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FLR technique exchange of methanol/fluorescent dye with water in water-saturated cement paste examined by NMR

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Abstract

A water saturated cement paste (w/c = 0.7) confined in a solution of methanol saturated with a fluorescent dye showed complete exchange of water after 10 days. However, after exchange the concentration of dye within the cement paste was less than 50% compared to the expected equilibrium value. This result is rationalized by the much larger solubility of dye in methanol compared to water, by more than two orders of magnitude. The diffusion of dye into the cement paste is thus a rather complex process, likely to involve precipitation at the water/methanol interphase, followed by an increasing solubility as more methanol enters the cement paste. The ^{1}H nuclear magnetic resonance spectral analysis suggests that methanol and/or dye reacts with the cement paste. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Spectroscopy; Diffusion

1. Introduction

Recently an impregnation technique based on a fluorescent dye dissolved in an alcohol has been proposed [1]. This method makes it possible to do plane section and thin section analysis on concrete of very low water/cement (w/c) ratio. The technique is called Fluorescent Liquid Replacement (FLR) and is based on the principle that the pore water is slowly replaced by an alcohol/fluorescent dye solution. The technique is shown to provide a significant increase in impregnation capability in concrete compared to traditional epoxy impregnation. The risk of introducing cracks and damage to the pore structure during impregnation is greatly reduced.

Of particular importance is the time needed for exchange of water (within the water-saturated cement paste) with the alcohol/fluorescent dye solution. This exchange process has been investigated in situ, by monitoring ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra of exchanging ethanol with water as a function of process time [2,3]. However, one subject not addressed in the previous studies concerns the fate of the fluorescent dye during the exchange process. Will the concentration of dye in alcohol within the cement paste be constant and independent of reaction time, or might the cement paste behave as a sort of chromatographic substance that changes this concentration? For instance, the diffusivity of the fluorescent dye may be smaller than the diffusivity of the alcohol due to differences in molecular size (or molecular weight). Also, cement pastes are known to have a broad distribution of pore sizes, ranging from a few nanometers to several micrometers, which may affect the distribution of methanol and dye within the cement paste differently. For very small pores, the dye molecule may be too large to enter these pores. Thus, knowledge of the molecular weight of the dye molecule, as well as information regarding the relative distribution of dye and methanol within the cement paste during and after the completion of the exchange process, is of importance.

Another parameter of significance is the relative solubility of dye in water and alcohol, respectively. Differences in these solubilities may lead to changes in the relative amount of dye and alcohol within the cement paste both in time and space.

In this preliminary work, ^{1}H and ^{13}C NMR spectroscopy will be applied to investigate the exchange of methanol/dye

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with water in a water-saturated cement paste having a w/c ratio of 0.7. Similar work on cement pastes with different w/c ratios and other alcohols is in progress and will be reported in the future.

2. Methods

2.1. Specimen

A sample of hydrated cement paste (HCP) with a w/c ratio of 0.70 was prepared from a Danish Super White Portland Cement certified as a British Standards Institution class 62.5N cement. The Bogue composition was 65.8% tricalcium silicate (C_3S), 21.0% dicalcium silicate (C_2S), 4.2% tricalcium aluminate (C_3A), 1.0% tetracalcium alumina ferrite (C_4AF), and 2.3% calcium oxide (C). The Blaine surface was 4,000 cm^2/g. The reason for using a white cement was its low content of paramagnetic constituents, like Fe_2O_3 and Mn_2O_3, that may contribute to the NMR relaxation [4]. The composition by weight of the cement was determined by X-ray fluorescence spectroscopy. The paste was mixed under slight vacuum (0.1 Bar) to avoid entrapped air and molded and sealed in cylindrical polytetrafluoroethane forms with diameters of 20 mm and lengths of 120 mm. The total weight of the mixture was checked before and after mixing to detect any loss of water resulting from the vacuum treatment. The paste was slowly rotated during the first 20 h of hardening to avoid separation between water and cement. After demolding, the paste was stored in water at room temperature. The sample was 3 months old at the time of testing, and was cut from the interior of the molded cylinders to avoid possible inhomogeneities in the paste caused by the proximity to the form walls.

The sample of hydrated cement paste was cut and ground to a diameter of approximately 3.5 mm and length of 12 mm to fit into the NMR tube. The sample was stored in 99.8% deuterated water for 14 days before measurements were initiated. The replacement of normal water with deuterated water was applied to reduce the strong background signal from normal water. Without this step, the water signal might mask the much weaker signal from the fluorescent dye, which may become unobservable (dynamic range limitations). For similar reasons, the methanol used was of 99.8% isotopic purity (d_4-methanol). The methanol solution was saturated with a fluorescent dye of unknown structure, molecular weight, and element composition.

Immediately before testing, the deuterated water on the external surface was wiped away with an absorbent tissue before the specimen was transferred to a 5-mm NMR tube. Approximately 80 mg of deuterated methanol/fluorescent dye solution was added to the sample tube, so that the upper level of the fluid methanol was located a few millimeters above the top of the cement paste. The tube was finally sealed with a rubber cap to prevent water and methanol vapor from escaping.

2.2. NMR

The ^1H and ^{13}C NMR spectra were acquired on a Varian VXR 300 NMR spectrometer, operating at 300 MHz proton resonance frequency, using a high-resolution 5-mm probehead. The number of transients was set to 16 (proton) and 1,400 (carbon) if not otherwise stated in the text. A radio frequency (rf) pulse of 45° tip angle and a repetition time between rf pulses of 30 s were used in both types of experiments. The repetition time was set to five times the longest T_1 (< 25 s) for both carbon and proton NMR measurements. The sweep width was set to cover 14 ppm (^1H NMR) and 250 ppm (^{13}C NMR), respectively.

To acquire quantitative spectra, the spin-lattice relaxation time (T_1) was determined by applying a conventional inversion recovery (180°-τ-90°) pulse sequence. The spin-lattice relaxation times of the dye molecule were all in the range of 0.9 to 2.4 s. The T_1 of the residual methyl proton peak was 4.9 s; the residual OH peak of deuterated methanol was (7.91 ± 0.02) s.

The ^{13}C NMR spectra were accumulated using gated decoupling (i.e., decoupling of the protons during acquisition time only) to exclude differential NOE effects[5].

3. Results and discussion

A key object of this work was to monitor in situ the concentration of dye in methanol within the cement paste as a function of exchange time. However, the relatively small amount of fluorescent dye in the solution combined with severe line broadening (due to susceptibility difference between the confined fluid and the solid cement matrix) made the dye within the cement paste undetectable. The concentration of dye in methanol within the cement paste can therefore only be monitored indirectly by observing the NMR signal intensity in the liquid phase surrounding the cement paste.

The ^1H and ^{13}C NMR spectra of a methanol solution saturated with the fluorescent dye are shown in Fig. 1.

During the exchange process, small particles became visible in the solution. The formation of solid particles has a deteriorating effect on the quality of the NMR spectrum (i.e., the spectral resolution becomes poorer), resulting in broad and overlapping peaks. We thus decided to let the exchange process continue in the NMR tube until termination, and to analyze the solution only after equilibrium was established.

To enable the exchange process to be monitored as a function of reaction time, a number of identical samples have to be prepared and inserted into solutions having the same reactant concentrations. Each cement sample must then be taken out of its respective solution at successive

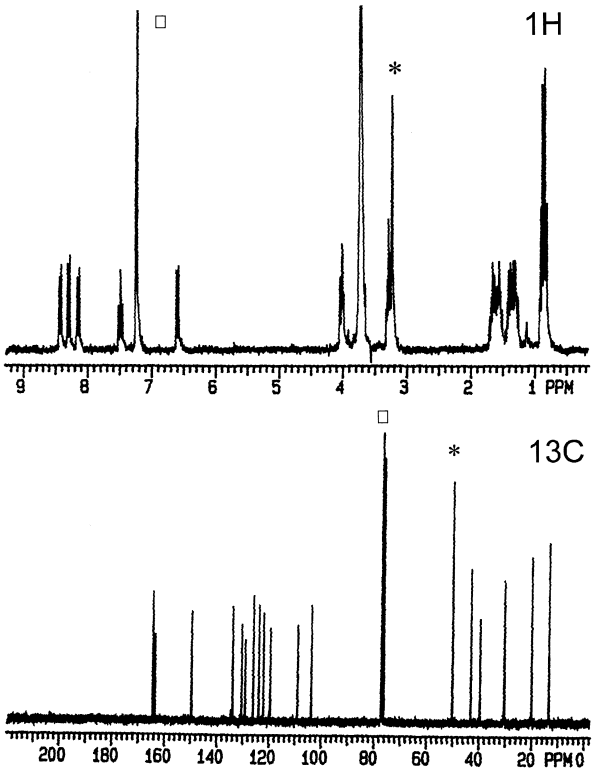

Fig. 1. ^{1}H NMR (A) and ^{13}C NMR (B) spectra of a methanol/dye solution dissolved in chloroform. The methanol and chloroform peaks are marked by (*) and (□), respectively.

times during the exchange process and the solutions analyzed separately. This approach will be addressed in a future communication.

3.1. Equilibrium ratio of dye and methanol in the cement paste at the end of the exchange process

After 10 days, the cement paste was taken out of the solution. To dissolve any precipitated dye, deuterated chloroform was added (chloroform has a much larger solubility for the fluorescent dye). The same amount of deuterated chloroform was added to an equivalent amount of methanol/dye solution that had not been in contact with any cement paste. That the actual amount of added chloroform was the same in the two solutions was verified by measuring the signal intensity of chloroform ($\delta = 7.25$ppm) in the two spectra. The ^{1}H NMR spectra of the two solutions are shown in Fig. 2. Only the chemical shift region of main interest is shown. The observed change in chemical shift of the triplet peak (dye) before and after exchange (Fig. 3) is simply due to a concentration effect (i.e., the concentration of reactants changes with time and affects the chemical shift of the corresponding resonance peaks). This will be discussed in more detail later in this text.

The volume of the methanol/dye solution is 0.0870 cm^3 (V_s). By heating the water-saturated cement sample to 105°C for 8 h, the pore water evaporates and enables the

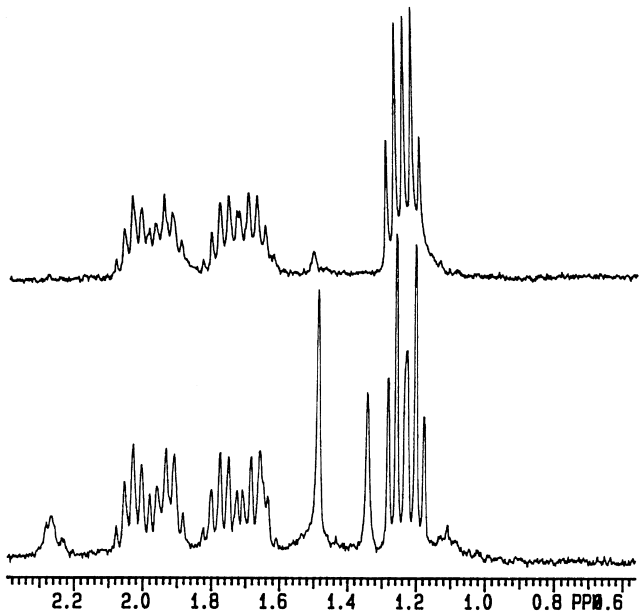

Fig. 2. Expanded view of the ^{1}H NMR spectra of a methanol/dye solution before (top) and after (bottom) exchange with water of a water-saturated cement paste.

pore volume V_C to be estimated (= 0.0653cm^3). If, after exchange, the dye (F) and methanol (M) are assumed to be evenly distributed between the cement paste (pores) and the surrounding liquid, then the observable NMR signal intensity (I_X) of the surrounding solution can be calculated from Eq. (1):

$$I_X = I_X^0 \cdot \frac{V_s}{V_s + V_c} \quad (1)$$

where X represents M and F and I_x^0 represents the signal intensity of X before exchange. These calculated intensities are denoted A(calc) in Table 1. The corresponding observed NMR signal intensities, A(obs) in Table 1, differ significantly from A(calc). Before discussing these discrepancies, we need to comment on the three additional peaks appearing in the high field region of the NMR spectrum after the exchange process has ceased (see Fig. 2).

From previous NMR measurements on identical cement pastes we can confidently state that these peaks do not arise from any contaminants within the cement paste. Moreover,

Table 1
Signal intensity of fluorescent dye (I_F) and methanol (I_M) within a methanol-dye solution before (B) and after (A) exposure to a cement paste of w/c = 0.7

Solution	I_F	I_M	I_F / I_M
B	28.6	58.4	0.49
A (calc)	16.4	33.4	0.49
A (obs)	22.1	31.9 (=23.9 + 8.0)	0.69

A(calc) represents expected signal intensity if a complete exchange of methanol/dye with water has taken place.

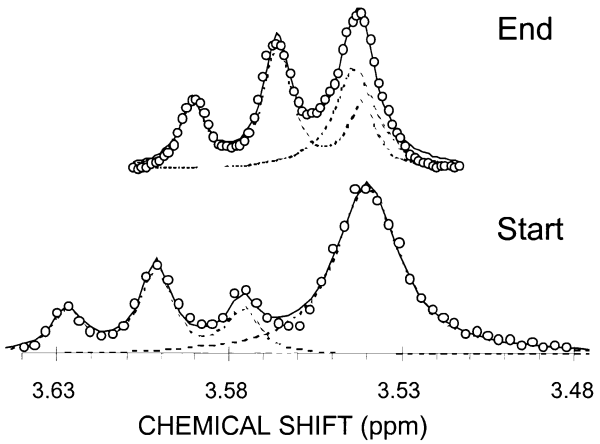

Fig. 3. High field chemical shift region of the ^{1}H NMR spectra in Fig. 2 before (top) and after (bottom) exchange. The triplet peak originates from the dye molecule. The single (actually a quintet) peak represents the residual single proton peak ($-CD_2H$) of deuterated methanol. The dotted curves are obtained by mathematical deconvolution of the spectra, assuming Lorenzian line-shape functions.

since no additional peaks are observed in a solution containing only methanol and dye, we have reason to believe that these resonance peaks originate from a reaction between methanol/dye and the surface of the cement paste. It remains to assign the three peaks in the ^{1}H NMR spectrum.

From the observed signal intensities (8, 28, and 14) and their corresponding chemical shifts ($\delta = 2.27$, 1.49, and 1.34 ppm), only the former resonance peak may be assigned with some confidence to a $-OCD_2H$ group. Hence, the two remaining peaks must be caused by some structural change(s) on the dye molecule due to a chemical reaction. This implies that the total signal intensity of the $-OCD_2H$ peak (methanol) after exchange is 31.9 ($= 23.9 + 8.0$) rather than 23.9. This intensity is shown within parentheses in Table 1.

Since the signal intensity of $-OCD_2H$ (methanol) and F must be conserved during the exchange process, we can estimate their signal intensities within the cement paste by a simple subtraction [i.e., I_X(cement) = I_X(B;obs) − I_X(A;obs) with $X = M$ and F]. The results are shown in Table 2.

Table 2
Amounts of fluorescent dye (F) and methanol (M) in eight different solutions

No.	F (mg)	M (mg)
1	0	471.6
2	1.1	416.7
3	1.3	449.2
4	2.7	404.5
5	3.2	406.5
6	5.8	388.2
7	8.0	400.5[a]
8	10.2	410.0[a]

[a] Precipitate observed.

From the calculated I_F/I_M ratios in Table 1 we can conclude unambiguously that the concentration of F in M within the surrounding solution increases with increasing exchange time. The corresponding I_F/I_M ratio within the cement paste (after the exchange reaction is completed) remains significantly smaller. The reason for this behavior is a difference in solubility of dye in methanol and water, respectively, and will be discussed next.

3.2. Solubility of fluorescent dye in methanol and water

The reason for the formation of solid particles in the liquid solution during the exchange process is believed to originate from a difference in solubility of the fluorescent dye in methanol and water, respectively. We have used ^{1}H NMR to investigate this. Eight solutions of dye dissolved in methanol were prepared. The relative amounts of dye and methanol in these solutions are tabulated below (Table 2).

Expanded regions (3.6 ppm > δ > 3.3 ppm) of the ^{1}H NMR spectra of solutions 1 to 8 are shown in Fig. 4.

Since the signal intensity (I) in NMR is directly proportional to the number of protons [i.e., the number of moles (n)], the following equation can be derived [see Eq. (2)]:

$$\frac{I(F)}{I(M)} \cdot \frac{1}{K} = \frac{n(F)}{n(M)} = \frac{m(F)}{m(M)} \cdot \frac{\overline{M}(M)}{\overline{M}(F)} \tag{2}$$

$\overline{M}$ (X) and $m(X)$ denote the molecular weight and mass of specie X ($= F, M$). K is an undetermined constant, which takes into account that a certain frac-

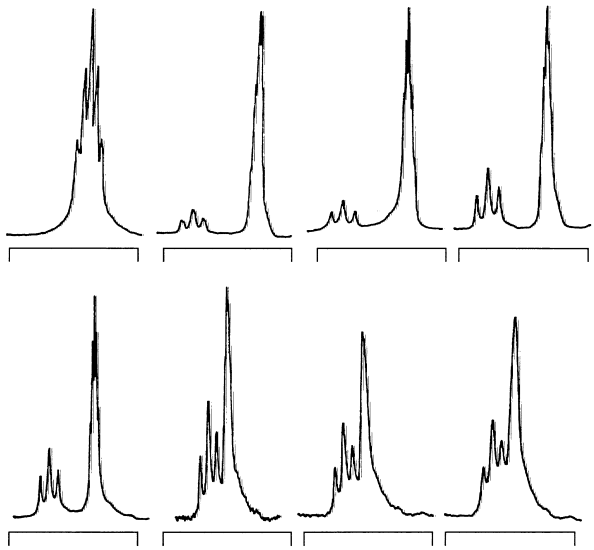

Fig. 4. ^{1}H NMR spectra between $\delta = 3.63$ and 3.33 ppm of the dye/methanol solutions in Table 1. The low field peak (triplet peak) represents a specific group of protons of the dye molecule. The high field peak corresponds to the residual methyl proton ($-CD_2H$; quintet) of deuterated methanol. The numbering of the spectra follows Table 2.

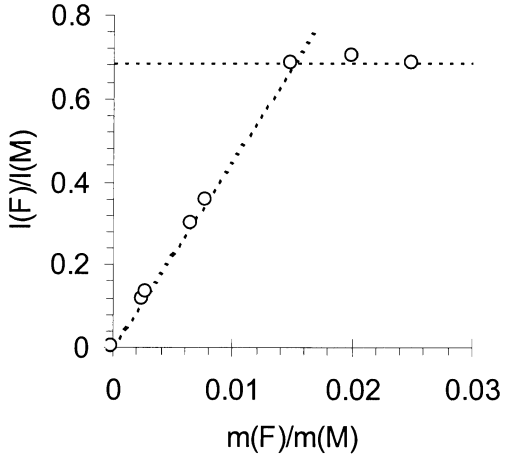

Fig. 5. ^{1}H NMR signal intensity ratio between dye and methanol, $I(F)/I(M)$, vs. the mass ratio of dye and methanol, $m(F)/m(M)$. The signal intensities are taken from Fig. 4. The straight lines represent linear least-squares fits to the observed data. See text for further details.

tion of the protons are replaced by nonobservable deuterium nuclei.

Also, the resonance peak ($\delta \approx 3.60$ ppm) chosen to represent the dye (F) molecule may contain more than a single proton atom. This number of protons is implemented in the parameter K. Whatever the value of K, Eq. (2) predicts a linear relation between $I(F)/I(M)$ and $m(F)/m(M)$. Fig. 5 shows a plot of $I(F)/I(M)$ as a function of $m(F)/m(M)$.

The straight lines in Fig. 5 represent linear least-squares fits and suggest that for values $m(F)/m(M) > 0.015$, the signal intensity ratio $I(F)/I(M)$ is constant. This means that solutions with $m(F)/m(M) > 0.015$ are saturated with dye, and that the dye simply precipitates out of the solution. Thus, $m(F)/m(M) = 0.015$ represents the maximum mass ratio of dye in methanol that may exist in solution (i.e., the solubility limit).

Fig. 4 suggests that the chemical shift of at least one of the resonance peaks belonging to the dye molecule ($\delta \approx 3.60$ ppm; triplet) changes with the relative concentration of dye in methanol. The numerical chemical shift value (δ) of the dye peak as a function of the relative amount of dye in methanol (m_F/m_M) is illustrated in Fig. 6.

Such a linear relation between chemical shift (δ_X) and concentration [X] of a specie X is frequently reported in the literature for small concentrations of X [i.e., see Eq. (3)]

$$\delta_X = \delta_X^0 + k_X[X] \tag{3}$$

where $\delta_X{}^0$ represents the chemical shift as $[X] \Rightarrow 0$. However, in the present case we have to consider the possibility that the dye (F) may react with methanol (M) to form an unspecified complex, denoted $F \cdot M$. Such a reaction may proceed according to [see Eq. (4)]

$$\mathrm{F} + \mathrm{M} \Longleftrightarrow \mathrm{FM} \tag{4}$$

The concentration of F and $F \cdot M$ can be estimated if the equilibrium constant (K) of Eq. (4) is known [i.e., see Eq. (5)]:

$$[F \cdot M] = K[M]_0 \frac{[F]_0}{1 + K[M]_0} \tag{5}$$

and [see Eq. (6)]

$$[F] = \frac{[F]_0}{1 + K[M]_0} \tag{6}$$

Eqs. (5) and (6) are valid if $[F]_0 << [M]_0$, which is satisfied in this work. Assuming a fast dynamic exchange (on an NMR time scale) between F and $F \cdot M$ to exist, we can express (from basic NMR theory) the observable chemical shift (δ) of the dye as seen in Eq. (7):

$$\delta = \frac{\delta_F[F] + \delta_{F\cdot M}[F \cdot M]}{[F] + [F \cdot M]} \tag{7}$$

Inserting Eq. (3) into Eq. (7), the following relation is obtained [see Eq. (8)]:

$$\delta = \frac{\delta_F^0 + \delta_{M\cdot F}^0 K[M]_0}{1 + K[M]_0} + (k_F + k_{F\cdot M}K^2[M]_0^2)\frac{[F]_0}{(1 + KM_0)^2} \tag{8}$$

Replacing $[F]_0$ and $[M]_0$ in Eq. (8) by their respective mass numbers ($[\mathrm{F}]_0 = n_F^0/V \approx m_F^o\rho_M/m_M^0 M_F$ and $[\mathrm{M}]_0 = \rho_M/\mathrm{M}_M$), Eq. (8) can be written as Eq. (9):

$$\delta = \frac{\delta_F^0 M_M + \delta_{M\cdot F}^0 K\rho_M}{M_M + K\rho_M} + (k_F + k_{F\cdot M}K^2\rho_M^2/M_M^2) \cdot \frac{\rho_M/M_F}{(1 + K\rho_M/M_M)^2} \cdot \frac{m_F^0}{m_M^0} \tag{9}$$

where M_X is the molecular weight of specie X ($= M$ and F), and ρ_M is the density of methanol. Eq. (9) predicts a linear relation between the chemical shift (δ) of the dye peak (triplet) and the relative mass ratio of dye and methanol ($m^0{}_F/m^0{}_F$). This is exactly what is observed (Fig. 6). The

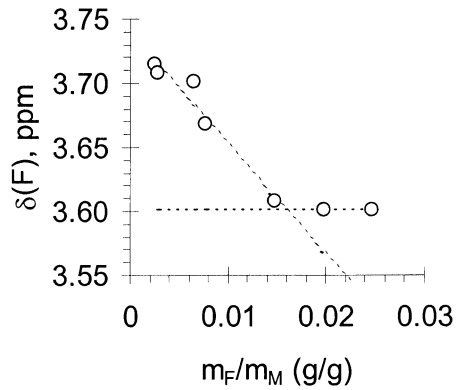

Fig. 6. Chemical shift (δ) of the triplet peak of the dye molecule (from Fig. 4) as a function of the mass ratio ($m^0{}_F/m^0{}_M$) between dye and methanol.

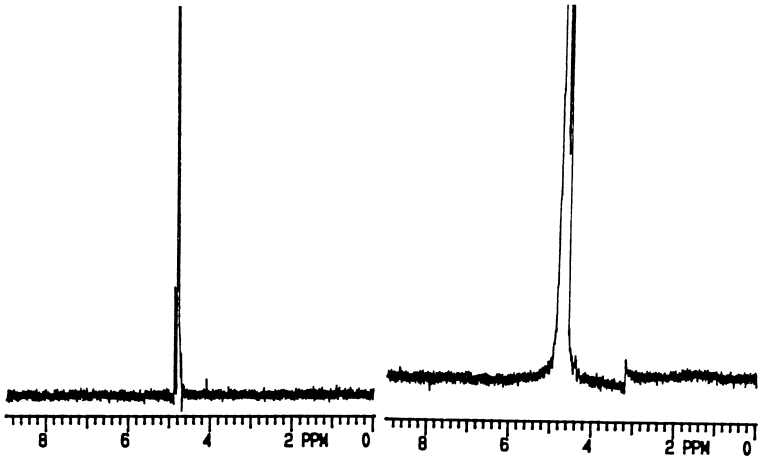

Fig. 7. ^{1}H NMR spectra of pure water (left) and water saturated with dye (right).

deviation from linearity for larger mass ratios (m^0_F/m^0_F) is due to precipitation of specie F from the solution, and enables the solubility of dye in methanol to be determined [i.e., $m(F)/m(M) = 0.015m$), which is the same number derived from Fig. 5.

The data in Fig. 6 suggest a minimum in the chemical shift of the dye-triplet peak to be approximately 3.60 ppm. However, in Fig. 3, the chemical shift of the corresponding dye peak (at the end of reaction) is even smaller by approximately 0.035 ppm. The probable reason for this small difference in chemical shift is that the latter solution also contains some water, which may affect the chemical shift of the dye peak.

To estimate the corresponding solubility of dye in water (precipitation of dye observed) ^{1}H NMR spectra were acquired (Fig. 7). No proton signal from the fluorescent dye can be detected. Taking into account the detection limit of this particular experiment (640 transients were accumulated), an upper limit of the solubility of dye in water can be estimated and amounts to $m(F)/m(M) < 10^{-4}$. The particles appearing in the solution during the exchange reaction therefore can be rationalized according to a solubility difference of dye in water and methanol. As the exchange reaction proceeds, more methanol than dye enters the cement paste, resulting in an increasing concentration of dye in the solution phase. The concentration of dye exceeds the solubility limit and precipitates out of the solution. Since the solubility of dye in water/methanol solutions is much lower than the solubility of dye in pure methanol, the increasing amount of water entering the solution phase (containing dye, methanol, and water) causes more dye to precipitate out as the exchange reaction proceeds.

Due to the more limited solubility of fluorescent dye in water compared to methanol, the diffusion process of dye molecules from a dye/methanol solution into a water-saturated cement paste is rather complex. The diffusion process involves precipitation of dye in all areas of the cement paste where methanol, dye, and water coexist (during the exchange process). However, as water leaves the cement paste during the exchange process, the corresponding concentration of methanol within the cement paste increases and the precipitated dye may again dissolve.

We also investigated the solubility of fluorescent dye in mixtures of methanol and water by ^{1}H NMR. The results are shown in Fig. 8.

The experimental approach was the same as previously described (see Fig. 4 and corresponding discussion). As can be seen from Fig. 8, the solubility decreases approximately exponentially with the mass fraction of water. The solubility of the fluorescent dye in a solution containing about equal amounts (by weight) of methanol and water is more than two orders of magnitude less than in pure methanol.

To estimate the molecular weight $\overline{M}(F)$ of the dye molecule from ^{1}H NMR, the K parameter in Eq. (2) must be determined. For nondeuterated methanol this parameter is equal to 1. However, using nondeuterated methanol

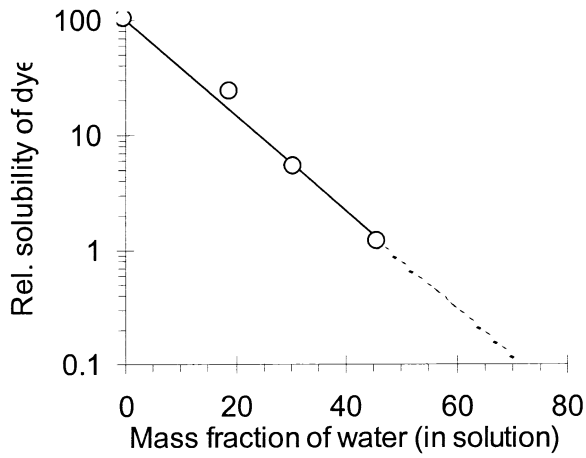

Fig. 8. Relative solubility of fluorescent dye in water/methanol solutions. Solubility in pure methanol is set to 100. The solid curve represents a best fit (exponential) to the observed data, with the solubility of dye fixed at 100 in pure methanol.

would result in a very strong signal from the methanol component and thus preclude the quantitative determination of the small signal arising from the dye molecules. A rough estimate of K can be made by noting that the degree of deuteration is approximately 99.8%, giving $K \approx 100/(100 - 99.8) = 500$. Inserting this number into Eq. (2) gives $\overline{M}(F)/\overline{M}(M) \approx 11.8$ [i.e., $\overline{M}(F) = 377$].

A more confident estimate of the molecular weight of the dye molecule, however, can be estimated from the ^{13}C NMR spectrum in Fig. 1. Using the observed values of $I_F = 0.85$, $I_M = 690$, $m(F)/m(M) = 0.015$, and $K = 1$ (all carbons are detected), we obtain $\overline{M}(F)/\overline{M}(M) = 12.3$ [i.e., $\overline{M}(F) = 393$]. This molecular weight is in surprisingly good agreement with the one obtained by ^1H NMR when keeping in mind the rough estimate of K used in the latter approach.

4. Conclusions

The solubility of dye in methanol can be monitored by ^1H NMR chemical shift and/or ^1H NMR signal intensity measurements. The solubility of dye in methanol is dependent on its water content and decreases approximately exponentially with the mole fraction of water in methanol. Due to this significant difference in solubility of dye in methanol and water, the exchange process of dye/methanol with water (in a water-saturated cement paste) is a rather complex process. It involves precipitation of dye at the water/methanol interface, followed by an increasing solubility of dye as additional methanol enters the cement paste. The concentration of dye within the cement paste (after exchange) is found to be less than the concentration of dye in the original dye/methanol bulk solution. Whether this originates from a chromatographic effect or not is at present unclear and needs further investigation. Of particular importance, ^1H NMR spectral analysis of the liquid solution before and after exchange suggests that methanol and/or dye react due to contact with the cement paste.

Acknowledgments

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