early stages of diffusion.

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References

[1] A. Joseph, A.E. Mathai, S. Thomas. *J Membr. Sci.*, **220**, 13 (2003).
[2] S.A. Kumar, S. Thomas, M.G. Kumaran. *Polymer*, **38**, 4629 (1997).
[3] R. Howley, B.D. MacCraith, K. O'Dwyer, P. Kirwan, P. McLoughlin. *Vib. Spectrosc.*, **31**, 271 (2003).
[4] S. George, K.T. Varughese, S. Thomas. *Polymer*, **41**, 579 (2000).
[5] R. Gobel, R. Krska, R. Kellner, R.W. Seitz, S.A. Tomellini. *Appl. Spectrosc.*, **48**, 678 (1994).
[6] J.E. Walsh, B.D. MacCraith, M. Meaney, J.G. Vos, F. Regan, A. Lancia, S. Artjushenko. *Analyst.*, **121**, 789 (1996).
[7] M. Janotta, A. Katzir, B. Mizaikoff. *Appl. Spectrosc.*, **57**, 823 (2003).
[8] J.S. Vrentas, C.M. Vrentas. *J. Appl. Polym. Sci.*, **93**, 92 (2004).
[9] L. Philippe, C. Sammon, S.B. Lyon, J. Yarwood. *Prog. Org. Coat.*, **49**, 315 (2004).
[10] M. Jakusch, B. Mizaikoff, R. Kellner. *Sensor Actuat. B-Chem.*, **38**, 83 (1997).
[11] B. Mizaikoff, K. Taga, R. Kellner. *Vib. Spectrosc.*, **8**, 103 (1995).
[12] R. Howley, B.D. MacCraith, K. O'Dwyer, H. Masterson, P. Kirwan, P. McLoughlin. *Appl. Spectrosc.*, **57**, 400 (2003).
[13] G. Roy, J.A. Mielczarski. *Water Res.*, **36**, 1902 (2002).
[14] M.C. Ertanlamontagne, S.R. Lowry, W.R. Seitz, S.A. Tomellini. *Appl. Spectrosc.*, **49**, 1170 (1995).
[15] J.F. Feller, Y. Grohens. *Sensor Actuat. B: Chem.*, **97**, 231 (2004).
[16] B. Mizaikoff. *Anal. Chem.*, **75**, 258A–267A (2003).
[17] M. Karlowatz, M. Kraft, B. Mizalkoff. *Anal. Chem.*, **76**, 2643 (2004).
[18] R. Gobel, R.W. Seitz, S.A. Tomellini, R. Krska, R. Kellner. *Vib. Spectrosc.*, **8**, 141 (1995).
[19] B. Murphy, P. Kirwan, P. McLoughlin. *Vib. Spectrosc.*, **33**, 75 (2003).
[20] H. Steiner, K. Staubmann, R. Allabashi, N. Fleischmann, A. Katzir, Y. Reichlin, B. Mizaikoff. *Water Sci. Technol.*, **47**, 121 (2003).
[21] C. Sammon, C. Mura, S. Hajatdoost, J. Yarwood. *J. Mol. Liq.*, **96–97**, 305 (2002).
[22] J.M. Chalmers, P.R. Griffiths (Eds). *Handbook of Vibrational Spectroscopy*, *Sampling Techniques*, Wiley, Chichester, UK (2002).
[23] M. Janotta, M. Karlowatz, F. Vogt, B. Mizaikoff. *Anal. Chim. Acta*, **496**, 339 (2003).
[24] L.R. Snyder, J.J. Kirkland, J.L. Glajch (Eds). *Practical HPLC Method Development*, 2, Wiley & Sons, New York (1997).
[25] B. Murphy, P. McLoughlin. *Int. J. Environ. Anal. Chem.*, **83**, 653 (2003).
[26] V. Dobbyn, R. Howley, P. Kirwan, P. McLoughlin. *Int. J. Environ. Anal. Chem.*, **83**, 643 (2003).
[27] M. Jakusch. Polymer coated infrared evanescent wave sensors: approaches for their systematic development. PhD thesis, Technical Institute of Vienna (2000).
[28] R. Clement, A. Jonquieres, I. Sarti, M.F. Sposata, M.A. Custal Teixidor, P. Lochon. *J. Membr. Sci.*, **232**, 141 (2004).
[29] M. Jakusch, B. Mizaikoff. *Adv. Environ. Chem. Sens. Tech.*, **4205**, 93 (2001).
[30] A.M. Shishatskii, Y.P. Yampolskii, K.V. Peinemann. *J. Membr. Sci.*, **112**, 275 (1996).
[31] G. Unnikrishnan, S. Thomas, S. Varghese. *Polymer*, **37**, 2687 (1996).
[32] S.C. George, S. Thomas, K.N. Ninan. *Polymer*, **37**, 5839 (1996).

[33] A.R. Berens, H.B. Hopfenberg. *J. Membr. Sci.*, **10**, 283 (1982).
[34] B. Murphy, P. Kirwan, P. McLoughlin. *Anal. Bioanal. Chem.*, **377**, 195 (2003).
[35] C. Sammon, C. Deng, C. Mura, J. Yarwood. *J. Mol. Liq.*, **101**, 35 (2002).
[36] A. Jonquieres, R. Clement, P. Lochon. *Prog. Polym. Sci.*, **27**, 1803 (2002).
[37] J. Crank, G.S. Park (Eds). *Diffusion in Polymers*, 2, Academic Press, London (1968).
[38] J.S. Vrentas, J.L. Duda, H.C. Ling. *J. Membr. Sci.*, **40**, 101 (1989).
[39] J. Yarwood, C. Sammon, C. Mura, M. Pereira. *J. Mol. Liq.*, **80**, 93 (1999).
[40] G.T. Fieldson, T.A. Barbari. *Polymer*, **34**, 1146 (1993).
[41] B. Murphy. Characterisation of polymer-modified sensor based upon internal reflection spectroscopy. PhD thesis, Waterford Institution of Technology (2003).
[42] S. Alsoy, J.L. Duda. *AIChE J.*, **48**, 1849 (2002).
[43] P. McLoughlin, K. Flavin, P. Kirwan, B. Murphy, K. Murphy. *Sensor Actuat. B-Chem.*, **107**, 170 (2005).
[44] F. Regan, M. Meaney, J.G. Vos, B.D. MacCraith, J.E. Walsh. *Anal. Chim. Acta*, **334**, 85 (1996).
[45] V. Acha, M. Meurens, H. Naveau, S.N. Agathos. *Biotechnol. Bioeng.*, **68**, 473 (2000).