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# Time-resolved ATR-FTIR studies on the release of solvents from cleaning gels into model systems of oil paint binding media

Lambert Baij<sup>\*ab</sup>, Katrien Keune<sup>ab</sup>, Joen Hermans<sup>a</sup>, Petria Noble<sup>b</sup> and Piet Iedema<sup>a</sup>

## Abstract

The use of gelled systems for the cleaning of paint surfaces aims to regulate the cleaning action by the controlled application of solvents. Benefits are assumed to include controlled solvent release at the surface and limited extraction of soluble paint constituents from the bulk of the painting. Rigid gels have the added benefit of reducing mechanical action and they typically leave no gel residues behind. In order to compare the diffusion of free (organic) solvents and solvents released from cleaning gels, we developed a method based on time-resolved attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR). Using model systems of oil paint binding media based on zinc and lead ionomers, the diffusion of free solvents and solvents released from three gels was accurately measured and compared. Minimal or no solvent retention caused by cleaning gels was found with this set of data, due to the slow diffusion of ethanol and water in the non-porous binding medium model.

## Introduction

Recently, the focus of cleaning science shifted towards the confinement of solvents into emulsions and solvent gels for the con-

trolled application of solvents<sup>1;2;3;4</sup>. These thickened solvents and gel systems not only reduce the mechanical action necessary for the cleaning of paint surfaces, but aim to provide the conservator with superior kinetic control of the cleaning process<sup>5;6</sup>. Nuclear magnetic resonance (NMR) mouse experiments on acrylic emulsion paints showed that the amount of water delivered into the paint by agar gels is on par with swab cleaning with water, while other gels showed higher water release<sup>4</sup>. Combined mass analysis and NMR experiments on oil paint mock-ups demonstrated a decreased uptake of solvent by the paint when using gelled systems<sup>7;8</sup> studied the water released by gels on paper by mass analysis and found the water released by the newly developed rigid gels to be significantly lower than that of the polyschararide gels agar and gellan. In this light, we study the kinetics of solvent delivery of three cleaning gels on our model systems for aged oil paint binding medium. These model systems are polymers based on a polymerized linseed oil matrix with Zn<sup>2+</sup> and Pb<sup>2+</sup> ions as an intergral part of the network, similar to aged binding medium in paintings<sup>9;10</sup>.

## Experimental

For this study we developed a method based on time-resolved ATR-FTIR that gives detailed chemical information over time and designed a sample cell that allows for careful control of the experimental conditions. Spec-

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tral processing and the application of a diffusion model allow for the determination of diffusion coefficients<sup>11</sup>. Using this method, the diffusion of a wide range of solvents commonly used for the cleaning of paintings is studied in binding medium models systems containing zinc (Zn<sup>2+</sup>) and lead (Pb<sup>2+</sup>) ions. In addition, the diffusion of water and ethanol from three conservation cleaning gels: Nanorestore<sup>®</sup> Max Dry, agar, and gellan, is studied and compared to free solvent diffusion from a solvent reservoir above the surface of the binding medium model. For free solvents, diffusion and swelling are governed by the equilibrium conditions at the interface of the solvent and polymer and inside the polymer. In contrast, the observed diffusion for liquids from gelled systems is the result of a combination of equilibrium conditions inside the gel, at the interface, and inside the polymer. If the process inside the gel or at the interface is rate-determining, this will be observed as 'retention'.

### Sample preparation

Binding medium model systems were made according to previously published procedures by<sup>10</sup> with a metal ion concentration in the polymer films of roughly 160 mM (or TAG : Pb/Zn = 1 : 0.44 in the initial uncured sample mixture). Agar was purchased from Sigma Aldrich and Gellan Kelcogel<sup>®</sup> CG-LA (LOT NO 3H7072A) was purchased from Azelis and used as received. Gels were made by mixing 4 wt% (agar) and 3 wt% (gellan) in deionized water at 100 °C while stirring for 15 min and subsequently cast on a flat surface. Nanorestore<sup>®</sup> Max Dry was used as received from CSGI (<http://www.csgi.unifi.it/>). Gels were kept in a sealed container loaded with ethanol or D<sub>2</sub>O for at least 12 hour before use. Complete exchange of

solvents inside the gels upon loading was not verified analytically. For agar and gellan, no detectable saccharide residues were found in the D<sub>2</sub>O supernatant as analysed by <sup>1</sup>H NMR while saccharide residues were found in the ethanol supernatant. All gels were blotted with paper tissue and flushed with a flow of N<sub>2</sub> until dry on the surface before application.

### Experimental setup

A Perkin-Elmer Frontier FT-IR spectrometer fitted with a Pike GladiATR module that included a heated top plate and a diamond ATR-crystal ( $\varnothing = 3$  mm) was used. In order to measure spectra of polymer samples while they were exposed to solvents or solutions, a custom built stainless steel cylinder was designed as illustrated in Figure 1 (a). As indicated in Figure 1 (b), a glass sheet was used to slow down solvent evaporation from the top of the gel.

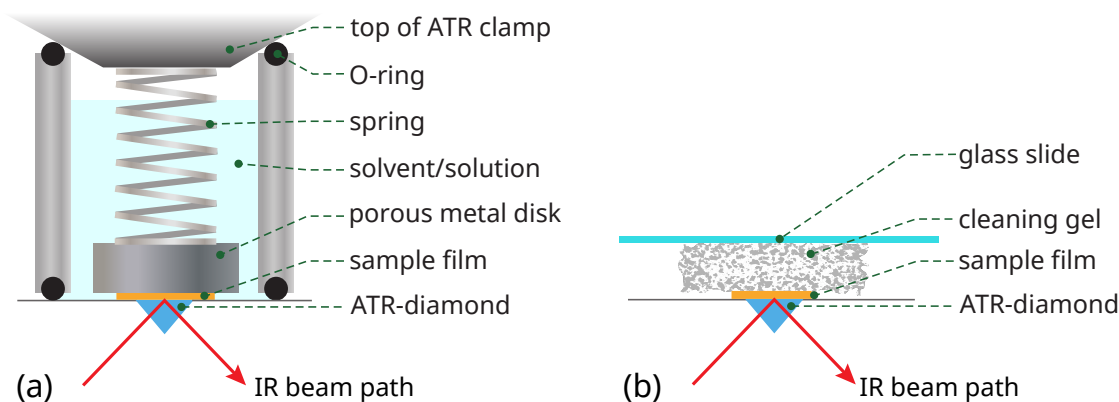
### Data processing

Diffusion in polymer films was measured for cyclohexane (904 cm<sup>-1</sup>), ethanol (879 cm<sup>-1</sup>), acetone (529 cm<sup>-1</sup>), D<sub>2</sub>O (2510 cm<sup>-1</sup>), methanol-*d*<sub>4</sub> (2485 cm<sup>-1</sup>), DCM (1265 cm<sup>-1</sup>), and toluene-*d*<sub>8</sub> (541 cm<sup>-1</sup>). The wavenumbers in parentheses for each solvent refer to the positions of a characteristic solvent band sufficiently isolated for accurate band integration. Time-dependent IR absorption band areas were calculated with Perkin-Elmer TimeBase software and used for model fitting without further processing.

## Results and discussion

### Diffusion of pure solvents in ionomer films

Solvent diffusion in model oil paint binding media was investigated for a range of sol-



**Figure 1** Illustration of (a) the sample cell used for time-dependent ATR-FTIR measurements of polymer films in contact with solvents or solutions and (b) the setup used for the release of solvent from cleaning gels. For setup (b) the glass sheet lowers evaporation of solvent from the top of the gel.

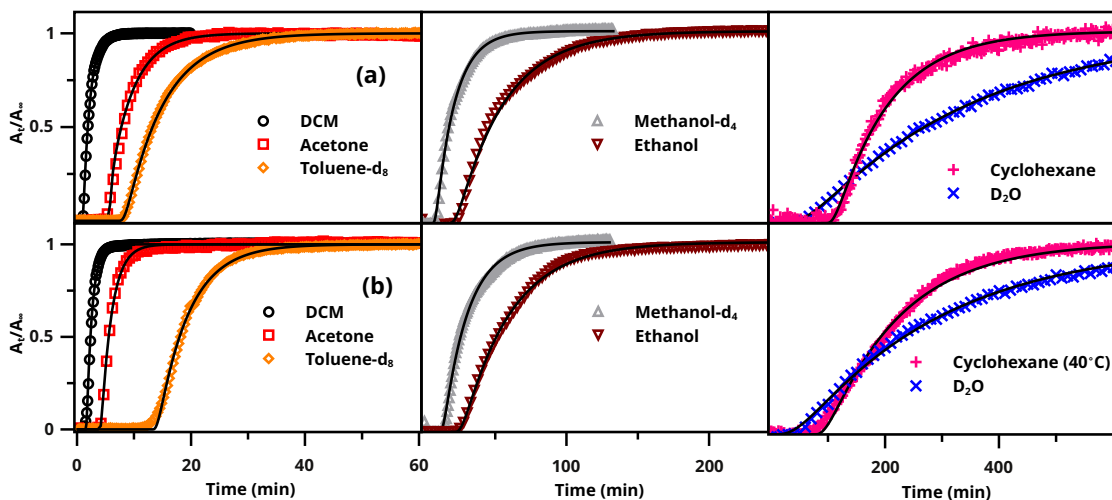
vents commonly used for the cleaning of oil paintings. Figure 2 shows the normalized concentration profiles over time of various solvents in zinc and lead ionomer systems. Values of diffusion coefficients were obtained by fitting the data to Fick's law for diffusion adapted for ATR-FTIR<sup>11</sup>. To account for the time before solvent reaches the detector, a lag time parameter  $\tau$  was employed as an extra parameter to define the onset of concentration increase after the initial swelling period. Fits of the diffusion data were obtained with the band area  $A_\infty$ , lag time  $\tau$  and diffusion coefficient  $D$  as independent parameters.

Figure 2 shows that the adapted Fickian diffusion model provides excellent fits for the diffusion of all investigated solvents. Therefore, once the solvent front reaches the detector (at  $t = \tau$ ), diffusion becomes Fickian, implying that solvent-polymer interactions remain constant<sup>12</sup>. Possible non-Fickian behaviour during solvent swelling (at  $t < \tau$ ) is accounted for by the lag time parameter  $\tau$ . The reproducibility of the concentration profiles was investigated by repeating the acetone diffusion experiment eight times on Zn-

pol films with a thickness varying between 124 and 159  $\mu\text{m}$ . The standard deviation in the diffusion coefficient in this set of measurements was 10 %.

In general, diffusion coefficients for solvents in zinc and lead ionomer systems were found to be similar. However, a great variation in the rate of diffusion between different solvents was found:  $D_{\text{DCM}}$  being roughly 200 times larger than  $D_{\text{D}_2\text{O}}$ . These values are similar to values determined by<sup>13;14</sup> for swelling experiments on thermally polymerized stand-oil films. The trend in diffusion rates for different solvents is correlated to the kinematic viscosity, with the more viscous solvents having the lowest diffusion coefficients. Similar observations were made by<sup>13;14</sup>. The diffusion of  $\text{D}_2\text{O}$  is much slower than what is expected from kinematic viscosity, but is comparable to values reported for water vapour diffusion in pigmented alkyd paints<sup>15</sup> and vapour diffusion in historical samples of prussian blue and basic lead carbonate<sup>16</sup>.

The lag time  $\tau$  is a function of film thickness  $L$  and the quantity  $L^2/\tau$  (lag time cor-



**Figure 2** Concentration profiles of several solvents in (a) zinc ionomer and (b) lead ionomer films of 135–160  $\mu\text{m}$  thickness. Solid black lines represent best fits of the adapted Fickian diffusion model with a lag time  $\tau$  as extra parameter. For  $\text{D}_2\text{O}$ ,  $\tau$  was estimated. Note the different time scales in each graph. Only a fraction of the collected data points are shown for clarity.

rected for film thickness) is known to be proportional to the diffusion coefficient<sup>17</sup>. Table 1 confirms this, although again water deviates from the trend. The unexpectedly small  $\tau$  for  $\text{D}_2\text{O}$  is clearly seen in Figure 2, where the water concentration profile starts before that of cyclohexane, while it is subsequently much slower to reach saturation. For a detailed discussion see also<sup>18</sup>.

The swelling capacity for each solvent was investigated by monitoring IR bands corresponding to the polymer sample. Taking the ratio of the difference in absorption of the ester carbonyl band ( $1740\text{ cm}^{-1}$ ) at saturation and at  $t = 0$  ( $\Delta A/A_{\text{min}}$ ), a measure is obtained for the degree of swelling. Table 1 shows that DCM swells the investigated model systems more than 110 %, while water hardly swells the polymer system at all (5–13 % for zinc and lead, respectively). Monitoring the decrease of IR absorption bands of the polymer confirms the low swelling capacity of water and reproduces trends in solvent

swelling power reported in the literature<sup>19;20</sup>.

### Diffusion of solvents from conservation cleaning gels

We have evaluated the diffusion of water and ethanol from three rigid gels that are used for the cleaning of paintings. This series consists of two polysaccharide gels, agar and gellan, and a type of conservation cleaning gel consisting of a polymer blend commercialized under the name Nanorestore<sup>2;8;21</sup>. While the overall structure remains intact<sup>22;23</sup>, minor mechanical and optical changes (decreased opaqueness, increased rigidity) were observed upon loading the agar gel (4 wt% in water) with ethanol. The gellan gel (3 wt% in water) was found to be incompatible with the loading of ethanol due to strongly increased rigidity and shrinking and could not be tested at this concentration.

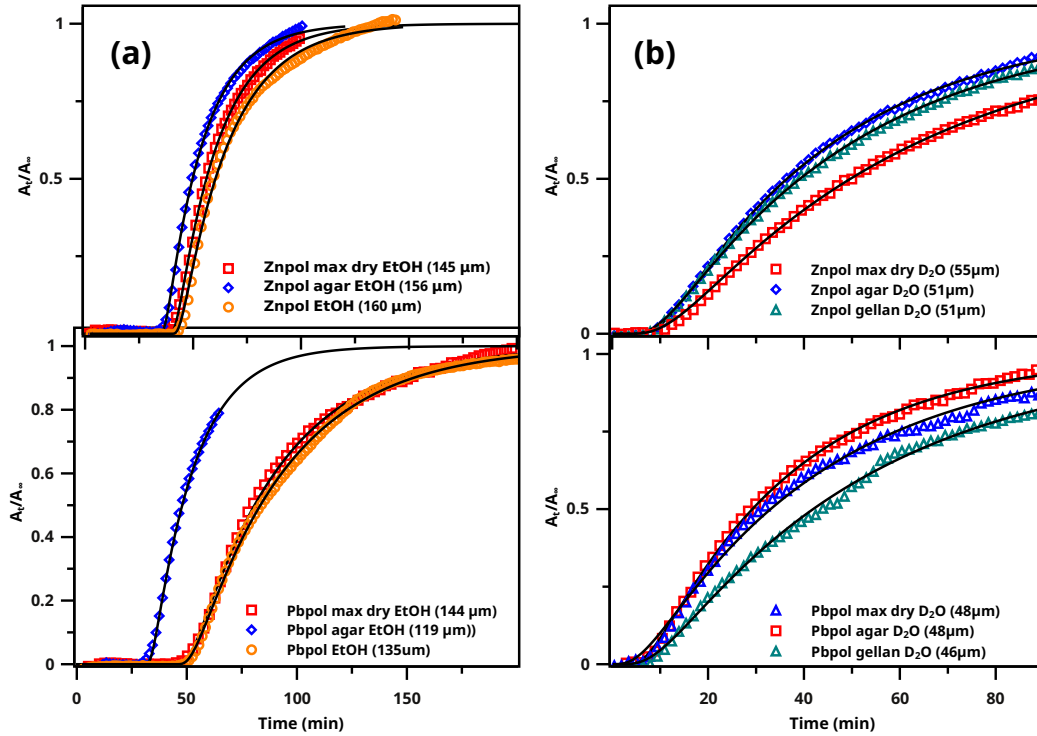
**Table 1** Diffusion coefficients ( $D$ ) and lag times corrected for thickness ( $L^2/\tau$ ) resulting from a fit Ficks law to the concentration profiles in Figure 2. Swelling factors ( $\Delta A/A_{\min}$ ) were calculated by taking the ratio of the highest and lowest intensity of the ester carbonyl band during swelling.

Sample	Solvent	$D$ ( $10^{-8}$ cm <sup>2</sup> /s)	$L^2/\tau$ ( $10^{-8}$ cm <sup>2</sup> /s)	$\Delta A/A_{\min}$
Znpol	DCM	138	320	1.21
	acetone	61	105	0.73
	toluene-d <sub>8</sub>	25	56	0.71
	methanol-d <sub>4</sub>	10	41	1.1
	ethanol	4.3	21	0.89
	cyclohexane	1.4	3.7	0.24
	D <sub>2</sub> O	0.61	8.2	0.05
Pbpol	DCM	140	270	1.13
	acetone	61	84	0.89
	toluene-d <sub>8</sub>	31	29	0.81
	methanol-d <sub>4</sub>	7.2	31	0.56
	ethanol	4.0	16	0.87
	cyclohexane	1.1	5.5	0.45
	D <sub>2</sub> O	0.63	8.2	0.13

### Diffusion of ethanol from gels

Figure 3 (a) shows the concentration profiles of ethanol in the binding medium model for free ethanol, Nanorestore Max Dry gels and 4 % agar gels loaded with ethanol. The difference of the parameter  $\tau$  between free solvent and solvent released from gels is used as a measure of solvent retention by gels. From Table 2, it is evident that the gelled systems do not show significant retention (for Zn-pol:  $L^2/\tau = 15 \pm 4$  for free ethanol and  $L^2/\tau \simeq 10$  for gelled systems). In general, the diffusion coefficient of solvents released from gels in the swollen polymer (at  $t > \tau$ ) is similar (*i.e.* within the experimental error) to the diffusion of free solvents. For example for Zn-pol, free ethanol diffusion has a value of  $D = 5.6 \pm 1.8 \times 10^{-8}$  cm<sup>2</sup>/s and ethanol released from gels has a value of  $D = 7.6 \pm 0.5 \times 10^{-8}$  cm<sup>2</sup>/s and  $D = 6.6 \pm 2.4 \times 10^{-8}$  cm<sup>2</sup>/s, for Nanorestore and agar 4 %, respectively. Likewise,

similar diffusion coefficients for free ethanol and ethanol released from gels were found for Pb-pol:  $D = 3.2 \pm 0.6 \times 10^{-8}$  cm<sup>2</sup>/s for free ethanol,  $D = 3.40 \pm 0.06 \times 10^{-8}$  cm<sup>2</sup>/s for Nanorestore and  $D = 5.4 \pm 0.3 \times 10^{-8}$  cm<sup>2</sup>/s for agar 4 %. Just as for Zn-pol, the experimental error in  $L^2/\tau$  for Pb-pol prevented us from concluding on significant solvent retention by gels (Pb-pol:  $L^2/\tau = 7.6 \pm 2.1$  for free ethanol,  $L^2/\tau \simeq 8$  for gelled systems). It should be noted that for the gels, evaporation of ethanol from the gel causes loss of contact between the sample and the detector (after  $\pm 100$  min for Zn-pol and  $\pm 60$  min for Pb-pol with agar) and complete solvent saturation is not reached. In contrast to the diffusion rates, this contact loss prohibited us from determining the exact *amount* of solvent (*e.g.* expressed as swelling) delivered by the gels quantitatively. Qualitatively though, the solvent delivery from gels appeared to be on par with the application of pure solvents at



**Figure 3** Concentration profiles of ethanol (a) and (b)  $D_2O$  in zinc and lead ionomer films. Solid black lines represent best fits of the Fickian diffusion model with a lag time  $\tau$  as extra parameter. For  $D_2O$ ,  $\tau$  was estimated. Only a fraction of all collected data points and are shown for clarity.

long timescales.

### Diffusion of water from gels

It was observed that gels are capable of accumulating water on the surface. If the gels are not properly dried before application, this surface-adhered water seems to be forced into the polymer. Consequently,  $\tau$  is close to zero and  $D$  is up to three times faster than for surface-dried gels. To correct for the error introduced by this hard to control effect, all values were averaged over two or more measurements. Considering the values of  $D_{D_2O}$  for all measurements, some gels (gellan and Max Dry for Zn-pol) show a small but significant decrease in  $D$  compared to free water (Table 2). We have no mechanistic explanation for this small decrease in  $D$  and it

is at present unclear if our dataset is large enough to make a solid statistical argument in favour of this difference. Comparing the retention ( $\tau$ ) of free water and water released by gels in Table 2, no significant increase in  $\tau$  was found when water was loaded into gels for Pb-pol, while for Zn-pol there seems to be very limited retention ( $L^2/\tau$  for Zn-pol is  $\simeq 8 \times 10^{-8} \text{ cm}^2/\text{s}$  for free water and  $L^2/\tau \simeq 6.5 \times 10^{-8} \text{ cm}^2/\text{s}$  for gels). Clear confirmation of this effect would require a larger data set.

The fact that there is minimal or no effect on  $\tau$  when water or ethanol is loaded into gels suggests that diffusion is rather determined by the nature (*e.g.* porosity) of the paint surface than by the method of solvent application (free solvent or gels). In order

**Table 2** Diffusion coefficients  $D$  and lag times corrected for thickness  $L^2/\tau$  resulting from a fit of Fick’s law to the concentration profiles in Figure 2. Values are averaged over two or more measurements. Standard deviations are indicated with  $\pm$ .

Sample	Solvent	$D$ ( $10^{-8}$ cm <sup>2</sup> /s)	$L^2/\tau$ ( $10^{-8}$ cm <sup>2</sup> /s)
Znpol	ethanol	$5.1 \pm 1.8$	$15 \pm 4$
Znpol + Max Dry	ethanol	$7.6 \pm 0.5$	$9.7 \pm 0.6$
Znpol + agar 4%	ethanol	$6.6 \pm 2.4$	$12.0 \pm 0.3$
Znpol	D <sub>2</sub> O	$0.56 \pm 0.08$	$8.4 \pm 0.3$
Znpol + Max Dry	D <sub>2</sub> O	$0.39 \pm 0.06$	$5.4 \pm 0.7$
Znpol + agar 4%	D <sub>2</sub> O	$0.44 \pm 0.07$	$6.2 \pm 0.2$
Znpol + gellan 3%	D <sub>2</sub> O	$0.39 \pm 0.06$	$6.5 \pm 0.4$
Pbpol	ethanol	$3.2 \pm 0.6$	$7.6 \pm 2.1$
Pbpol + Max Dry	ethanol	$3.40 \pm 0.06$	$8.1 \pm 0.0$
Pbpol + agar 4%	ethanol	$5.4 \pm 0.3$	$9.1 \pm 1.0$
Pbpol	D <sub>2</sub> O	$0.58 \pm 0.06$	$7.0 \pm 0.5$
Pbpol + Max Dry	D <sub>2</sub> O	$0.42 \pm 0.14$	$6.8 \pm 0.3$
Pbpol + agar 4%	D <sub>2</sub> O	$0.42 \pm 0.13$	$6.4 \pm 1.4$
Pbpol + gellan 3%	D <sub>2</sub> O	$0.32 \pm 0.01$	$6.7 \pm 0.9$

to inhibit solvent retention from the gels, the diffusion of solvent into the paint must be slower than the diffusion of solvent out of the gel. In that case, small amounts of solvent accumulate on the interface of the gel and the surface. This is a key observation for cleaning with gels: it is the paint surface that largely determines the rate of solvent uptake. This argument holds only for non-porous paints, powdery or cracked paints are expected to show faster diffusion by capillary action. Preliminary experiments on a 40 year old porous paint sample confirmed this fast diffusion but posed new analytical challenges that will be the topic of forthcoming research.

## Conclusion

We have described a time-dependent ATR-FTIR method using a custom sample cell to study solvent diffusion and film swelling in linseed oil-based binding medium mod-

els containing lead or zinc (lead or zinc ionomers). The method was successfully used to study the diffusion of a range of seven solvents. Similar diffusion behaviour in zinc and lead ionomers was found. After an initial short non-Fickian phase, all solvents fitted a Fickian concentration profile, with diffusion coefficients similar to literature values. The method was extended to study the diffusion of solvent from Nanorestore<sup>®</sup> Max Dry, agar and gellan gels. We conclude that within this dataset, solvent retention caused by the use of cleaning gels cannot be qualified as significant.

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