

A new empirical diffusion model for solvents in sprayed seals based on evaporation measurements

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A new empirical diffusion model for solvents in sprayed seals based on evaporation measurements

Prediction of solvent diffusion and evaporation rate in the initial days after construction of a sprayed seal is of special concern for pavement performance assessment. It is still a major challenge as solvent evaporation is a very complicated process. In this study, laboratory tests were conducted on bitumen-solvent binder films, under different experimental conditions and varying solvent properties. A solution of Fick's diffusion equation was then used to calculate solvent diffusion coefficient (D) values for the initial 7 days. While a strong correlation was found between D and solvent viscosity as well as D and solvent distillation range, no relationship was found between D and solvent aniline point nor aromatic content. These findings were utilized in developing a multiple linear regression (MLR) diffusion model for the initial 7 days of evaporation. The evaluation of the model indicated close agreement between the predictions and experimental values ($R^2 = 0.95$). The model enables road agencies to predict solvent diffusion and residual solvent for the early life of a sprayed seal without needing to conduct extensive experiments thereby saving time and labour cost. Accurate prediction of residual solvent via the developed model will further ensure long-term performance of sprayed seals.

Keywords: Sprayed seal; Chip seal; Diffusion; Evaporation; Residual solvent; Performance prediction and evaluation.

1. Introduction

Bituminous binders are an important component in the paving industry, being extensively used in pavement construction, surface treatment of pavements and aggregate pre-coating. In these applications, it is necessary to reduce the viscosity of the bituminous binder either temporarily or permanently so that it will coat and adhere to the aggregate. The addition of heat, solvent and water to bitumen are the most widely used methods for temporarily reducing the viscosity of bitumen in different branches of pavement construction, such as sprayed seal (Chester, 1987; Dickinson, 1989; P. Herrington &

Patrick, 1998; Holtrop, 2008; Roads Corporation (Vic.) & GeoPave, 2004; You et al., 2019). Sprayed seal, which is also referred to as chip seal, typically consists of a single layer of bituminous binder and a layer of aggregate (Kodippily, Henning, & Ingham, 2014; You et al., 2019). This is among the most popular and cost-effective methods for sustainable road surfacing (Bagshaw, Herrington, & Wu, 2015; Kodippily et al., 2014; Mamlouk & Dosa, 2014) and pavement preservation (Kumbarger, Boz, & Kutay, 2019; Lee & Kim, 2014; Montoya, Jason Weiss, & Haddock, 2017). Around 90% of the surfaced road network in Australia and New Zealand consists of sprayed seals constructed on granular pavements (Austroads, 2019; Bagshaw et al., 2015; Chai, van Staden, Chowdhury, & Loo, 2014; González, Jameson, de Carteret, & Yeo, 2013; Holtrop, 2008). Sprayed seals are also widely used in countries such as South Africa, the United Kingdom, and Canada (Gransberg & James, 2005; Kodippily, Henning, & Ingham, 2012) as a surfacing and in the United States as pavement preservation strategies (Gransberg & James, 2005; Haider, Boz, Kumbarger, Kutay, & Musunuru, 2019; Wasiuddin et al., 2013).

When sprayed seals are constructed at low temperatures (under 45 °C), a liquid petroleum solvent (also called ‘cutter’) is added to the binder to decrease the viscosity of the binder temporarily in the sprayed seal. The blend of bitumen and solvent is referred to as cutback bitumen or cutback asphalt (Wang, Xiao, Chen, Li, & Amirhanian, 2017). The solvent added to the binder is evaporated from the sprayed seal over time. If solvent **evaporates more slowly** than required, flushing occurs due to excess solvent in the seal which reduces the structural integrity and safety **performance by having** low skid resistance (Kodippily et al., 2014; Lawson & Senadheera, 2009). If solvent **evaporates** too fast and aggregates are not properly wetted by the binder, stripping i.e. loss of aggregate occurs (Abo-Qudais & Al-Shweily, 2007; P. R. Herrington & Henderson,

2004). Pavement maintenance and construction costs globally more than four-hundred-billion dollars each year (Torres-Machí, Chamorro, Pellicer, Yepes, & Videla, 2015). To reduce the maintenance cost and obtain optimal sprayed seal performance, it is essential to properly select a solvent with specific properties that will yield the required functionality in practice. In the literature, inconsistent findings are reported between researchers (Chester, 1986; Donbavand, 1984; P. Herrington & Patrick, 1998; Meydan, 1997) regarding the effect of solvent distillation properties on the rate of loss of solvent from sprayed seals. From thermographic analysis of the concentration of solvent in sprayed seals in New Zealand, Donbavand (1984) found that diesel fuel (with high final boiling point) evaporated at a quicker rate and kerosene (lower final boiling point) at a slower rate, than in accordance with the common viewpoint, which is that diesel retains in the binder seal for years, whereas kerosene remains for weeks only. Chester (1986, 1987) reported similar findings from his studies using a gravimetric method to measure the evaporation of various solvents from sprayed seals in Victoria, Australia. However, Meydan (1997) reported from his study that he could not observe any differential effect of the type of solvent on the residual concentration of solvents. There is discrepancy among findings by researchers (Chester, 1986, 1987; Meydan, 1998) regarding the relation between the aromatic content of solvents and the associated **evaporation rate in sprayed seals**. Further, some solvents used in the past are no longer available and it is necessary to conduct research on the current generation of solvents available in Australia. As a result, all these challenges necessitate additional studies with different solvent types having diverse ranges of specific properties cited in AS 3568 (Standards Australia, 1999), to determine key properties that correlate with the desired evaporation rate of solvents.

The evaporation of these solvents from bitumen/solvent binder is hypothesized to be governed by diffusion phenomena (Donbavand, 1984; Fayazi, Kryuchkov, & Kantzas,

2017; Meydan, 1997; Oliver, 1974). Several models have been developed to describe the diffusivity behaviour of solvents in sprayed seals. Oliver (1974) used an ideal model compound dodecylbenzene to assess the diffusion process in a thin film of bituminous binder. Dickinson (1986) developed a model for a concentration-dependent diffusion coefficient by combining theoretical and empirical equations and fitted the model using only one solvent. However, these models did not represent a commercial oil fraction where a range of diffusion coefficients is expected. Later, Dickinson (1987) extended the previous diffusion model to two commercial solvents – lighting kerosene and flux oil (diesel). Nevertheless, the magnitude of the unknown parameters of this model could not be used for a wide range of commercial solvents. Meydan (1997) proposed two equations for the fraction of remaining solvent in a sprayed seal using a laboratory dataset of six solvents. However, to predict the behaviour of the solvent loss using these existing equations, an experimental data set would be required to determine the value of D , which would be time-consuming and inefficient. In addition, these equations have limitations with respect to covering a wide range of temperatures and solvent percentages. To reduce these limitations, a new general model is required incorporating solvent properties and other external parameters such as temperature.

In this study, the effect of different types and percentages of solvents, as well as the temperature and the chemical properties of the solvent, on the rate of diffusion, has been investigated. Using the correlational analysis from the investigation, an empirical diffusion model for solvent evaporation has been developed for the initial 7 days after construction of sprayed seal using multiple linear regression analysis based upon both theory and experimental data. Solvent properties, solvent percentage and temperature of the surrounding atmosphere were used as covariates in developing the models based on wide-ranging experimental database. Ten (10) statistical metrics were calculated to

evaluate the predictive performance of the models proposed in this study. The evaluation of the proposed model produced satisfactory results, demonstrating the efficiency and predictive capability of the model.

2. Methods and materials

2.1 Diffusion equation

In a sprayed seal, diffusion of hydrocarbon solvent occurs through a very thin film (typically 1-3 mm). As the surface area on top of a seal is very large compared to the thickness of the seal, diffusion can be considered as one dimensional, i.e., diffusion occurs **only across the thickness of the sprayed seal**. The diffusion and subsequent evaporation of a solvent from a sprayed seal (i.e. aggregates + binder) involve multiple factors in the process. This makes it a very complex scenario to characterise. Hence, only the binder film consisting of bitumen and hydrocarbon solvent is considered in terms of characterising the diffusion process in this study. Figure 1 illustrates the diffusion occurring in a cutback bitumen binder film with the thickness l , contained in a circular dish.

The following assumptions were made **for the mathematical** derivation:

- One-dimensional mass transfer occurs;
- No volume change occurs upon mixing the solvent and bitumen;
- Uniform temperature and pressure are maintained throughout the experiment;
- The initial concentration of solvent (C_0) is constant throughout the binder film;
- During the diffusion process, the solvent concentration on the surface (C_l) is constant; and
- Non-steady diffusion occurs.

Fick's diffusion equation for non-steady diffusion is described by:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad \text{Eq. (1)}$$

where C = Concentration at any distance x

D = Diffusion coefficient

t = Time

x = Space coordinate measured normal to the film surface

In this study, the initial and boundary conditions for diffusion in the thin film of binder contained in a circular dish without a lid (bottom surface closed, top surface open) would be:

$$\text{Initial condition:} \quad C(x, 0) = C_0 \quad 0 \leq x \leq l, \text{ at } t = 0 \quad \text{Eq. (2)}$$

$$\text{Boundary condition:} \quad C = C_1 \quad \text{at } x = l, t > 0 \quad \text{Eq. (3)}$$

$$\frac{\partial C}{\partial x} = 0 \quad \text{at } x = 0, \text{ for all } t \quad \text{Eq. (4)}$$

To find the solution of Eq. (1) for the above initial and boundary conditions, the separation of variables method was employed. The solution obtained is given below, which is also mentioned by Crank (1975), Hines and Maddox (1985).

$$\frac{C - C_0}{C_1 - C_0} = 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n + 1} e^{-\frac{D(2n+1)^2\pi^2t}{4l^2}} \cos \frac{(2n + 1)\pi x}{2l} \quad \text{Eq. (5)}$$

2.2 Fraction of residual solvent

Eq. (5) can be simplified further for a zero-surface concentration and Eq. (6), an equation for the residual fraction of solvents, α (generally defined as weight of remaining solvent divided by initial weight of solvent), can be obtained as a function of time. Here, a zero-surface concentration is based on the assumption that evaporation rate into the atmosphere is much faster than diffusion rate through the bitumen film.

$$\alpha = \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2\pi^2} e^{-\frac{D(2n+1)^2\pi^2 t}{4l^2}} \quad \text{Eq. (6)}$$

2.3 Materials

C170 bitumen and seven types of solvents were used for characterisation in this study. C170 bitumen was obtained from Puma Energy and tested against key requirements of Australian standard AS 2008 (Standards Australia, 2013). The C170 bitumen had a viscosity of 192 Pa.s at 60 °C and a density of 1.0483 g/cm³ at 15 °C.

The seven solvents were selected in this study based on recommendations from Australian state road authorities. Jet A1, high flash cutter, diesel and Enersol HFK were selected as they represent commercial solvents in current use in sprayed seal construction. Mineral turpentine, Enersol kerosene and Enersol K were selected as they represented commercially available solvents which showed a variety of different AS 3568-1999 test properties (Standards Australia, 1999). The later three solvents could also be feasibly used to reduce the viscosity of bitumen in sprayed seals. Among these solvents, Jet A1, high flash cutter and diesel were supplied by Viva Energy Australia Pty Ltd. Mineral turpentine was supplied by Recochem Inc. Enersol kerosene, Enersol K and Enersol HFK were supplied by IOR Energy Pty Ltd. The composition of the solvents, as well as their

typical range of properties, are given in Table 1 and Table 2. All solvents were tested against key requirements of the relevant Australian standard AS 3568 (Standards Australia, 1999) and their properties are given in Table 3.

2.4 Experiments

Evaporation tests on the selected bitumen-solvent blends were conducted at the Australian Road Research Board (ARRB) laboratory, using different temperatures to characterise the diffusion mechanism. During the evaporation tests, the weight of the remaining solvent in the bitumen-solvent mixtures at several mix ratios (2%, 4% and 6% w/w solvent-bitumen ratio) was measured to determine the diffusion coefficient value for each type of blend.

2.4.1 Compatibility test of solvents with C170 bitumen

First, assessment of the relative solubilities of the solvents with C170 bitumen was conducted on 60% w/w C170 bitumen with 40 % w/w solvent blends, following a modified version of the test method AS/NZS 2341.27. During the test, blends were poured into emulsion sedimentation jars and stored at room temperature, away from sunlight, for 3 days. Then, the top and bottom 50 mL from each sedimentation jar were collected. The Brookfield viscosities of the top and bottom samples from each blend were then measured at 40 °C and 60 °C following the Brookfield test method (AS/NZS 2341.4). The difference in viscosities between the top and bottom samples at 40 °C were all within $\pm 1\%$ of the original viscosity of each blend, and at 60 °C, all were within $\pm 2\%$ of the original viscosity of each blend (Table 4). These results indicated that each of the solvents was completely miscible with bitumen (i.e. the solvents and bitumen were compatible), as no separation of components had occurred after 3 days' of storage.

2.4.2 Making up blends

The cutback bitumen blends were prepared by mixing C170 bitumen as the main binder with 2%, 4% and 6% w/w of each of the 7 solvents as the diluent. The process of making the blends involved heating C170 bitumen in an oven at 120 °C until it was fluid enough to stir and pour, meanwhile pouring the required amount of solvent into empty tin. The bitumen was then added to the tin on top of the solvent followed by stirring. The blend was then placed in an oven for 5 minutes and re-stirred to ensure the blend was a homogeneous mixture. A preliminary test containing 94% w/w C170 bitumen and 6% w/w mineral turpentine (as mineral turpentine was the most volatile solvent included in the study and 6% w/w was the highest solvent concentration used) indicated that the blend preparation procedure resulted in less than 0.04% w/w loss of mineral turpentine during the mixing process. Therefore, the loss of solvent during the mixing process was assumed negligible.

2.4.3 Evaporation tests on solvent-bitumen systems

Evaporation tests were performed using 2 mm thin binder films of each of the bitumen-solvent blends. These films were prepared in 78.6 mm diameter metal dishes. Dishes containing each type of binder (without a lid) were placed on a bench in a controlled temperature room (Figure 2) operating at a specific temperature for 30 days. During this time, the mass loss of solvent from the binder films was monitored over time for a total of 22 blend types (C170 bitumen and 21 C170/solvent blends at 2%, 4% and 6% w/w solvent-bitumen ratio). Duplicate samples for each binder were used to account for any deviation of data. A trial test showed that there was no variation of solvent loss for the same type of binder at different locations on the bench. As a result, no fixed positions were maintained for the dishes throughout the test. Weight measurements were taken

using a four decimal point analytical balance at 0 hour, 2 hours, 4 hours and then each working day to calculate the amount of solvent loss which occurred for up to 30 days. In this way, evaporation tests on the 22 types of blends were carried out at three different temperatures, 40 °C, 50 °C and 60 °C in the same controlled temperature room mentioned above.

3. Results and discussion

3.1 Evaporation trend of solvents

From the laboratory data, α values at different times were calculated by assuming that bitumen weight remained constant over time. This is because an initial test on a sole bitumen binder film had indicated that the bitumen did not evaporate over time. Rather it appeared to become slowly oxidised, as a very insignificant amount of weight gain was observed (a maximum of 0.3%) after 30 days of heating.

The experimental α values at different times up to 30 days for 2%, 4% and 6% w/w Jet A1- C170 blends at 40 °C, 50 °C and 60 °C temperatures are presented in Figure 3a, Figure 3b and Figure 3c, respectively. Only the plots associated with the Jet A1 solvent are included, as similar trends were observed for the other solvents. From the plots of α vs. time, a general trend of linear rate of solvent mass loss over the initial time period (≤ 7 days) is observed. After that, the rate of change in α becomes exponential over time. This trend of initial faster evaporation rate followed by a slower rate of evaporation aligns with previous literature (Meydan, 1997, 1998). It is however noticeable that, with the studied percentages of solvent (resembling road practice), the solvent is not completely evaporated from the binder film after 1 month. Several months may be required to achieve nearly full solvent evaporation and it is highly likely that complete loss of solvent is never achieved.

The differences between the measured mass loss of the seven solvents in this study were not insignificant contrary to the results reported by Meydan (1997). There was around 10% solvent mass loss difference among the six solvents after 28 days at 60 °C in the laboratory test conducted by Meydan (1997) whereas around 22% solvent mass loss difference after 28 days at 60 °C was observed among the seven solvents in this study. From the experimental α values, it was observed that diesel evaporated at the slowest rate. After 30 days, around 36% diesel remained in the 6% C170/diesel film whereas only around 16% Jet A1 remained in the 6% C170/Jet A1 film at 60 °C. Due to this difference, diesel is suggested for use in lower trafficked rural roads, where the slower solvent evaporation will not result in any damage to a sprayed seal. The second lowest evaporation rate was detected for Enersol HFK. Around 24% Enersol HFK remained in the 6% C170/Enersol HFK film at 60 °C after 30 days. The slower evaporation rates of these two materials can be attributed to their higher final boiling point.

There was an anecdotal presumption that high flash point (HFP) cutters remain in the seal for longer duration compared to low flash point cutters, thus making the binder less resilient to traffic. As in the case of observations by Meydan (1997), this study found no indication that a higher flash point of solvent had any impact on solvent evaporation by comparing the experimental α values for all the binder films.

3.2 Effect of solvent properties on diffusion

Arrays of calculated α values were employed to determine the diffusion coefficient (D) values using Eq. (6) for each solvent. The D values of the solvents were calculated over an evaporation duration of the initial 7 days, considering that the diffusion coefficient was constant. D was estimated for the initial 7 days, because an analysis of D as a function of time, using the experimental data in this study, showed that D remained nearly constant

for the initial 7 days of each experiment. The estimated constant D values for the initial 7 days gave a better fit to the experimental data (lowest value of $R^2 = 0.95$ for 7 days compared to 0.85 for 30 days), yielding a more reliable correlation between D and solvent properties. In determining the D values from the α values, the golden section search and parabolic interpolation algorithm were used (Brent, 1972; Forsythe, Malcolm, & Moler, 1977). The D value was obtained in such a way that the mean squared error (MSE) for the calculated α was at a minimum. During the optimisation process of D, the termination tolerance on D was set to 10^{-8} , which refers that the calculation stopped when the change in D beyond 8 decimal places could generate the same minimum value of MSE. 1000 number of terms (n_{\max}) in the infinite series were used to determine the D values. A trial-and-error process was used to select the values of termination tolerance and n_{\max} to reduce the runtime, as beyond those values no significant change in D was noticed (no change in α values up to 7 decimal places was observed for $n_{\max}=1,000$ compared to $n_{\max}=10,000$). The obtained D values for the initial 7 days are presented in Table 5.

A correlational analysis was performed between the estimated constant D values and the solvent properties: aniline point, aromatic content, boiling point and dynamic viscosity of the solvent, to investigate which properties of the solvents controlled the diffusion of solvents in the sprayed seal. It was observed that aniline point and aromatic content had no correlation with solvent diffusion over time (Figure 4). This finding contrasts with reports in some literature (Chester, 1987) that the higher the aromatic content, the greater would be the reduction in viscosity of the bituminous binder and the higher the evaporation. This study found no link between high solvent aromatic content and faster evaporation, in agreement with the findings of Meydan (1997). It appeared that some other properties of the solvents rather than aniline point or aromaticity might have an effect on diffusion and subsequent evaporation.

From the plot of D vs. solvent viscosity at 40 °C in Figure 6, it appears that solvent viscosity has an inversely linear relationship on the diffusion coefficient, i.e. the diffusion and subsequent evaporation of the solvent (a similar trend was observed at 60 °C). The lower the viscosity of the solvent, the higher the rate of diffusion was observed from the analysis. This result indicates that solvent viscosity should be a key specification property in solvent selection for a sprayed seal.

A nearly inverse correlation was observed between solvent final boiling point (T_{FBP}) and D (Figure 5) but no noteworthy correlation could be found between D and solvent 50% recovery point. This trend suggests the selection of T_{FBP} as another required property for the specification of solvents for use in sprayed sealing applications.

3.3 Diffusion model

In this study, an experimental database containing 1617 α values for different solvent properties and experimental conditions were used to develop a model for α . Multiple linear regression (MLR) was used in this study to correlate D with the four most influential parameters, found by the analysis of the experimental data (section 3.2), for the initial 7 days of solvent evaporation. Parameters considered included the dynamic viscosity of the solvent at 60 °C (μ_{60}) in mPa.s, the final boiling point of the solvent (T_{FBP}) in °C, the solvent percentage (w_s) in %w/w and surrounding temperature (T) in °C. It was assumed that D remained constant for the duration of the model development (7 days), as D remained nearly constant for the initial 7 days of each experiment.

Several models of D were developed by regression analysis of the experimental data incorporating combinations of two, three or four of the above-mentioned parameters. The equations developed for D were then used in Eq. (6) to predict the values of α during the first 7 days of the experiment. Scatter plots of the experimental vs. predicted α values

for the duration of the models are presented in Figure 7 and Figure 8 to give some insight into model performance. The 1:1 line on each graph represents the ideal model, whereas the 1:2 and 2:1 dashed lines denote a factor of two scatter (Barmpadimos, Hueglin, Keller, Henne, & Prévôt, 2011; Sayegh, Munir, & Habeebullah, 2014). The R^2 values that are included in the graphs show the strongest linear relationship between the observed α values and the modelled α values when an equation containing the parameters μ_{60} , w_s and T is used (t, i.e. time, was used in all models and is not mentioned here).

To conduct an insightful performance evaluation of the models, ten statistical parameters were calculated. These are mean bias error (MBE), mean absolute error (MAE), mean absolute percentage error (MAPE), mean squared error (MSE), mean squared percentage error (MSPE), mean percentage error (MPE), root mean squared error (RMSE), R^2 , adjusted R^2 (R^2_{adj}) and index of agreement (IA). MBE and MPE indicate whether a model underestimates or overestimates the observations. MAE estimates the average magnitude of error produced by the model, whereas MAPE indicates the deviations of the predictions from the corresponding actual value. MSE and RMSE give relatively high weight to large errors/outliers. R^2 gives an insight into how well a model fits actual data. As R^2 increases with additional variables in the model, adjusted R^2 (R^2_{adj}) is used to evaluate the validity of models having different numbers of variables. IA was proposed by (Willmott, 1981) as a measure of the degree of model prediction error. It can vary between 0 and 1, with 1 indicating a perfect match.

The numerical values of these statistical parameters are summarised in Table 6. The small negative MBE and the positive MPE indicate that all the models slightly underestimated the actual values. As indicated by the other error indices, the model containing the parameters μ_{60} , w_s and T appears to perform much better than the other linear models. The MAPE of this model implies that there is an average of 4.23%

deviation of predictions from the actual value. The MSPE value for this model is only 0.42%, indicating a small number of outliers. An R^2_{adj} value of 0.95 suggests that the predictions match up considerably well against the actual values.

The best-modelled equation for D obtained from the MLR analysis in this study is expressed in Eq. (7), that can be substituted into Eq. (6) to determine the values of α covering the initial 7 days of the experiment. However, the application of this equation is limited to temperatures higher than or equal to 40 °C and solvents that have a dynamic viscosity lower than 1.5 mPa.s at 60 °C.

$$\begin{aligned}
 D = & 2.3630 \times 10^{-2} \mu_{60} - 7.4775 \times 10^{-2} w_s + 6.2365 \times 10^{-4} (T - \mu_{60} T) \\
 & + 2.0978 \times 10^{-3} w_s T + 1.4480 \times 10^{-2} \mu_{60} w_s \\
 & - 4.8333 \times 10^{-4} \mu_{60} w_s T - 2.4238 \times 10^{-2}
 \end{aligned} \tag{Eq. (7)}$$

where μ_{60} = Dynamic viscosity of solvent at 60 °C in mPa.s

w_s = Solvent percentage in the mixture in % w/w

T = Surrounding temperature in °C

D = Diffusion coefficient in mm²/day

4. Summary and conclusions

In this study, the diffusion and evaporation trend of standard and non-standard solvents in sprayed seals have been investigated. Based on the observed relation between solvent diffusion and solvent properties, a new empirical diffusion model has been proposed using the experimental database obtained in this study for solvents used in sprayed seals. The key conclusions obtained from this study can be summarised as follows:

- It was observed that solvent distillation range and viscosity had a significant impact on the diffusion of solvent in thin cutback bitumen films of sprayed seals. Aniline point and aromatic content had no impact on diffusion and subsequent

evaporation. These properties have been mentioned with a required specification in AS 3568-1999 (Standards Australia, 1999) for solvent selection in sprayed seal application. The findings of this study demonstrate the necessity of updating the Standard which should make no provision of aniline point or aromatic content requirement.

- Based on the relation between solvent diffusion and solvent properties as well as experimental conditions, a multiple linear regression diffusion model for the initial 7 days evaporation duration has been proposed in this study, for solvents used in sprayed seal construction.
- Using a combination of the proposed diffusion model and solution of Fick's diffusion equation, fractions of residual solvents have been predicted, where a close agreement between the experimental and predicted values has been observed ($R^2 = 0.95$).
- The model can be used to predict α , at temperatures higher than or equal to 40 °C and solvents with the dynamic viscosity lower than 1.5 mPa.s at 60 °C.
- The initial days of a sprayed seal after construction is the most crucial time for ensuring a sustainable road surface. The proposed diffusion model can be used by road authorities and practising engineers to specify the diffusion rate of solvent from sprayed seals and subsequent solvent loss during the first week after construction. Furthermore, the model has the advantage that diffusion of solvents and residual solvent amount can be predicted without needing to conduct experiment thereby eliminating the shortcomings of the existing solutions. As a result, the pavement industry and practising engineers can benefit from the use of the proposed model in this study by saving their time and labour cost as well as designing and constructing sustainable pavements.

5. Limitations and directions for future work

Bitumen-solvent binder of the sprayed seal is a complex mixture of different hydrocarbon types and the characterisation of such a complex system is a very complicated task. Using a conventional method to model this type of intricate system is time-consuming and labour intensive. The proposed model in this study was developed using a traditional method, where several assumptions and simplification of the system were adopted. Due to this limitation, this study recommends using artificial intelligence techniques in future for the development of prediction models for the diffusion of solvents. Computer-aided modelling can help to generate a more precise and reliable model.

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Disclosure statement

No potential conflict of interest.

Nomenclature

D	Diffusion coefficient
l	Binder film thickness
t	Time
α	Fraction of remaining solvent
C	Concentration
C_0	Initial concentration of solvent
C_1	Solvent concentration on the surface
HFP	High flash point
T_{FBP}	Final boiling point
T	Temperature
w_s	Solvent percentage
μ_{60}	Dynamic viscosity at 60 °C
R^2	Coefficient of determination

References

- Abo-Qudais, S., & Al-Shweily, H. (2007). Effect of aggregate properties on asphalt mixtures stripping and creep behavior. *Construction and Building Materials*, 21(9), 1886-1898. doi:<https://doi.org/10.1016/j.conbuildmat.2005.07.014>
- Austroroads. (2019). *Guide to pavement technology: part 2: pavement structural design* (Vol. AGPT02-17). Sydney, NSW: Austroroads.
- Bagshaw, S. A., Herrington, P. R., & Wu, J. P. (2015). Preliminary examination of chipseals prepared with epoxy-modified bitumen. *Construction and Building Materials*, 88, 232-240.
- Barmpadimos, I., Hueglin, C., Keller, J., Henne, S., & Prévôt, A. (2011). Influence of meteorology on PM10 trends and variability in Switzerland from 1991 to 2008. *Atmospheric Chemistry and Physics*, 11(4), 1813.
- Brent, R. P. (1972). *Algorithms for minimization without derivatives*. Englewood Cliffs, N.J.: Englewood Cliffs, N.J., Prentice-Hall.
- Chai, G., van Staden, R., Chowdhury, S., & Loo, Y. (2014). A study of the effects of pavement ageing on binder deterioration. *International Journal of Pavement Engineering*, 15(1), 1-8.
- Chester, J. L. (1986). *Flux and cutter oils and their rates of loss from sprayed seals*. Paper presented at the Australian Road Research Board (ARRB) Conference, 13th, 1986, Adelaide, Australia.
- Chester, J. L. (1987). Cutter oils and their use in spray sealing.
- Crank, J. (1975). *The mathematics of diffusion* (2nd ed. ed.). Oxford [England]: Oxford England : Clarendon Press.
- Dickinson, E. J. (1986). The rate of evaporation of cutter from films of cutback bitumen. *Australian Road Research*, 16(3).
- Dickinson, E. J. (1987). Evaporation of cutters and fluxes from sprayed seals. 17, 1-12.

- Dickinson, E. J. (1989). *The rate of evaporation of volatile diluents (cutter) from cutback bitumen sprayed seals.*
- Donbavand, J. (1984). An Investigation into the Use of Thermogravimetry and Derivative Thermogravimetry for the Analysis of Bituminous Materials. *Australian Road Research, 12*(2).
- Fayazi, A., Kryuchkov, S., & Kantzas, A. (2017). Evaluating Diffusivity of Toluene in Heavy Oil Using Nuclear Magnetic Resonance Imaging. *Energy & Fuels, 31*(2), 1226-1234. doi:10.1021/acs.energyfuels.6b02464
- Forsythe, G. E., Malcolm, M. A., & Moler, C. B. (1977). *Computer methods for mathematical computations* (Vol. 259): Prentice-hall Englewood Cliffs, NJ.
- González, A., Jameson, G., de Carteret, R., & Yeo, R. (2013). Laboratory fatigue life of cemented materials in Australia. *Road Materials and Pavement Design, 14*(3), 518-536.
- Gransberg, D. D., & James, D. M. (2005). *Chip seal best practices* (Vol. 342): Transportation Research Board.
- Haider, S. W., Boz, I., Kumbarger, Y., Kutay, E., & Musunuru, G. (2019). Development of performance related specifications for chip seal treatments. *International Journal of Pavement Engineering, 1*-10.
- Herrington, P., & Patrick, J. (1998). *Fluxing Of Chipseal Binders*. Paper presented at the Road Engineering Association of Asia and Australasia (Reaaa), Conference, 9th, 1998, Wellington, New Zealand, vol 1.
- Herrington, P. R., & Henderson, R. (2004). Bitumen Film Thicknesses and Confinement Ratios in Chip Seal Surfacing. *Road Materials and Pavement Design, 5*(2), 251-264. doi:10.1080/14680629.2004.9689972
- Hines, A. L., & Maddox, R. N. (1985). *Mass transfer: fundamentals and applications* (Vol. 434): Prentice-Hall Englewood Cliffs, NJ.
- Holtrop, W. (2008). Sprayed sealing practice in Australia. *Road & Transport Research: A Journal of Australian and New Zealand Research and Practice, 17*(4), 41.
- Kodippily, S., Henning, T. F., & Ingham, J. M. (2012). Detecting flushing of thin-sprayed seal pavements using pavement management data. *Journal of Transportation Engineering, 138*(5), 665-673.
- Kodippily, S., Henning, T. F., & Ingham, J. M. (2014). Using a multi-phase model to predict flushing of sprayed seal pavements. *International Journal of Pavement Engineering, 15*(3), 267-278.
- Kumbarger, Y. S., Boz, I., & Kutay, M. E. (2019). Investigating the effect of binder and aggregate application rates on performance of chip seals via digital image processing and sweep tests. *Construction and Building Materials, 222*, 213-221.
- Lawson, W. D., & Senadheera, S. (2009). Chip seal maintenance: solutions for bleeding and flushed pavement surfaces. *Transportation Research Record, 2108*(1), 61-68.
- Lee, J., & Kim, R. Y. (2014). Evaluation of polymer-modified chip seals at low temperatures. *International Journal of Pavement Engineering, 15*(3), 228-237.
- Mamlouk, M. S., & Dosa, M. (2014). Verification of effectiveness of chip seal as a pavement preventive maintenance treatment using LTPP data. *International Journal of Pavement Engineering, 15*(10), 879-888.
- Meydan, A. (1997). *Evaporation of Cutters from a Chip Seal*. Paper presented at the AAPA International Flexible Pavements Conference, 10TH, 1997, Perth, Western Australia, VOL1.
- Meydan, A. (1998). *Effect of the Boiling Point of a Flux Oil on its Evaporation from Bitumen*. Paper presented at the Focussing On Performance: AAPA Pavements Industry Conference, 1998, Surfers Paradise, Queensland, Australia.

- Montoya, M. A., Jason Weiss, W., & Haddock, J. E. (2017). Using electrical resistance to evaluate the chip seal curing process. *Road Materials and Pavement Design*, 18(sup4), 98-111. doi:10.1080/14680629.2017.1389090
- Oliver, J. W. (1974). Diffusion of oils in asphalts. *Industrial & Engineering Chemistry Product Research and Development*, 13(1), 65-70.
- Roads Corporation (Vic.), & GeoPave. (2004). *Bituminous sprayed surfacing manual*. (Technical Bulletin No. 45). Melbourne: VicRoads, 2004
- Sayegh, A. S., Munir, S., & Habeebullah, T. M. (2014). Comparing the performance of statistical models for predicting PM10 concentrations. *Aerosol and Air Quality Research*, 14(3), 653-665.
- Standards Australia. (1999). *Oils for reducing the viscosity of residual bitumen for pavements* (AS 3568-1999). Sydney, NSW: Standards Australia. Retrieved from <http://www.saiglobal.com>
- Standards Australia. (2013). *Bitumen for pavements* (AS 2008-2013). Sydney, NSW: Standards Australia Retrieved from <http://www.saiglobal.com>
- Torres-Machí, C., Chamorro, A., Pellicer, E., Yepes, V., & Videla, C. (2015). Sustainable pavement management: Integrating economic, technical, and environmental aspects in decision making. *Transportation Research Record*, 2523(1), 56-63.
- Wang, J., Xiao, F., Chen, Z., Li, X., & Amirhanian, S. (2017). Application of tack coat in pavement engineering. *Construction and Building Materials*, 152, 856-871.
- Wasiuddin, N. M., Marshall, A., Saltibus, N. E., Saber, A., Abadie, C., & Mohammad, L. N. (2013). Use of sweep test for emulsion and hot asphalt chip seals: laboratory and field evaluation. *Journal of Testing and Evaluation*, 41(2), 289-298.
- Willmott, C. J. (1981). On the validation of models. *Physical geography*, 2(2), 184-194.
- You, L., Jin, D., You, Z., Dai, Q., Xie, X., Washko, S., & Cepeda, S. (2019). Laboratory shear bond test for chip-seal under varying environmental and material conditions. *International Journal of Pavement Engineering*, 1-9.

Table 1. Composition of the solvents.

Material	Composition	Proportion (volume%)
Jet A1	Kerosene	0-100%
High flash cutter	Kerosene (petroleum), hydrodesulphurised	90-100%
	Naphthalene	<3%
Diesel	Fuels, diesel	95-100%
	Fatty acids, vegetable oil, methyl esters	0-5%
Mineral turpentine	Solvent naphtha, light aromatic; low boiling point naphtha	<40%
	Low aromatic white spirit	<70%
	Kerosene	>99.9%
Enersol kerosene	n-Hexane	<0.1%
	Benzene	<0.1%
Enersol K	Kerosene	100%
Enersol HFK	Kerosene	100%

Table 2. Typical range of properties of the solvents (obtained from the solvent suppliers).

Material	Boiling point, °C	Density at 15 °C (kg/m ³)	Flash point (°C)	Vapour pressure	Kinematic viscosity at 40 °C
Jet A1	90-300	-	48	1-21 kPa at 37.8 °C	1-2.5 mm ² /s
High flash cutter	195-260	800-830	82 (typical 75)	-	2-4.5 mm ² /s
Diesel	170-390	820-850	79.5 (typical 63)	<100 Pa at 20 °C	3.1 mm ² /s
Mineral turpentine	148-200	780-820	31	0.5 kPa at 20 °C	-
Enersol kerosene	140-270	730-790	>37 (typical 42)	<2.1 kPa	-
Enersol K	180-295	760-810	>60.5	-	-
Enersol HFK	175-340	790-810	>65	-	2-4.5 mm ² /s

Table 3. AS 3568-1999 properties of the solvents which were used in this study.

Property	Test method	Jet A1	High flash cutter	Diesel	Mineral turpentine	Enersol kerosene	Enersol K	Enersol HFK	
Solvent Description		Standard cutter oil	Standard HFP cutter oil	Standard flux oil	Non-standard solvent	Non-standard solvent	Non-standard solvent	Non-standard solvent	
Aniline point (°C)	ASTM D611	59.2	62.8	71	23.4	74.4	80.8	83	
Aromatic content (%v/v)	ASTM D1319	15.4	16.9	24.3	44.9	2.7	7	6.9	
Density at 15 °C (kg/m ³)	ASTM D4052	795.1	814.3	847.4	813.0	760.7	794.3	796.5	
Viscosity at 40 °C (mPa.s)	ASTM D445	0.9	1.26	2.82	0.66	0.83	1.66	1.85	
Viscosity at 60 °C (mPa.s)		0.74	0.95	1.91	0.55	0.66	1.2	1.32	
Initial boiling point (°C)		161.8	202.0	193.1	149.2	148.2	194.0	184.3	
% volume recovered at (%)	150 °C	ASTM D86	0	0	0	0	0	0	
	200 °C		66	0	1	100	78	0	2
	250 °C		100	100	15	100	100	54	46
	300 °C		100	100	68	100	100	100	83
	350 °C		100	100	96	100	100	100	100
Final boiling point (°C)		232.3	236.3	357.9	184.0	233.5	285.7	335.8	

Table 4. Compatibility test results.

Bitumen-solvent blend	60% C170/40% solvent						
	Jet A1	High flash cutter	Diesel	Mineral turpentine	Enersol kerosene	Enersol K	Enersol HFK
Observations after storage test	NP*	NP*	NP*	NP*	NP*	NP*	NP*
Top 50 mL viscosity at 40 °C (Pa.s)	0.0585	0.0917	0.2359	0.0393	0.0526	0.1160	0.1295
Bottom 50 mL viscosity at 40 °C (Pa.s)	0.0584	0.0920	0.2348	0.0391	0.0530	0.1162	0.1293
Top 50 mL viscosity at 60 °C (Pa.s)	0.0264	0.0375	0.0809	0.0188	0.0238	0.0451	0.0498
Bottom 50 mL viscosity at 60 °C (Pa.s)	0.0262	0.0375	0.0802	0.0192	0.0239	0.0455	0.0499
Viscosity at 40 °C of initial blend	0.0555	0.0894	0.2273	0.0388	0.0521	0.1089	0.1252
Viscosity at 60 °C of initial blend	0.0251	0.0367	0.0794	0.0190	0.0238	0.0434	0.0484
% Top and bottom viscosity difference at 40 °C	0.2	-0.4	0.5	0.5	-0.8	-0.2	0.1
% Top and bottom Viscosity difference at 60 °C	0.8	0.0	0.8	-1.9	-0.4	-0.8	-0.1
*NP = No precipitation							

Table 5. Estimated D values for the initial 7 days of the evaporation test.

Solvent name	D (mm ² /day)								
	T = 40 °C			T = 50 °C			T = 60 °C		
	SP =2%	SP =4%	SP =6%	SP =2%	SP =4%	SP =6%	SP =2%	SP =4%	SP =6%
Jet A1	0.0144	0.0279	0.0414	0.0290	0.0655	0.1012	0.0706	0.1485	0.2244
Mineral turpentine	0.0200	0.0366	0.0560	0.0445	0.0788	0.1196	0.0918	0.1797	0.2631
Diesel	0.0027	0.0048	0.0078	0.0095	0.0190	0.0336	0.0290	0.0690	0.1078
High flash cutter	0.0133	0.0233	0.0325	0.0364	0.0596	0.0776	0.0915	0.1417	0.2204
Enersol kerosene	0.0183	0.0363	0.0523	0.0373	0.0848	0.1275	0.0982	0.1918	0.2793
Enersol K	0.0114	0.0199	0.0377	0.0328	0.0821	0.1387	0.0843	0.2118	0.3073
Enersol HFK	0.0084	0.0149	0.0250	0.0200	0.0327	0.0692	0.0561	0.1253	0.1747

* T = Temperature; SP = Solvent percentage;

Table 6. Model predictions of α for initial 7 days of evaporation.

Error metrics	μ_{60} , T_{FBP} , w_s & T	T_{FBP} , w_s & T	μ_{60} , w_s & T	w_s & T	T_{FBP} & T	μ_{60} & T	T_{FBP} & w_s	μ_{60} & w_s
MBE	0.00	0.00	-0.01	-0.01	-0.01	-0.01	-0.02	-0.02
MAE	0.03	0.03	0.03	0.04	0.05	0.05	0.07	0.07
MAPE (%)	4.38	4.52	4.23	5.37	7.49	7.40	10.16	10.16
MSE	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01
MSPE (%)	0.43	0.46	0.42	0.70	1.35	1.36	2.44	2.38
MPE (%)	0.49	0.12	0.64	0.35	0.73	0.41	0.27	0.29
RMSE	0.04	0.04	0.04	0.06	0.07	0.07	0.09	0.09
R^2	0.94	0.94	0.95	0.89	0.83	0.83	0.71	0.72
R^2_{adj}	0.94	0.94	0.95	0.89	0.83	0.83	0.71	0.72
IA	0.99	0.98	0.99	0.97	0.95	0.96	0.92	0.92

*Error metrics calculation equations:

$$\text{Mean bias error, } MBE = \frac{1}{n} \sum_{i=1}^n P_i - O_i$$

$$\text{Mean absolute error, } MAE = \frac{1}{n} \sum_{i=1}^n |O_i - P_i|$$

$$\text{Mean absolute percentage error, } MAPE = 100 \times \frac{1}{n} \sum_{i=1}^n \left| \frac{O_i - P_i}{O_i} \right|$$

$$\text{Mean squared error, } MSE = \frac{1}{n} \sum_{i=1}^n (O_i - P_i)^2$$

$$\text{Mean squared percentage error, } MSPE = \frac{100}{n} \sum_{i=1}^n \left(\frac{O_i - P_i}{O_i} \right)^2$$

$$\text{Mean percentage error, } MPE = 100 \times \frac{1}{n} \sum_{i=1}^n \frac{O_i - P_i}{O_i}$$

$$\text{Root mean squared error, } RMSE = \sqrt{\frac{1}{n} \sum_{i=1}^n (O_i - P_i)^2} \text{ or } \sqrt{MSE}$$

$$\text{Adjusted } R^2, R^2_{\text{adj}} = 1 - \frac{(1-R^2)(n-1)}{n-k-1}$$

$$\text{Index of agreement, } IA = 1 - \frac{\sum_{i=1}^n (O_i - P_i)^2}{\sum_{i=1}^n (|P_i - \bar{O}| + |O_i - \bar{O}|)^2}$$

Here, P_i = Predicted value

O_i = Observed value

\bar{O} = Mean of the observed value

n = Total number of observations

k = Number of independent variables in the model



Figure 1. Schematic representation of diffusion occurring through a thin binder film in a circular dish.



Figure 2. Evaporation test: metal dishes containing 2 mm thin bitumen/solvent binder films kept on table inside a controlled temperature room to continue testing for 1 month.

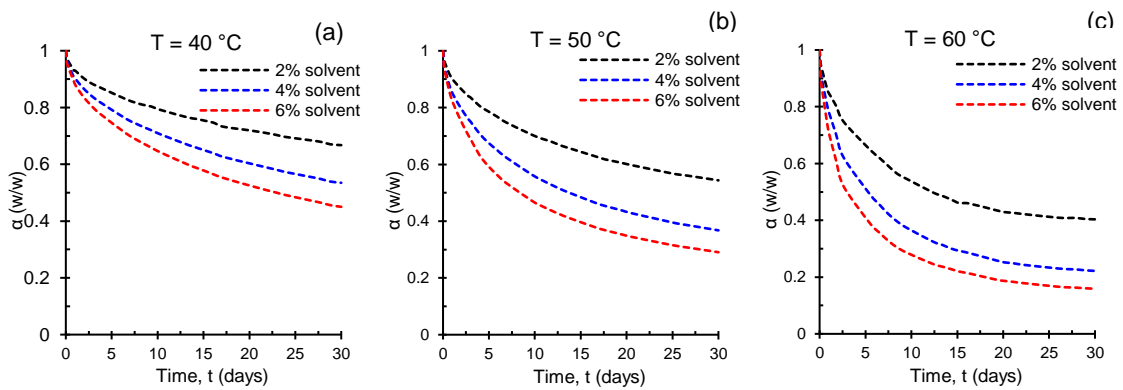


Figure 3. Plot of experimental fraction of remaining solvent, α vs time (t) for Jet A1 at temperatures (T) of- (a) 40 °C, (b) 50 °C and (c) 60 °C.

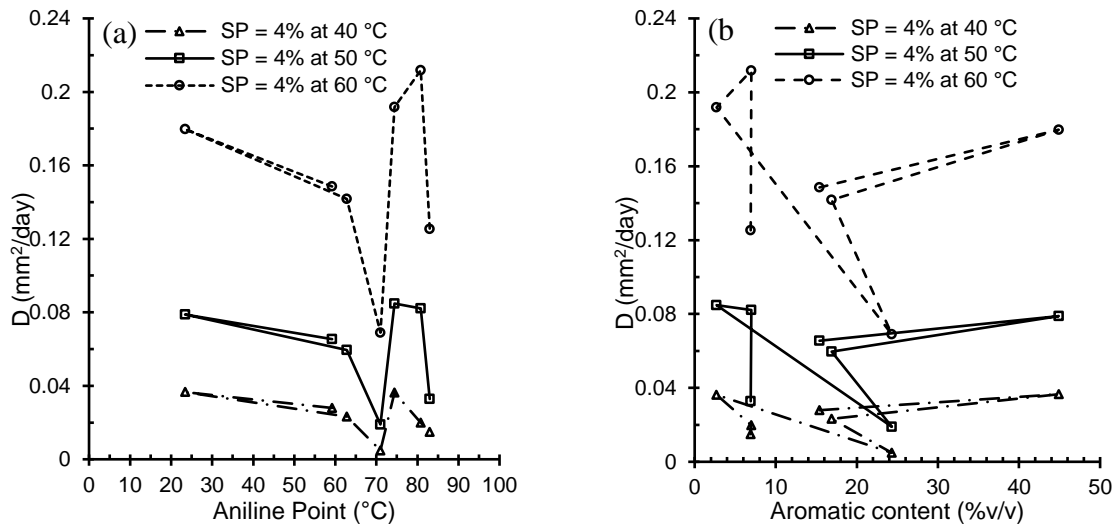


Figure 4. D versus (a) solvent aniline point, (b) aromatic content.

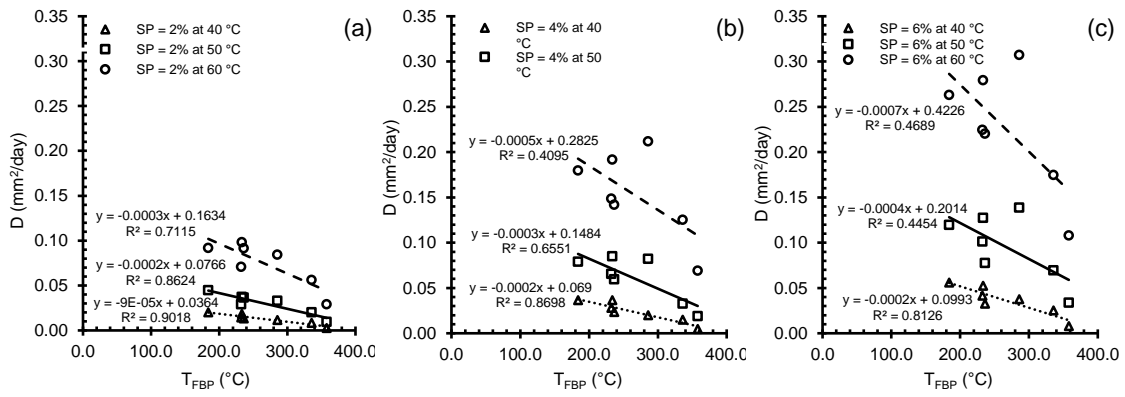


Figure 5. D versus solvent final boiling point (T_{FBP}) at solvent percentages (a) 2%, (b) 4% and (c) 6%.

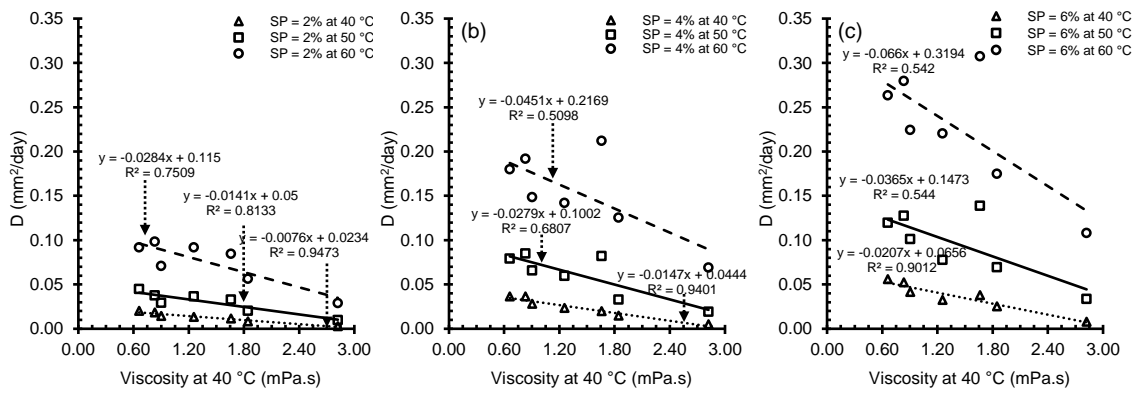


Figure 6. D versus solvent viscosity at solvent percentages of- (a) 2%, (b) 4% and (c) 6%.

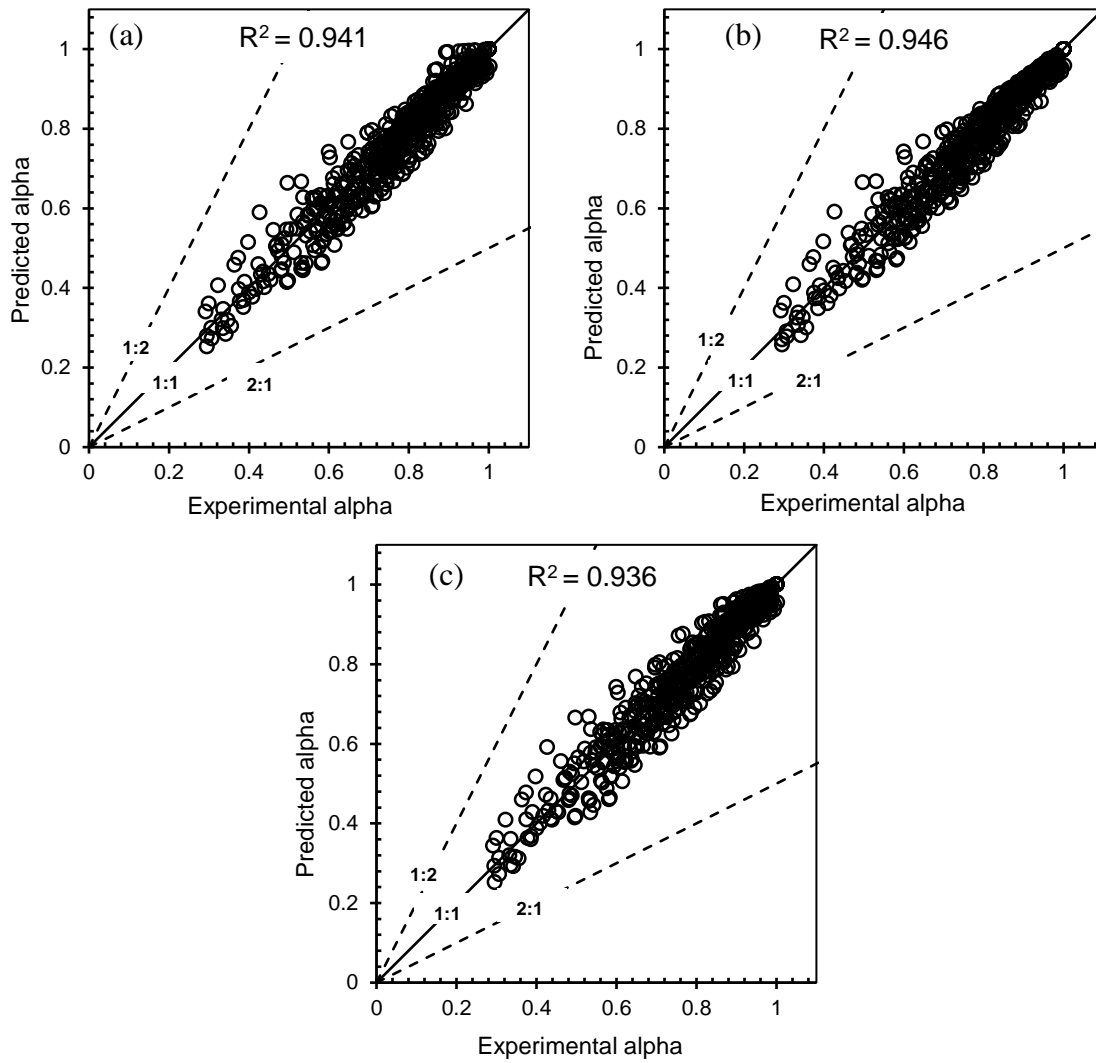


Figure 7. Experimental vs predicted α values for the 7-day MLR diffusion models with independent variables (a) μ_{60} , T_{FBP} , w_s , T & t , (b) μ_{60} , w_s , T & t , (c) T_{FBP} , w_s , T & t .

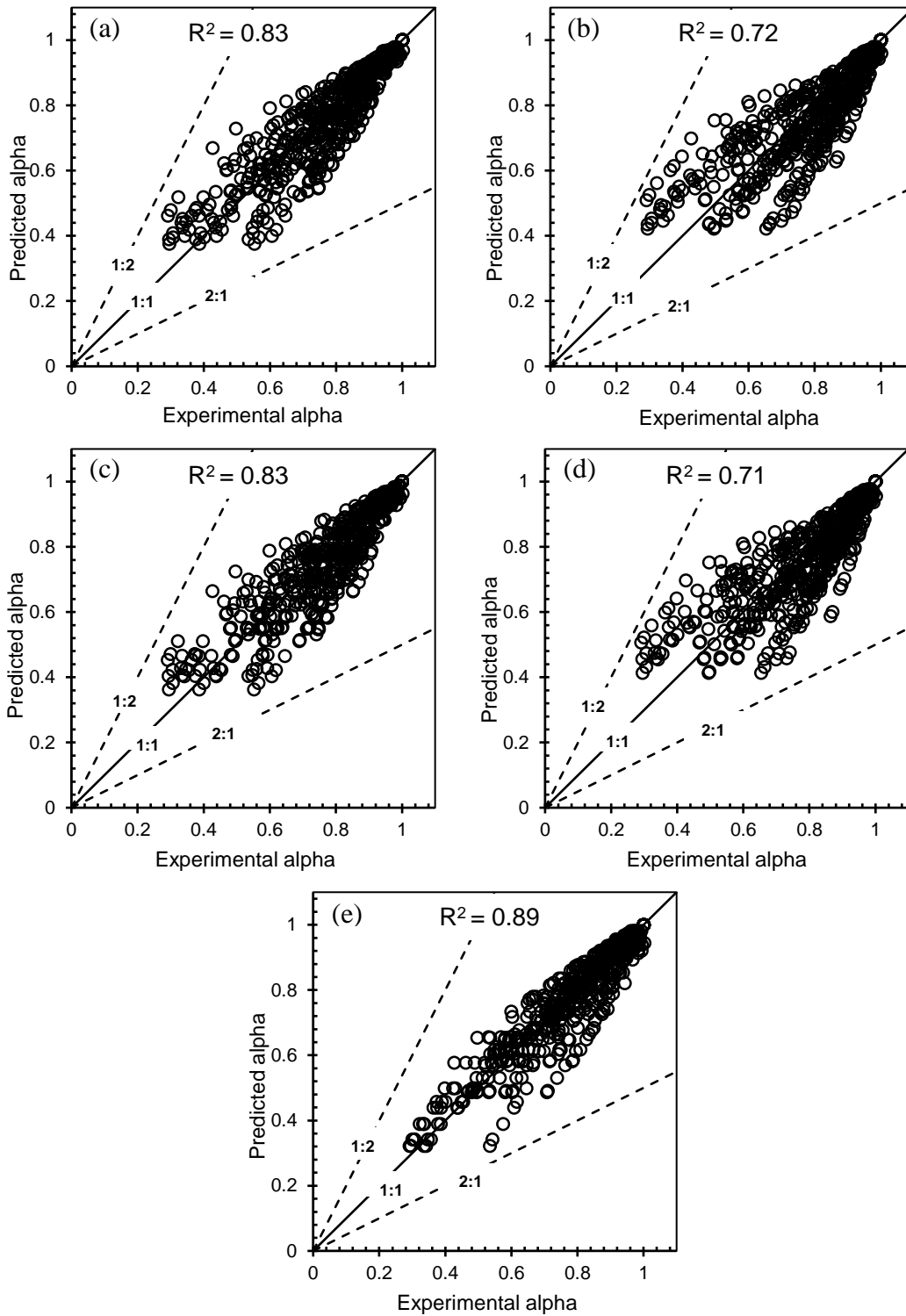


Figure 8. Experimental vs predicted α values for the 7-day MLR diffusion models with independent variables (a) μ_{60} , T & t, (b) μ_{60} , w_s & t, (c) T_{FBP} , T & t, (d) T_{FBP} , w_s & t, (e) w_s , T & t.