

Determining coefficients for mass-transfer models for volatile organic compound emissions from architectural coatings

D. Won*, C.Y. Shaw

Institute for Research in Construction, National Research Council, Ottawa, Ontario, Canada

ABSTRACT

This research is to develop a mass-transfer model for describing the emission of volatile organic compounds (VOCs) from architectural coatings, which accounts for both surface evaporation and internal diffusion during the drying period. To apply this model, it is necessary to know the evaporation and diffusion coefficients of VOC emitted from the coating materials. An experimental method was, therefore, developed to determine both the evaporation and diffusion coefficients for six aliphatic hydrocarbons and six aromatic hydrocarbons from oil-based paint. It was shown that diffusion coefficients are inversely proportional to molecular weight, while evaporation coefficients are proportional to vapour pressure of the VOCs.

INDEX TERMS

Architectural coating; VOCs; Mass-transfer model; Emissions; Indoor air

INTRODUCTION

Hydrocarbon-based solvents in architectural coatings can significantly contribute to the levels of VOCs in indoor environments, in particular, during the drying period. The VOC emissions from the coatings are controlled by two mass-transfer mechanisms. At the early stage of drying, which is characterized by a high emission rate, the emission process is mainly controlled by surface evaporation. When solvent mobility becomes restricted by the resins in the coating material during the drying period, i.e., as the film forms and thickens, the emission rate decreases with time and diffusion increasingly replaces evaporation as the dominant mechanism controlling the emission process.

Two models have been commonly used to describe the emission processes from architectural coatings. The empirical models, which were developed by fitting the measured time–concentration data from a chamber study, ignore the principle of the emission process, and therefore, are case-specific. The vapour pressure and boundary layer model developed by the US Environmental Protection Agency is a more advanced model than empirical models, but it does not account for internal diffusion (Guo *et al.*, 1998). This paper is to develop a more fundamental model based on mass-transfer mechanisms for VOC emissions from architectural coatings. It also describes a method developed for determining the diffusion and evaporation coefficients for the use of the model.

METHODS

Model Development

The chemical emissions from a wet material such as a painted wall can be described using a one-dimensional diffusion equation. Since the diffusion coefficient is dependent on the concentration, the governing equation is:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial C}{\partial x} \right) \quad (1)$$

* Corresponding author. E-mail: doyun.won@nrc-cnrc.gc.ca

where C is the concentration of a chemical in the specimen (mg/m^3), x is the distance upwards from the substrate, t is the time and D is the diffusion coefficient of a chemical in the specimen (m^2/s). During a short time period, it is assumed that the concentration of a chemical is relatively constant and, therefore, the diffusion coefficient in Eqn (1) is constant.

The following initial and boundary conditions are used to solve Eqn (1):

$$C = C_0 \quad \text{at } t = 0 \quad (2)$$

$$\frac{\partial C}{\partial x} = 0 \quad \text{at } x = 0 \quad (3)$$

$$-D \frac{\partial C}{\partial x} = \alpha (C^* - C) \quad \text{at } x = l \quad (4)$$

where C_0 is the initial concentration of a chemical in the coating (mg/m^3); C^* is the concentration that would be in equilibrium with the vapour pressure in the atmosphere remote from the surface (mg/m^3); α is the evaporation coefficient (m/h); and l is the coating thickness (m) (Crank, 1983). The initial boundary condition can be obtained independently. The first boundary condition indicates that there is no mass flow at the bottom of the system, while the second boundary condition is from the assumption that the mass flux by diffusion is equal to the mass flux by evaporation at the surface.

Solving Eqn (1) using the Laplace transform for the above initial and boundary conditions can lead to Eqn (5):

$$\frac{C - C_0}{C^* - C_0} = 1 - \sum_{n=1}^{\infty} \frac{2L \exp\left(-\beta_n^2 Dt / l^2\right) \cos\left(\beta_n x / l\right)}{(\beta_n^2 + L^2 + L) \cos(\beta_n)} \quad (5)$$

where β_n are positive roots of $\beta \tan \beta = L$ and $L = l\alpha / D$.

Based on Eqn (5), the total amount of a chemical left the system at time t (M_t) is:

$$\frac{M_t}{M_{\infty}} = 1 - \sum_{n=1}^{\infty} \frac{2L^2}{\beta_n^2 (\beta_n^2 + L^2 + L)} \exp\left(-\beta_n^2 Dt / l^2\right) \quad (6)$$

For a large t , the first term of the infinite series in Eqn (6) is important and, therefore, Eqn (6) becomes:

$$\ln\left(1 - \frac{M_t}{M_{\infty}}\right) = \ln\left[\frac{2L^2}{\beta_1^2 (\beta_1^2 + L^2 + L)}\right] - \frac{\beta_1^2 D}{l^2} t \quad (7)$$

where M_{∞} is M_t for an infinite t , which is the product of A , l and C_0 ; and A is the area of the coating (m^2). Plotting the logarithmic term on the left-hand side of Eqn (7) versus time can lead to the diffusion coefficient using the following equation:

$$D = -\frac{S l^2}{\beta_1^2} \quad (8)$$

where S is the slope estimated from the $\ln(1 - M/M_{\infty})$ profile.

To calculate D from Eqn (8), α and β_1 need to be determined first. The evaporation coefficient (α) can be described by Eqn (9) for the case where the surrounding air concentration is low, i.e., C^* is close to zero. In a chamber experiment, this condition can be satisfied right after a specimen is introduced into the chamber.

$$ER_0 = -\alpha C_0 A \quad (9)$$

where ER_0 is the initial emission rate (g/h). Therefore, β_1 can be calculated from Eqn (10) by manipulating Eqn (8) and $\beta_1 \tan \beta_1 = L$ and $L = l\alpha / D$.

$$\frac{\tan \beta_1}{\beta_1} = -\frac{\alpha}{S l} \quad (10)$$

A tool such as Solver in Excel can be used to solve Eqn (10).

Experiments

Oil-based paint purchased at a local outlet store was spiked with six aliphatic hydrocarbons (heptane, octane, nonane, decane, undecane, and dodecane) and one aromatic hydrocarbon (toluene). Adding chemicals was intended to include more diverse chemicals in addition to the original chemicals, which are mostly branched alkanes with 8–12 carbons. A Petri dish containing 2.3 g of the paint mixture was introduced into a 400 l stainless chamber operated with a flow rate of 3.33 l/min, 50% relative humidity and 23°C.

The chamber consists of an outer and inner chamber for a better control of airflow pattern over the paint specimen. An electronic balance was used to monitor the weight loss of the paint sample. The weight loss data were converted into TVOC concentrations (TVOC_{balance}). The advantage of electronic balance is that it can provide almost continuous data. For individual VOCs, discrete air samples were taken on sorbent tubes at the exhaust of the chamber. The sampled tubes were analysed with a thermal desorber and GC/MS. Integrating all peaks of a chromatograph and quantifying them against the toluene response led to another TVOC value (TVOC_{GC/MS}). The concentration of TVOC_{balance} ($C_{a,t}$) was estimated from the weight loss data (W_t) using the following equation:

$$C_{a,t} = C_{a,t-1} - \Delta t \frac{Q}{V} C_{a,t-1} + \frac{1}{V} (W_{t-1} - W_t) \quad (11)$$

where Q is the chamber flow rate (m³/h) and V is the chamber volume (m³). The total mass emitted during time t (M_t) for individual VOCs was estimated based on the measured chamber concentration, using the following equation:

$$M_t = V C_{a,t} + \frac{1}{2} \sum_{i=1}^n Q (C_{a,t} + C_{a,t-1}) \Delta t \quad (12)$$

The term M_∞ was estimated based on the initial concentration of a chemical in the coating, which was independently measured from the chamber experiment. A volume of 1 µl of paint mixture was injected into the glass wool blocking a sorbent tube. Clean air was then drawn through the sorbent tube at a flow rate of 100 ml/min for 2 min. The sorbent tube was analysed with the same method for the chamber air analysis. The initial emission rate (ER_0) was estimated using the first data point of M .

$$ER_0 = \frac{M_1}{t_1} \quad (13)$$

The coating thickness, l , was estimated as 640 µm based on the area of the Petri dish and the amount of paint used.

RESULTS

Figure 1 shows the chamber air concentrations of TVOC, six aliphatic carbons mentioned previously, and six aromatic hydrocarbons (toluene, ethyl benzene, 1,2-dimethylbenzene,

1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, and 1,2,4,5-tetramethylbenzene). Individual VOC levels were smoothed by taking averages of adjacent three data points. A good agreement between $\text{TVOC}_{\text{balance}}$ and $\text{TVOC}_{\text{GC/MS}}$ proves the validity of converting the weight data to the concentration data and vice versa.

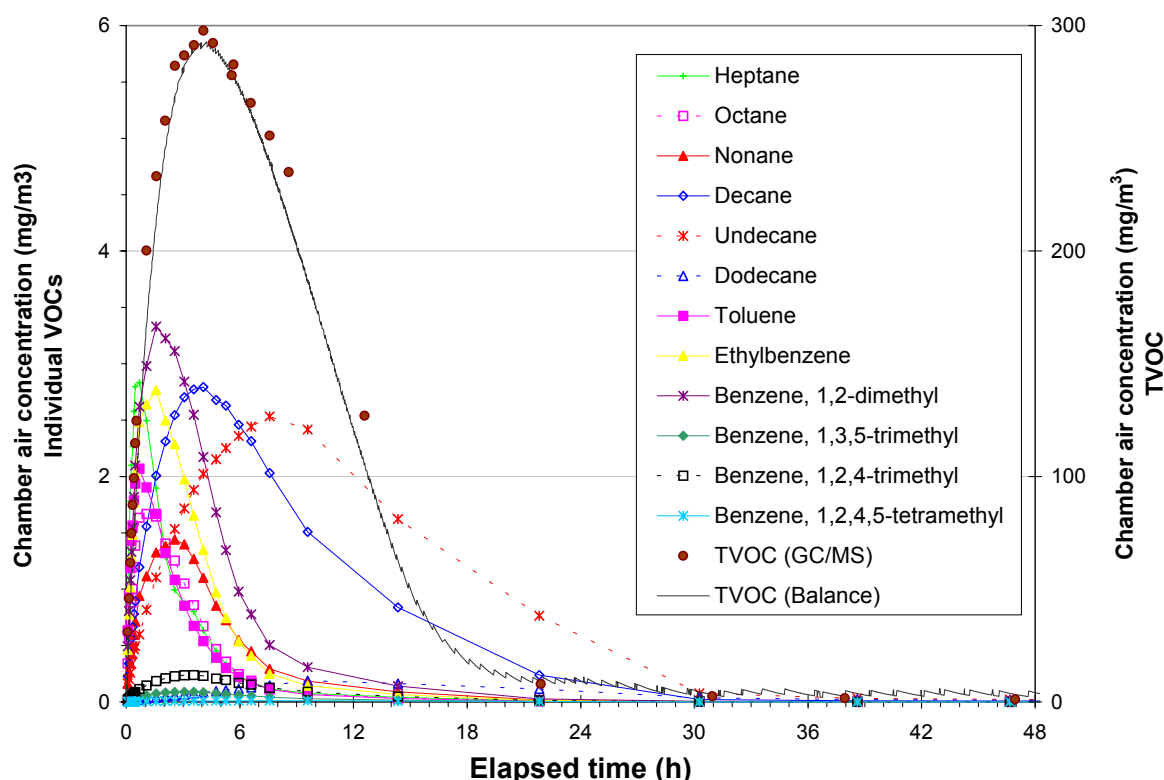


Figure 1 Chamber air concentration for TVOC and selected VOCs.

Figure 2 shows the normalized total mass emitted during time t (M/M_∞) and the emission rate for TVOC. The results suggest that the profile can be divided into four regions probably based on the mass-transfer mechanism, starting from an evaporation-controlled region (<0.2 h) characterized by a very fast decay rate, followed by a transition region ($0.2 < t < 2$ h), a diffusion-controlled region ($2 < t < 16$ h) with a slow decay rate and a negligible mass-transfer region ($t > 16$ h). The observed duration of the evaporation-controlled region is in good agreement with that from a numerical simulation (Yang *et al.*, 2001). Based on the data within the diffusion-dominated region, the slopes of the $\ln(1 - M/M_\infty)$ profiles were calculated for TVOC and individual VOCs. Also, the values of α and β_1 were calculated from Eqns (9) and (10). These results were then used to calculate the diffusion coefficients from Eqn (8). Table 1 summarizes the calculation results.

An attempt was made to relate two model coefficients with chemical properties. As shown in Figure 3, diffusion coefficients tend to be inversely proportional to molecular weight, while evaporation coefficients appear to be proportional to vapour pressure. A linear model was adopted to relate diffusion coefficient with molecular weight and a hyperbola model was chosen for evaporation coefficient and vapour pressure. The R^2 values indicate that there is a strong relationship, in particular, between evaporation coefficient and vapour pressure.

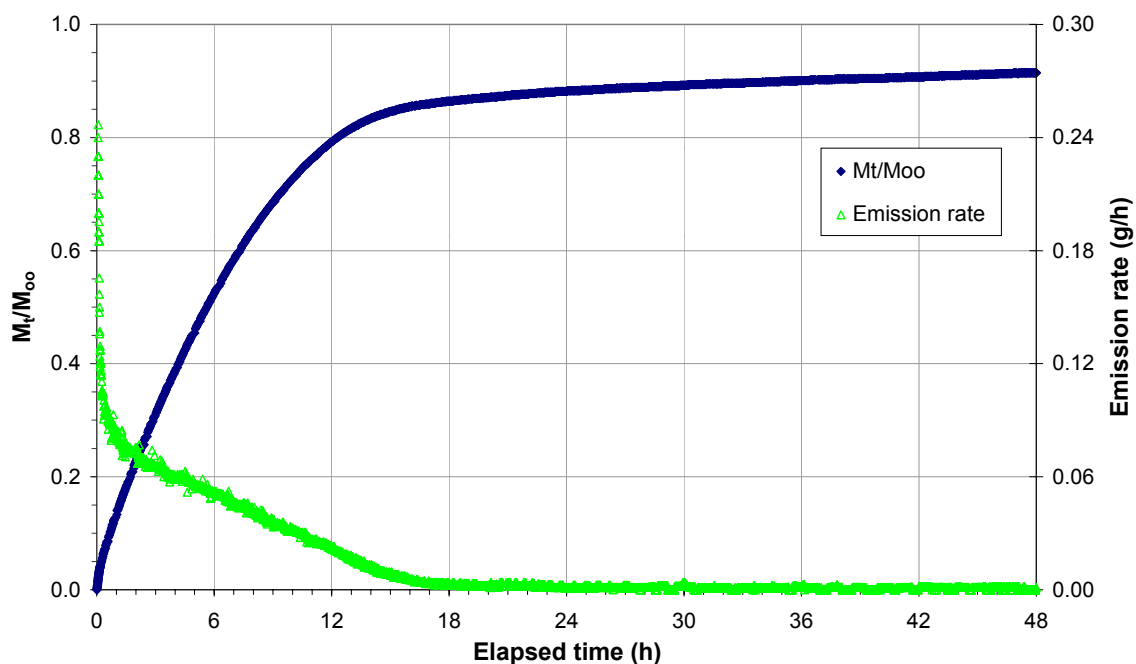


Figure 2 The normalized total mass emitted (M/M_{∞}) and the emission rate of TVOC.

Table 1 Result of plotting $\ln(1-M/M_{\infty})$ versus time t , evaporation, and diffusion coefficients.

	Molecular weight	Vapor Pressure (mmHg)	Slope	Intercept	R^2	α (m/h)	D (m^2/s)
Heptane	100.20	46.00	-0.327	-0.054	0.979	1.39E-03	1.47E-11
Octane	114.20	14.10	-0.294	-0.085	0.997	1.10E-03	1.34E-11
Nonane	128.30	4.45	-0.195	-0.088	0.984	5.07E-04	9.59E-12
Decane	142.29	1.43	-0.129	-0.004	1.000	2.45E-04	7.01E-12
Undecane	156.31	0.41	-0.061	-0.004	0.977	7.43E-05	4.29E-12
Dodecane	170.34	0.14	-0.011	-0.046	0.960	1.40E-05	7.86E-13
Toluene	92.10	28.40	-0.576	-0.135	0.990	2.50E-03	2.58E-11
Ethylbenzene	106.20	9.60	-0.306	-0.097	0.994	1.23E-03	1.38E-11
12-DMB	106.20	6.77	-0.296	-0.103	0.993	9.08E-04	1.40E-11
135-TMB	120.20	2.48	-0.142	-0.036	0.993	3.74E-04	6.96E-12
124-TMB	120.20	2.10	-0.147	0.022	1.000	3.94E-04	7.18E-12
1245-TMB	134.22	0.53	-0.028	-0.170	0.960	1.62E-04	1.20E-12
TVOC			-0.0678	-0.0202	1.000	1.86E-04	3.29E-12

12-DMB = 1,2-dimethylbenzene, 135-TMB = 1,3,5-trimethylbenzene, 124-TMB = 1,2,4-trimethylbenzene, 1245-TMB = 1,2,4,5-tetramethylbenzene.

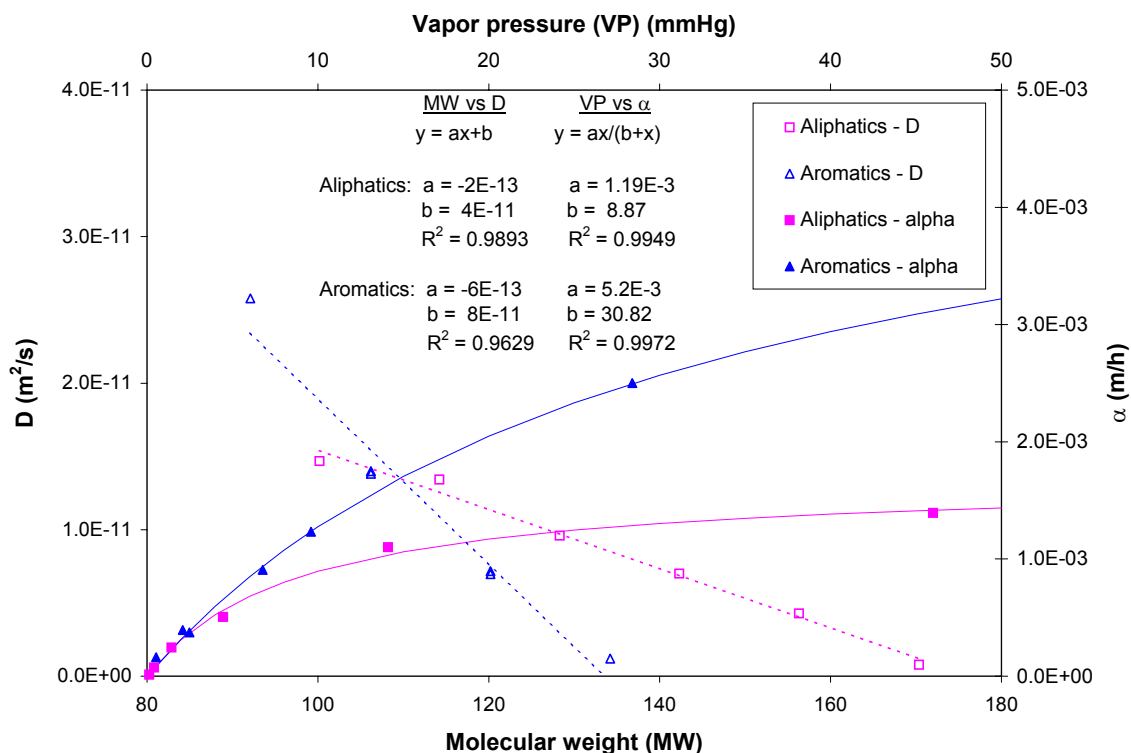


Figure 3 Relationship between coefficients and chemical properties.

CONCLUSIONS

A mass-transfer model with evaporation and diffusion coefficient was developed to describe VOC emissions from architectural coatings. A chamber experiment was used to determine the coefficients for six aliphatic and six aromatic hydrocarbons from oil-based paint. Diffusion coefficient was found to be inversely proportional to molecular weight, while evaporation coefficient was proportional to vapour pressure. The strong correlation between model coefficients and chemical properties suggests that the mass-transfer model may be used to describe emissions for more compounds without costly experiments. Further research is required to validate the suggestion.

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