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Laboratory studies of diffusion in bitumen using markers

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Performance of recycled asphalt pavements depends, among other things, on the degree of mixing of old and new binders. One of the factors contributing to the mixing is diffusion, which increases the homogeneity of recycled binders. In this study, FTIR-ATR (Fourier Transform Infrared Spectroscopy with Attenuated Total Reflectance) has been applied to investigate influence of temperature, viscosity of the diffusion medium, and diffusant size and polarity on diffusion characteristics. Several substances, referred to as markers, have been monitored when diffusing through different binders. By careful selection of markers, the importance of diffusant size and polarity on rate of diffusion has been demonstrated. Diffusion has been modelled using Stoke-Einstein's equation and compared with experimental data obtained by FTIR-ATR. The equation has shown useful in explaining the effects of temperature, viscosity and molecular size on diffusion. © *2003 Kluwer Academic Publishers*

1. Introduction

1.1. Background

Diffusion is an important concept considering processes in bituminous binders such as oxidative ageing (oxygen diffusion), stripping (water diffusion) and rejuvenation in asphalt recycling (mixing of binders). Hitherto, diffusion in bitumen has attracted only a few researchers (cf. Section 1.3 below). The investigation presented in this paper originates from an interest in knowing, if the time of mixing during hot in-place asphalt recycling is sufficient for homogeneous mixing of old and new binders. It is assumed that mechanical mixing, compatibility between old binder and rejuvenator, as well as diffusion are the key parts of the process of achieving a homogeneous recycled binder. This paper is the latest one in a series of three papers on diffusion measurements using FTIR-ATR (Fourier Transform Infrared Spectroscopy using Attenuated Total Reflectance). In the first paper [1], the FTIR-ATR method is described (cf. Section 2.2), and factors influencing diffusion, such as temperature and binder film thickness, investigated, while in the second paper [2], the influences of ageing and maltene phase composition on diffusion rate were studied. The study described in this paper is focused on more general aspects related to diffusion of components compatible with bituminous binders, especially how properties of the diffusing substances influence diffusion. Most of the experimental work has been performed by monitoring diffusion of selected well-defined substances, referred to as markers. The methodology used is also assessed in this paper.

Bitumen is a multi-component system consisting of an immense number of substances. Models of bitumen suggest that bitumen consists of a solvent phase, often referred to as maltenes, and microstructures and/or colloidal particles dispersed, often referred to as asphaltenes [3, 4]. The complex composition of bitumen adds to the complexity of the diffusion process. Some examples of the encountered difficulties, when studying diffusion in bituminous binders, are:

- At the best, only a few molecules, if any, can be identified as originating from a given binder.
- All substances diffuse at different rates depending on, for example, molecular size, shape and polarity.
- The composition of the media in which diffusion takes place changes during diffusion.

Generally, studies of diffusion can either be performed by labelling one of the binders or finding some identifiable differences between the binders. For both methods, it could be debated how the measurements reflect the real distribution of diffusion coefficients in the mixture of the two binders. Labelling of binders means that the molecules are manipulated in such a way, that they can be detected and recognised. This manipulation could either be done by altering the atoms (for example use of neutron radiation to produce C13 or D isotopes) or by slightly changing the chemical composition of the substances (for example by chemical reactions to create or add IR-detectable functional groups). However, the manipulation is likely to show influence on the diffusion

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properties of the labelled substances, which means that they may no longer be representative of the original binder. Generally, differences in infrared absorbance exist between two binders. In this paper, the methyl-methylene and carbonyl bands are used to study diffusion of bituminous binders. However, in the major part of the work, another approach is used. Well-defined substances, referred to as markers, are used to study how molecular properties such as size and polarity influence diffusion. By using markers with distinguishable infrared absorbance and a variation in molecular properties, more general knowledge of diffusion in bitumen is obtained.

1.2. Theory

The Stoke-Einstein equation is commonly used to predict diffusion coefficients in both gases and liquids. It gives a good principal understanding of the parameters governing diffusion processes and is written

$$D = \frac{k_B T}{6\pi \mu \langle R \rangle} \tag{1}$$

where the term $k_B T$ is the internal heat energy in which k_B is Boltzmann's constant (1.3807×10^{-23} J/K) and T absolute temperature. The internal heat is responsible for, and proportional to, the Brownian motions, which drives diffusion. Furthermore, the equation implies, that the rate of diffusion, D, for a given material at a given temperature, is proportional to the reciprocal of the mean molecular radius, $\langle R \rangle$, of the diffusing molecule. According to Stoke-Einstein equation, the diffusion coefficient is also inverse proportional to viscosity, μ, given the substance and temperature. Regarding temperature, the effect on the rate of diffusion is difficult to identify, since temperature influences both Brownian motions and viscosity. A relationship between temperature and diffusion rate can be derived using the heat energy activation approach resulting in

$$D = k_1 \cdot e^{k_2/T} \tag{2}$$

where k_1 and k_2 are constants and T absolute temperature in K. It has been shown by Oliver [5] and others [1], that Equation 2 is useful for characterising diffusion rate in bitumen.

According to the Stoke-Einstein equation, the rate of diffusion is inversely proportional to the mean radius of the diffusing molecules (or agglomerates of molecules), which means that diffusion is influenced by the size of diffusing molecules but also the shape, as the shape contributes to the mean molecular radius. In this respect, intermolecular interactions are important and act in two ways to slow down diffusion. Firstly, strong molecular interactions lead to association of molecules into agglomerates. Secondly, increased interactions between molecules leads to increased "friction" between the molecules and the diffusion medium. In gels (or other media which have a transient or rigid network of molecules), diffusion is slowed down due to obstruction and exclusion of large molecules [6].

The influence of molecular shape on diffusion rate can be considered by assuming that the molecules show idealised shapes, as prolate and oblate ellipsoids. The mean molecular radius, $\langle R \rangle$, of a prolate ellipsoid (shape of American football) is

$$\langle R \rangle = \frac{(a^2 - b^2)^{1/2}}{\ln\left(\frac{a + (a^2 - b^2)^{1/2}}{b}\right)} \tag{3}$$

and an oblate ellipsoid (disc-shaped)

$$\langle R \rangle = \frac{(a^2 - b^2)^{1/2}}{\tan^{-1}\left(\left(\frac{a^2 - b^2}{b^2}\right)^{1/2}\right)} \tag{4}$$

where a and b are the major and minor axes of the ellipsoid [7].

In terms of molecular weight, M, Stoke-Einstein equation implies that the diffusion coefficient is proportional to $M^{-1/3}$, since the equation is based on diffusion of a sphere. When diffusion of a polymer in polymers is modelled, the friction between the entangled, long molecules is becoming of increased importance. For long chain molecules, as polymers, a common experimental result is that the diffusion coefficient is proportional to M^{-2} [8]. This relationship is used below in the discussion of test results obtained in this study (cf. Section 4.2).

1.3. Review of previous work

FTIR-ATR has previously been applied to functional group analysis of bitumen [9], as well as studies of diffusion of oxygen into bitumen [10], water through bitumen onto siliceous material [11], and various substances into thin polymer films [12–15]. In the case of diffusion into polymer films, the method is similar to the method described in this paper (cf. Section 2.2). The diffusion through a thin film is detected by quantifying the change in absorbance at wavenumbers characteristic of the diffusing substances. In the thin polymer film tests, the diffusing substance is flushed over the polymer film, keeping the concentration steady at the surface of the film.

In [10], FTIR-ATR was also used to study oxidative ageing of bitumen by monitoring the increase in carbonyl content. The samples were prepared by applying thin binder films on aluminium foils, which were aged at different temperatures and oxygen pressure. The increase in carbonyl content was measured on both sides of the binder film by pushing them onto the ATR prism.

An application of FTIR-ATR to studies of water diffusion through thin bitumen films has been presented by Nguyen *et al.* [11]. By constantly flushing water over a siliceous ATR prism covered with bitumen and measuring the increase in infrared absorbance of water on the ATR prism, the process of water transport and replacement of bitumen on the siliceous interface was studied. The method was considered promising for investigations of resistance to stripping with regard to factors, such as type of binder, use of anti-stripping agents or influence of contaminants on the aggregate surface.

Oliver [5] studied diffusion of dodecylbenzene and two oil fractions into three different bitumens, using a method of tritium labelling. The study was undertaken to investigate the possibility of replacing weathered binder at the pavement surface with an oversprayed oil formulation, thereby extending the life of the surfacing. To determine the diffusion coefficient, a thin layer ($<1\ \mu$m) of diffusant was applied to the top of a bitumen cylinder, 1.25 cm diameter and 0.5 cm high. The tritium labelled diffusant was then allowed to penetrate the bitumen for some time, after which the bitumen was sliced using a microtome. The radioactivity was measured at different depths, and the diffusion coefficient was calculated. One of the conclusions of this study was, that the diffusion rate could be increased by adding diluent oil fractions or by raising the temperature. Oliver also concluded that the diffusion coefficient depends on the temperature in an Arrhenius type relationship (cf. Equation 2). Moreover, the diffusion rate was unaffected by a skin on top of the bitumen cylinder caused by photo-oxidation. It was also stated, that for the oils, constituting of molecules of different size and configuration, only an average diffusion coefficient could be determined. Furthermore, Oliver performed diffusion experiments on oil fractions obtained by size exclusion chromatography (SEC) and liquid chromatography (LC). From these studies Oliver concluded, that the more aliphatic fractions obtained from LC diffused more rapidly than naphthenic and condensed aromatic fractions.

A number of issues related to diffusion in bitumen have been investigated by Karlsson *et al.* [1, 2]. For example, consequences of Fick's law governing the diffusion process was demonstrated, which, among other things, means that the time needed for a diffusion process to occur is proportional to the square of the binder layer thickness [1]. Factors influencing diffusion, such as temperature, ageing and refining of bitumen (bitumen obtained from one and the same crude oil by various degree of distillation) have also been studied [1, 2]. Evidences have been put forward to support a hypothesis claiming that the maltene phase is the medium in which diffusion takes place. The evidences were among others that:

- Ageing of bitumen did not significantly affect diffusion, in spite of increasing viscosity several orders.
- Ageing appeared to turn some maltenes into viscosity builders, while most of the maltenes kept on showing the same viscosity and molecular size distribution.
- Measurements of the viscosity of extracted maltenes seemed related to diffusion through Stoke-Einstein equation over a wide range of temperatures.

2. Experimental

2.1. Materials

Ten different bitumens as shown below were used:

- B180 from Mexico, denoted A-180 (180 denotes a binder penetration of 180 dmm at 25°C)
- B180 from Saudi Arabia, denoted B-180
- B60 from Venezuela, Laguna, denoted C-60
- SHRP-AAC, denoted D-85
- SHRP-AAD, denoted E-128
- SHRP-AAF, denoted F-46
- B15, B55 and B180 from Laguna refined from the same crude to different stiffness (without oxidation), denoted G-15, G-55 and G-180
- Binder recovered from field aged wearing course, denoted H-12.

Table I shows a list of eight different substances used as markers. For comparison, and as a bearer of markers, one rejuvenator, Nynas V115 (denoted R-115), a heavy naphthenic petroleum distillate, was also used.

Maltenes of A-180 were extracted using n-hexane (C6, 1% by weight) precipitation and denoted C6-A-180. The solution was stirred for two hours, after which the solution was centrifuged at 3000 rpm. The solution with the dissolved maltenes was poured into an extraction flask and the maltenes recovered by distillation (50°C and 200 mbar).

2.2. Characterisation of diffusion using FTIR-ATR

FTIR-ATR was used to continuously monitor diffusion of one binder (or marker) into another. ATR exploits the total internal reflectance of infrared light in a non-absorbing prism. Any absorbing substances in contact with the prism surface will attenuate the internally reflected light and, as a consequence, an infrared absorbance spectrum is obtained, corresponding to a spectrum recorded as if the light passed through the surface layer of the material studied.

To determine diffusion rates of a rejuvenator penetrating a bitumen, thin layers of the two compounds were applied on top of a zinc selenide (ZnSe) ATR prism (Fig. 1). The application was accomplished by gluing brass frames on top of the prism. The thicknesses of the frames were either 200 or 500 μm. Using two frames, with different slot widths on top of each other, two thin layers of binder were created by scraping. After application of the layers, the temperature was set and infrared absorbance recorded.

To be able to monitor the diffusion process continuously over a time span of up to 72 h, computer programs were written for automating the data acquisition and processing. Diffusion coefficients were determined by curve fitting of a mathematical solution of Fick's law to experimental data. The diffusion coefficient is

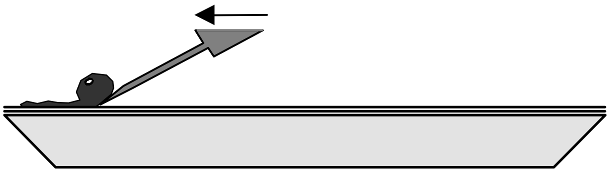

Figure 1 Schematic picture showing the application of the two-layer system using frames glued onto the ATR ZnSe prism and a scraper.

the single parameter in Fick's law describing the rate of diffusion given certain initial (concentration, layer thickness) and boundary conditions (no flow of matter into or out of the sample). Using such a single diffusion coefficient, the effects of the binders, being complex with largely distributed chemical compositions, on the diffusion process cannot be fully described. Examples of such effects are softening of a stiff binder by a rejuvenator or distribution of diffusion rates due to variation in molecular size and polarity. Therefore, the diffusion coefficient obtained should be considered as a mean value representing the system of the two binders tested.

The instrument used was a Mattson Infinity 60 AR spectrophotometer fitted with a Graseby Specac ATR heatable to 200°C. The number of scans taken was 256 (up to 100°C) or 64 (above 100°C) with a resolution of 4 cm^{-1}. The absorbance at certain wavenumbers was calculated using the integrated peak area or the peak height. Further details of the test method used are given in [1].

3. Results

A series of tests were performed to study the influence on diffusion of properties of diffusants such as molecular size and polarity, as well as the properties of diffusion media, such as the viscosity (cf. Sections 3.2 and 3.3). However, before these tests were performed, a set of tests aiming at investigating the method of using markers for diffusion studies was carried out.

3.1. Introductory tests using a marker

Measurements of diffusion rates of selected substances, in this paper called markers, will not be the true diffusion coefficients of the binders studied. By careful selection of markers, the results of the measurements can instead be used to compare the rates of diffusion when varying parameters such as temperature, binder and marker properties.

It is necessary to be aware of some of the factors influencing the results. Below is given an example of diffusion results obtained using a marker (diphenylsilane, DPS), where effects of softening by DPS and evaporation are considered.

Diffusing molecules will affect the diffusion media and thereby change the rate of diffusion. Consequently, different concentrations of a marker will render slightly different diffusion coefficients. To show the dilution effect, 1, 3 and 6% by weight of DPS was mixed with R-115 and then applied on top of bitumen A-180. The effect of evaporation of the marker was also manifested in this test. The IR absorbance of DPS (at 743 cm^{-1}) obtained during the test over a period of time is illustrated in Fig. 2. In Fig. 2a, which uses an ordinary time scale, equilibrium appears to have been reached after about 200 min. However, in Fig. 2b, the logarithmic time scale reveals, that evaporation of DPS causes the IR absorbance to decrease. When fitting the theoretical curves of diffusion to obtain diffusion coefficients, the fits are somewhat poor. After the maximum absorbance, the theoretical curve is no longer applicable. The diffusion coefficients obtained were 2.4, 2.4 and 4.1 × 10^{-12} m^2/s for 1, 3 and 6% of DPS, respectively.

If one assumes that the evaporation of DPS is proportional to the concentration of DPS at the surface, the effect of evaporation can be considered, and the measured values corrected. In Fig. 3, the measured IR absorbance of DPS is corrected for evaporation and scaled to correspond to the curve obtained for 6% DPS (by weight). In this way, it was possible to show, as expected, that a higher concentration of DPS increases the rate of diffusion. The rates of diffusion for 3 and 6% DPS are roughly 35 and 80% faster compared to 1% DPS. The diffusion coefficients obtained if corrected for evaporation are slightly lower than the ones obtained if the effect of evaporation is ignored (1.5, 2.0 and 2.7 × 10^{-12} m^2/s, respectively).

3.2. Diffusion coefficients

3.2.1. Rejuvenator softening of bitumen

It has been suggested that one important property of an effective rejuvenator is its ability to soften the old binder and thereby speed up the diffusion process [5]. In Section 3.1, it was indicated how increasing

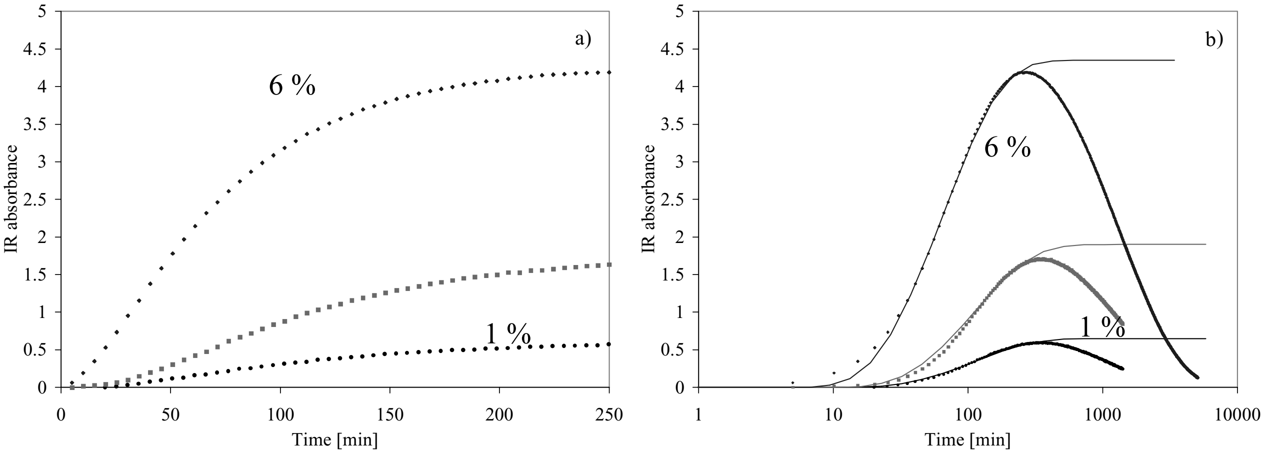

Figure 2 Infrared absorbance of diphenylsilane (DPS) vs. time (a) and with the time scale logged (b). Theoretical curves are fitted to experimental data in (b).

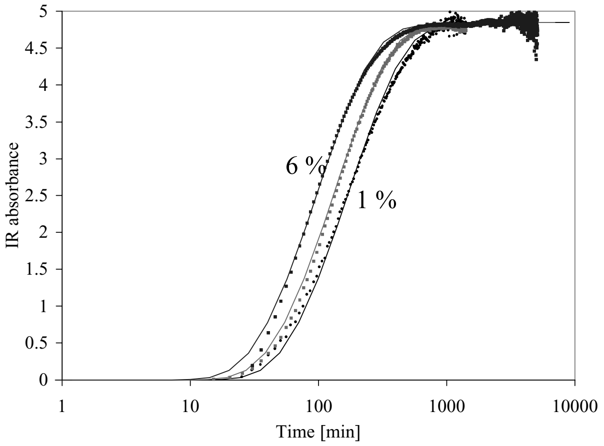

Figure 3 Diffusion of DPS through bitumen A-180 corrected for evaporation and normalised to corresponding values obtained using 6% DPS.

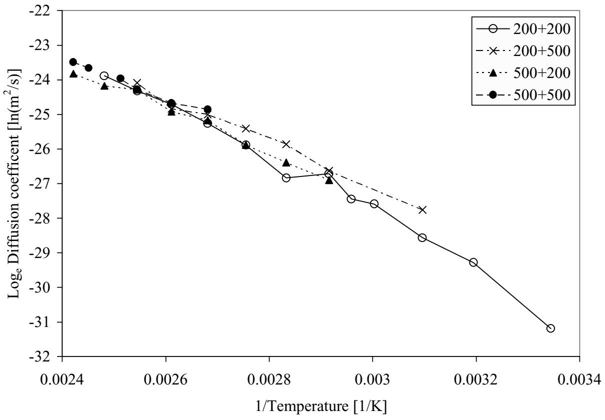

Figure 4 Natural logarithm of diffusion coefficients vs. inverse absolute temperature for tests performed using different layer thicknesses of bitumen and rejuvenator.

concentration of small molecules speed up the diffusion process. In Fig. 4, data from diffusion tests performed on different layer thickness of bitumen A-180 and rejuvenator R-115 is shown. The layer thicknesses were $200 + 200$, $200 + 500$, $500 + 200$ and $500 + 500$ μm (the first figure refer to the bitumen and the second one to the rejuvenator). The rejuvenator was applied on top of the bitumen, and the rate of diffusion was determined by recording the infrared absorbance of the methyl-methylene bands. The data is presented using the inverse absolute temperature on the horizontal axis and the natural logarithmic of the diffusion coefficients on the vertical axis. As discussed in [1], this representation usually results in a straight line over a limited range of temperatures. The data presented in Fig. 4 indicate, that there could exist a significant difference below a temperature of 90°C (above 0.00268 1/K), between the layer configuration using 200 μm of bitumen and 500 μm of rejuvenator, and the other configurations. This difference could be due to the softening effect of the rejuvenator on the bitumen, even though this effect is small compared to the effect of temperature. It appears, that a comparably large concentration of rejuvenator is required to obtain a significant softening effect on rate of diffusion.

3.2.2. Influence of addition or removal of low molecular weight components

Diffusion of a marker through a binder diluted with n-dodecane and lauric acid was studied, as well as through binders refined from one source by distillation to different grades of penetration. These two sets of studies showed that the rate of diffusion was increased by adding a diluent and decreased by the refining process, as illustrated in Fig. 5. In Fig. 5a, bitumen A-180 was altered by adding n-dodecane and lauric acid (5, 10 and 20% by weight). Using DPS as a marker, it was observed, that both lauric acid and n-dodecane did affect the rate of diffusion (the higher the concentration of substance added, the higher the diffusion rate). The effect of n-dodecane was about the double compared to lauric acid. The effect of the refining process is shown in Fig. 5b. Rate of lauric acid and DPS diffusion was measured through bitumens refined from one and the same crude to different penetration grades (G-15, G-55 and G-180, respectively). As shown in Fig. 5b, the diffusion rate decreases as the penetration of the binder decreases for both markers used. As already mentioned in Section 1.3, a hypothesis has been launched [2] claiming that the diffusion rate to a great extent is determined by the viscosity of the maltene phase. This hypothesis was supported by the results presented in Fig. 5b, as the maltene phase viscosity was found to increase with decreasing penetration grade [2].

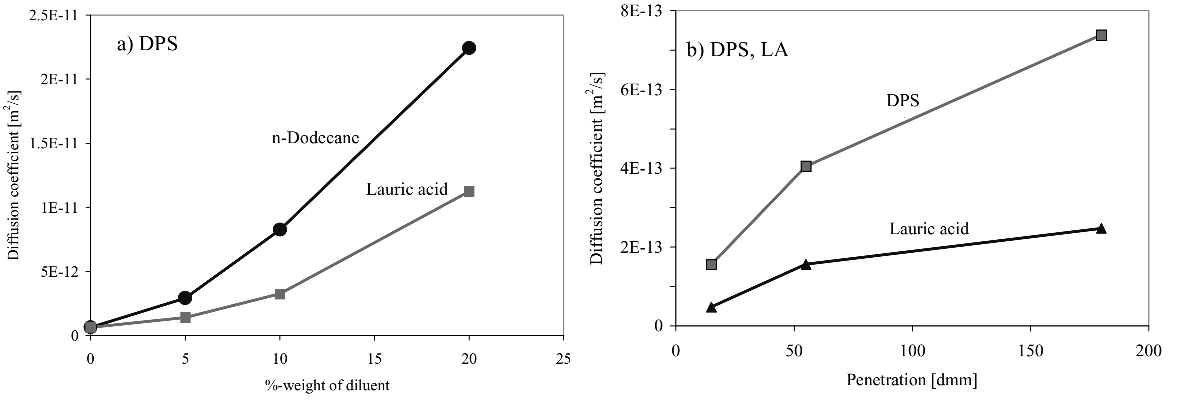

Figure 5 Diffusion coefficients obtained using DPS and bitumen A-180 diluted with n-dodecane and lauric acid, respectively (a). Diffusion coefficients of DPS and lauric acid through bitumen refined to different grades of penetration (b).

TABLE I Selected substances used as markers and their rate of diffusion in bitumen A-180 at 50°C. Molecular weight, melting, flash and boiling points from Merck [16].

Name	MW (g/mol)	Melting point (°C)	Flash/boil. point (°C)	IR-peak studied (cm^{-1})	Diffusion coeff. (m^2/s)
Glycerol	92	18	∼180/120	1016	3.1×10^{-13}
Iso octanol	130	−76	75/185	1016	1.5×10^{-12}
Diphenyl silane (DPS)	184		98/123–126	743	3.0×10^{-12}
Diphenyl sulfide	186	−40	>110/296	743, 1024, 1584	1.4×10^{-12}
Lauric acid (LA)	200	42–45	>160/299	1728	8.0×10^{-13}
Polystyrene	440			756, 3025	1.9×10^{-13}
Polystyrene	520			″	7.5×10^{-14}
Polystyrene	1010			″	2.8×10^{-14}

3.2.3. Influence of molecular size and polarity

In Table I, diffusion coefficients obtained using different markers and bitumen A-180 are presented. To ensure that no other substances than the markers diffused (not considering self diffusion), the markers where mixed (3% by weight) in bitumen A-180, and then applied on top of pure A-180. In this connection, it should be mentioned, that application of binders of equal stiffness on top of each other was associated with some difficulties, but in spite of that, the sample preparation was considered as satisfactorily. It can be seen in Table I, that increased size and polarity leads to decreased rate. As expected, the heaviest substances, the polystyrenes, diffused at the slowest rate. However, the second slowest diffusing substance was the lightest one, glycerol. The reason for this result is probably due to the ability of glycerol to form multiple strong intermolecular bonds by its three hydroxyl groups.

The effects of temperature and type of diffusant on rate of diffusion through C-60 are shown in Fig. 6. The rejuvenator R-115 (methyl-methylene peak) diffuses at a slightly faster rate than C6-maltenes obtained from bitumen A-180, but considerably slower compared to the markers DPS and lauric acid (LA). The influence of temperature seems to be about the same for all four diffusants, as expected, since temperature has a major influence on the diffusing media and its viscosity. The magnitude of the diffusion coefficients are approximately distributed as 10:3:1.8:1 in the order DPS:LA: R-115:C6-A-180.

Also within a binder itself, a difference in diffusion rate exists between different components. This can be observed by comparing the diffusion coefficients obtained from different IR bands. Diffusion coefficients of rejuvenator R-115 diffusing through bitumen A-180 and B-180 were determined using both methyl-methylene and carbonyl peaks. More details about the measurements are found in [1]. The accuracy of detecting C═O is lower compared to C─H, but, since as many as 42 tests were analysed, a statistically significant influence of the difference in diffusion rate was observed. The diffusion coefficients from these 42 tests are presented in Fig. 7 with open and filled symbols representing diffusion coefficients determined using the methyl/methylene and carbonyl bands, respectively. The 95% confidence intervals for the mean curves of C─H and C═O diffusion are also given. As shown, the difference between the two sets of data is significant, since the intervals do not overlap.

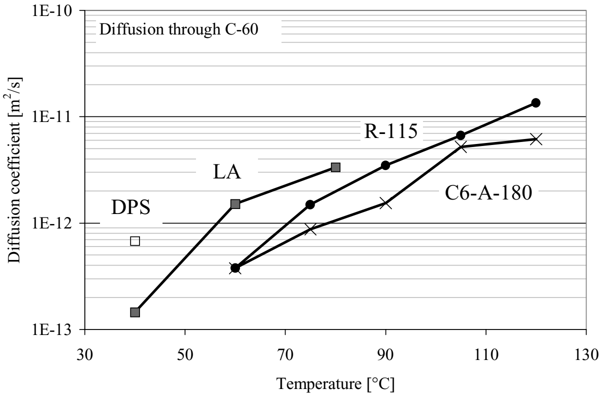

Figure 6 Rate of diffusion of different substances through bitumen C-60 at different temperatures.

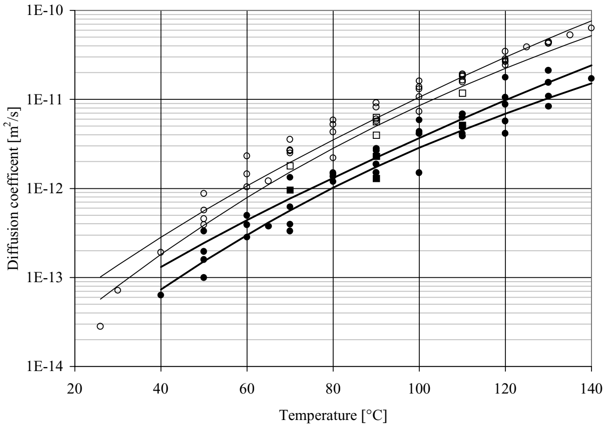

Figure 7 Diffusion of R-115 through A-180 (circles) and B-180 (squares) measured using methyl-methylene (open) and carbonyl (filled) peaks, respectively.

3.2.4. Variation between binders

Diffusion of R-115 through six binders was monitored in order to get an idea of the variation in rate of diffusion in different binders. The results are presented in Fig. 8. The maximum difference in rate of diffusion between the six binders is about one order. Diffusion of DPS and LA through different bitumen showed the same pattern (cf. Table II). It was indicated in a previous paper [2], that artificial TFO-ageing does not affect the rate of diffusion significantly. Among the results in Table II, a test with DPS is also included using a binder, referred to as H-12, which was recovered from a drilled

TABLE II Diffusion of diphenylsilane (DPS) and lauric acid (LA) through different binders at 40°C

Binder	Diffusion coefficient (m^2/s) DPS	Diffusion coefficient (m^2/s) LA
A-180 (fastest diff.)	1.6×10^{-12}	5.8×10^{-13}
C-60	4.0×10^{-13}	–
D-128	6.0×10^{-13}	1.4×10^{-13}
F-46	7.4×10^{-13}	1.0×10^{-13}
G-15[a] (slowest diff.)	2.0×10^{-13}	4.7×10^{-14}
G-55[a]	4.2×10^{-13}	1.6×10^{-13}
G-180[a]	7.0×10^{-13}	2.5×10^{-13}
H-12	5.5×10^{-13}	–

[a] Same values as in Fig. 5b.

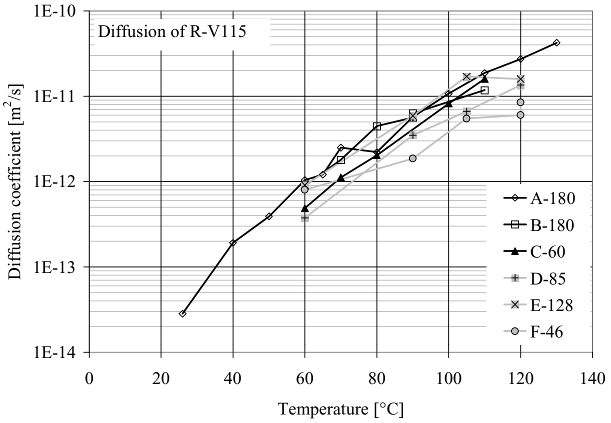

Figure 8 Diffusion of R-115 through six binders over a range of temperatures.

core sample taken from an old wearing course. Ageing during service life had decreased the grade of the binder from more than 60 dmm down to 12 dmm (penetration at 25°C). The diffusion rate of DPS through H-12 was not exceptionally lower than through the other binders.

3.3. Molecular weight distribution using HPSEC

The High Performance Size Exclusion Chromatography (HPSEC) tests were performed to determine the mean molecular weight of A-180, C6-A-180 and R-115. The HPSEC system used was a Waters 515 HPLC pump equipped with a Waters 410 differential refractometer. Tetrahydrofuran (THF) was used as the mobile phase with a constant flow of 1 ml/min. Three ultra-styragel columns were arranged in the order of pore size of 10^4, 10^3 and 500 Å. Narrow molecular weight polystyrene standards were used to calibrate the instrument. Before analysis, the sample was dissolved in THF (5% by weight).

The mean molecular weights of main peaks (non-associated maltenes) were 730 amu for A-180 and C6-A-180, and 270 amu for R-115. As illustrated in Fig. 9, the difference between the molecular size distribution of A-180 and C6-A-180 is only manifested above 3000 amu (if the graphs are scaled to the same height).

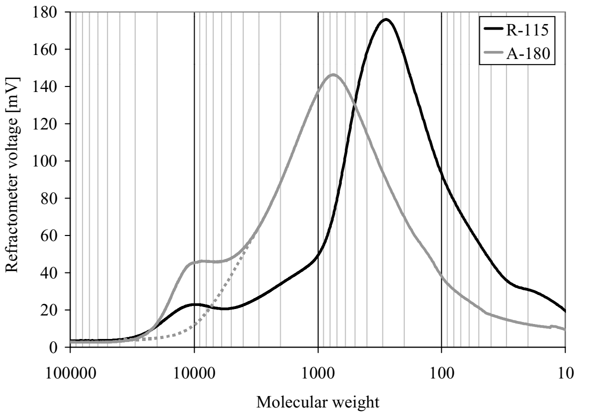

Figure 9 Molecular weight distribution of R-115 and A-180 measured by HPSEC. The dotted line indicates the molecular size distribution of the n-hexane maltenes of A-180 (C6-A-180).

4. Discussion

In Section 4.1, the use of markers in diffusion studies is demonstrated and some advantages and drawbacks are discussed. Section 4.2 is devoted to analyses based on experimental results presented in Chapter 3, aimed at enlighten diffusion in bituminous binders.

4.1. Use of markers for diffusion measurements

By monitoring selected substances (markers) diffusing through bitumen, valuable information can be obtained. The advantage of using markers is, that they, opposite to bituminous binders, show well-defined properties. The molecular size and shape of markers, as well as type of functional groups, can be varied. The functional groups are of interest, since they influence the molecular interactions. Markers have earlier been used [2] to study influence of ageing on diffusion.

When selecting markers and evaluating results obtained, some sources of interference should be kept in mind, such as melting point, volatility, interaction with bitumen, detectability and handling. Substances may separate from the binder, if the melting point or rate of evaporation is not low enough. In Section 3.1, it was shown how the influence of evaporation and concentration of a marker can be analysed and, to some extent, taken into consideration (Figs 2 and 3). Influence of marker concentration on the rate of diffusion can be demonstrated using different concentrations (cf. Fig. 3), but also modelled as discussed below (Section 4.2).

The marker itself interacts with the binder in several ways. Besides chemical reactions, which of course must be avoided by choice of marker, the marker changes the physical properties of the binder, for example the viscosity, and thereby influences the rate of diffusion. The influence can be minimised by using as low marker concentration as possible.

When infrared spectra are collected over a long period of time to monitor diffusion, variations in absorbance not originating from diffusion of markers is likely to occur. To facilitate the recording of marker diffusion, the infrared absorbance characteristics of binder and marker should be as different as possible. Furthermore, it is of great advantage, if the IR bands analysed are not in the range where interfering substances, such as water and carbon dioxide in the air or aged binder components (containing mainly carbonyls and sulphoxides) absorb, as discussed elsewhere [1, 17]. It was found that small and non-polar markers (fast diffusing) were easier to detect, since the time required for measuring diffusion is shorter and consequently, the interference of changes in external factors, such as atmospheric humidity, is comparably small. Furthermore, the fast diffusion of this type of marker also means that the interference from the slower diffusing bitumen components is relatively small.

Regarding sample preparation, application of a binder layer on top of another one is easier to perform, if the upper binder layer shows lower viscosity in order to avoid deformation of the lower layer. Therefore, application of markers was generally made by pre-blending of the marker with the (soft) rejuvenator used.

4.2. Diffusion in bituminous binders

Temperature, diffusant properties and properties of the media in which the diffusion takes place are three key parameters, when studying diffusion. Below, the influence of these factors is discussed.

4.2.1. Influence of temperature

The apparent great effect of temperature on diffusion originates from its influence on viscosity. This can be illustrated by an example. Since the diffusion coefficient according to Stoke-Einstein's equation (Equation 1) is proportional to the absolute temperature, a rise in temperature from 20°C (293 K) to 150°C (423 K) corresponds to an increased diffusion coefficient of 44%. This increase is negligible in comparison to the recorded increase in diffusion rate.

4.2.2. Influence of diffusion media

Stoke-Einstein's equation accounts for the influence of the diffusion media by considering resistance to diffusion proportional to viscosity of the media using a hydrodynamic approach. The decrease in viscosity, when raising temperature from 20 to 150°C, is normally in the magnitude of several orders for most bitumen. In [2], it was shown, using Stoke-Einstein's equation, that maltene phase viscosity rendered better predictions of diffusion coefficients compared to viscosity of pure bitumen. The methods used for extracting maltenes, measuring viscosity and relating the viscosity to diffusion coefficients could be debated, especially as maltenes are difficult to distinctly define. Research described by Branthaver *et al.* [18] shows, that fractions of bitumen obtained by heptane precipitation, size exclusion chromatography and ion exchange chromatography render a wide range of viscosities, even though some similarities can be observed. In this context, the most important conclusion drawn by Branthaver *et al.* is, that a minor fraction of a bitumen (asphaltenes) normally is responsible for the main viscosity building. Consequently, the major fraction of a binder comprises components with weaker intermolecular interactions and/or smaller molecules, referred to as the maltene phase. As mentioned in Section 1.3, a hypothesis has been formulated, which claims that diffusion is mainly influenced by the properties of the maltene phase. Some of the experimental work presented in Section 3 was aimed at investigating the diffusion media. These results, and their possible contribution to the understanding of the process of diffusion in bitumen, are discussed below.

One way to bring about indications of properties of the diffusion media is to manipulate the media by addition of known substances and measure how these substances influence diffusion (cf. Fig. 5a). In order to model the increase in rate of diffusion when a soft substance is added, Equation 5 was used for predicting viscosity of mixtures of liquids and binders [19].

$$\ln \mu_{\text{mix}} = c_1 \cdot \ln \mu_1 + c_2 \cdot \ln \mu_2 + c_1 \cdot c_2 \cdot G_{12} \qquad (5)$$

Indexes 1 and 2 denote two different liquids or binders, and x_1 and x_2 denote volume, mass or molar fraction of liquids/binders 1 and 2. The parameter G_{12} considers the effect of the intermolecular interaction between the binders and can vary substantially between different sets of binders [10]. The viscosity of the mixture of binders can be used in Stoke-Einstein's equation and Fick's law to model the diffusion process. When applying this approach to viscosity data of n-dodecane and lauric acid obtained from [20] and of n-hexane maltenes presented in [2], the theoretical and experimental diffusion coefficients of Fig. 5a coincide when $R = 8 \times 10^{-11}$ m (0.8 Å), and $G_{12} = -10$. Apparently, the mean molecular radius of DPS (0.8 Å) obtained in this manner is too small, since it is even smaller than the lengths of the covalent bonds present (1–2 Å [21]). The same approach can also be used to model diffusion of DPS as shown in Figs 2 and 3. For example, the procedure described can be used to extrapolate the diffusion coefficients obtained in Fig. 3 for different concentrations of DPS (1, 3 and 6% by weight). The diffusion coefficient obtained in this way at 0% DPS is 1.4×10^{-12} m^2/s, which is almost equal to the diffusion coefficient obtained at 1% DPS (1.5×10^{-12} m^2/s).

4.2.3. Influence of diffusant properties

The size and shape of diffusing molecules or agglomerates of molecules (the diffusants) is of great importance with regard to diffusion rate. The importance of shape has been described in Section 1.2 and is demonstrated by the following example. Association of molecules should theoretically show a minor influence on the rate of diffusion, if the enlargement is equal in all dimensions, but substantial, if molecules are associated into oblong shapes. This effect of shape can be exemplified using Equation 3. If the volume of a sphere is increased 100 times, the radius becomes 4.6 times larger. If the sphere instead becomes an oblong ellipsoid, where in an extreme case $a = 100 * b$, the mean molecular radius will increase almost 20 times.

The experimental work and results described in this paper regarding influence of diffusant properties on diffusion has mainly been performed using markers of different size and polarity. When the diffusion coefficients presented in Table I are plotted against molecular

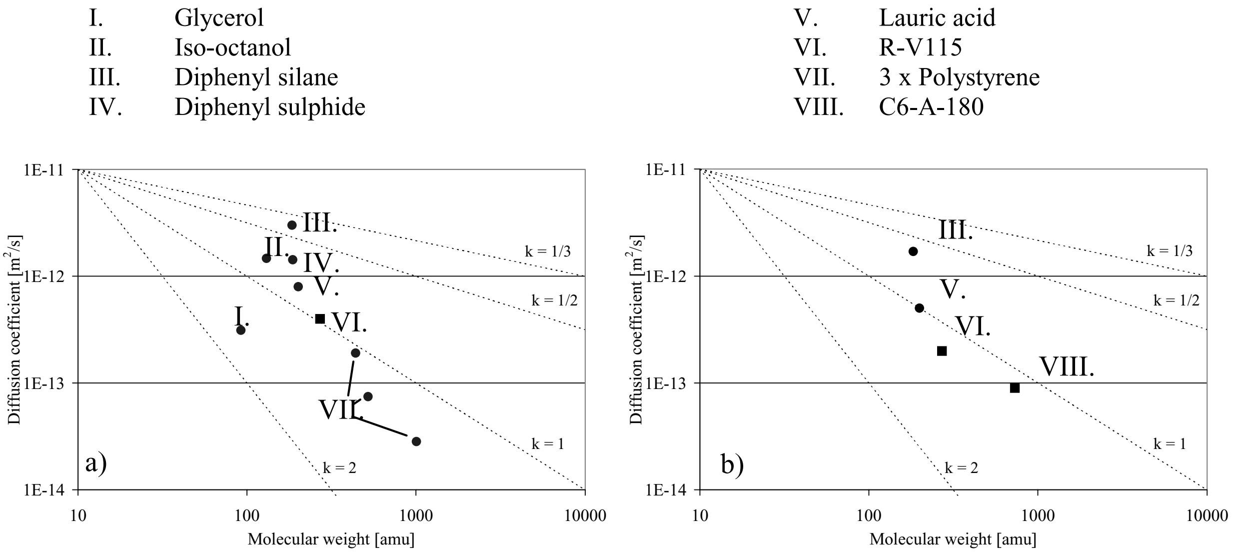

Figure 10 Influence of marker molecular size on diffusion rate in bitumen A-180 at 50°C (a). For comparison, data given in Fig. 6 for diffusion through bitumen C-60 is transformed to 50°C (b).

weight, a trend can be observed (cf. Fig. 10). As earlier indicated in Section 1.2, it is not obvious how the size (M) and shape of a diffusing molecule will influence its rate of diffusion (D). Assuming that the relationship between D and M follows a power law, that is $D \propto M^{-\mathrm{k}}$, the coefficient k should be between 1 and 1/3, if the molecules of the diffusion media are small [7]. k equal to 1/3 corresponds to a spherical diffusant and k equal to 1 to a linear diffusant. If polymers diffuse in a polymer solvent, i.e., if large molecules diffuse in a solvent of large molecules, the molecules are hindered by entanglement [7, 8]. This would explain why experimental results of polymer diffusion render k to be about 2. Since $D \propto M^{-k}$ is a straight line in a log-log diagram, the lines $k = 1/3$, 1/2, 1 and 2 are plotted in Fig. 10 for the purpose of comparing with experimental results. Besides glycerol, it can be observed, that the diffusion coefficients are lined up corresponding to a slope of k around 2. It was expected, that glycerol would diffuse at a slower rate than expected from its molecular weight, since it contains three hydroxyl groups and may form strong multiple bonds with other molecules.

It was difficult to come upon large size markers showing preferred properties. There is a possibility, that the three polystyrenes used in this study could influence the slope observed (k value) too much due to their similarities regarding constitution. Other substances in the same range of molecular weights could behave differently depending on, for example, shape and polarity.

If the diffusion coefficients shown in Fig. 6 are plotted as a function of molecular weight and transformed to 50°C, the same trend is observed, cf. Fig. 10b. However, the diffusion rate of C6-A-180 was higher than expected from the molecular weight distribution shown in Fig. 9 (peak molecular weight 730 amu).

All the radii of the molecules and agglomerates constituting bituminous binders are in principal widely

TABLE III Mean molecular sizes predicted by Stoke-Einstein equation (Equation 1) using experimentally determined maltene viscosity and diffusion coefficient data

Diffusant	Diffusion coefficient(s) in	Temperature (range) (°C)	Diffusing media/ range of viscosity (Pa · s)	Mean molecular radius (Å)
Rejuvenator R-115	Figs 4, 8	30–130	A-180 maltenes[a] 14–0.02	3
Rejuvenator R-115	Fig. 8	60–80	C-60 maltenes[a] 1.8–0.48	3
Rejuvenator R-115	Fig. 8	60–90	F-46 maltenes[a] 0.57–0.15	8
DPS	Table II	40	A-180 maltenes[a]/ 4.5	0.8
Lauric acid	Table II	40–80	A-180 maltenes[a]/ 4.5–0.23	1.5
Lauric acid	Table II	60–80	G-15 maltenes[b]/ 17–3	0.4
Lauric acid	Table II	80	G-55 maltenes[b]/ 2	0.5
Lauric acid	Table II	40–80	G-180 maltenes[b]/ 72–1.2	0.3

[a] Maltene viscosity obtained using dynamic shear rheometer.

[b] Maltene viscosity obtained using Brookfield viscometer.

distributed, and, consequently, a wide variation in diffusion coefficients should exist. The influence of polarity and the ability to associate with other molecules are of great importance for the apparent size of diffusing agglomerates. The rate of diffusion of non-polar DPS is higher compared to lauric acid, which contains one carboxyl group. Glycerol with three hydroxyl groups is by far the slowest among the smaller markers studied. Similarly, the influence of polarity should be manifested in diffusion of bituminous components. In Fig. 7, it is indicated that the carbonyl containing diffusants in general diffuses at a rate, which is approximately 1/4 of the one measured by monitoring methyl/methylene absorbance.

Calculations of values of mean molecular radii of diffusants based on Stoke-Einstein's equation and maltene viscosities may be of limited value, since, for example, the maltene viscosities obtained are dependent on the method of extraction. In Table III, some mean molecular radii calculated using Stoke-Einstein's equation and experimental results on maltene viscosity presented in [2] are given. These radii are smaller compared to estimations of the mean molecular radius, for example, using Equation 3 and assuming lauric acid to be of oblong shape (about 3 Å).

5. Conclusions

Based on the results and discussion presented in this paper the following conclusions were drawn:

- The use of selected substances as markers for studies of diffusion in bituminous binders has proven useful.
- Stoke-Einstein's equation (Equation 1) has been useful in interpreting the test results. However, it was difficult to show good agreement between diffusion coefficients predicted by Stoke-Einstein's equation and experimentally determined coefficients. One main reason behind the difference observed between predicted and measured values is probably due to the difficulty to accurately measure viscosity of the maltene phase.
- The interpretation of results presented regarding the influence of molecular weight, M, on diffusion rate was ambiguous and further studies are needed. From Stoke-Einstein equation, an approximate relationship was derived, relating the diffusion coefficient, D, to M^{-k}, where the k value varied between 1 (oblong shape) and 1/3 (sphere). The diffusion tests using markers indicated k to be around 2, which means, that the influence of molecular weight is higher than the diffusion rate predicted by Stoke-Einstein's equation.
- Polarity of molecules can show substantial influence on the rate of diffusion. Glycerol, the constitution of which makes multiple strong bonds possible, clearly diffused at a much slower rate than other substances of about the same size.
- For a given diffusant, the maximum variation in rate of diffusion in eight different binders studied was found to be about one order.
- The hypothesis proposed in [2], that the viscosity of the maltene phase is a main factor influencing the rate of diffusion in bitumen, is supported by findings presented in this paper.

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