



Transient evaporation of multicomponent liquid mixtures of organic volatiles through a covering porous layer

Francesco Gioia^{*}, Fabio Murena, Antonio Santoro

Dipartimento di Ingegneria Chimica, Università di Napoli Federico II, Piazzale Tecchio, 80125 Napoli, Italy

Received 27 February 1997; accepted 22 September 1997

Abstract

The release into the atmosphere of volatile organic components, evaporating from a multicomponent liquid mixture covered by a porous layer, is studied theoretically and experimentally. The modelling has been developed on the basis of fundamental principles and the most appropriate approximations have been suggested by the physics of the problem. The results of the investigation indicate that in most cases, neglecting the bulk flow induced by diffusion in the Fick's equation is a good approximation. Moreover, a criterion is established which may even quantify the accuracy of this approximation. On the contrary, it is shown that the change in the liquid composition during the evaporation plays a predominant role on the predictive capability of the

Abbreviations: *Parameters*: c , total molar concentration in gas phase, $c = P / \mathfrak{R}T$ (mol cm⁻³); c_i , gas-phase molar concentration of component i (mol cm⁻³); D_{ia} , gas-phase effective diffusivity of i in air in the bed (cm² s⁻¹); \mathcal{D}_{ia} , gas-phase free diffusivity of component i in air (cm² s⁻¹); H , bed height (cm); k_i , see Eq. (22) (mol s⁻¹); L , moles of liquid at any t (mol); m , mass of liquid at any t (g); M_i , molecular weight of compound (g); N_i , molar flux relative to stationary coordinates [mol (cm² s⁻¹)]; P , pressure (bar); Pe_i^o , Peclet number evaluated at $t = 0$ (see Eq. (12)); \overline{Pe} , Peclet number as calculated by means of Eq. (33); p_i^* , vapor pressure (mm Hg in Table 2, bar in equations); \mathfrak{R} , gas constant; $\mathfrak{R} = 83.14$ [(bar cm³) (mol K)⁻¹]; S , cross-sectional area of the bed (cm²); T , temperature (K); T_m , average temperature during the experimental run (°C); t , time (s, min in figures); V , volume of the bed (cm³); V_p , volume of the particles loaded in the apparatus (cm³); v^* , molar average velocity (see Eq. (6)) (cm s⁻¹); W_p , weight of particles of the bed (g); x_i , liquid-phase mole fraction; y_i , gas-phase mole fraction; z , distance in the vertical direction (cm); ∇ , nabla operator (cm⁻¹); *Greek symbols*: γ_i , activity coefficient; θ , free cross-section fraction of the bed; ε , intraparticle porosity in the bed; τ , H/v , dimensionless time; ν , characteristic molar velocity, $\nu = v^*|_{t=0}$ (cm s⁻¹); ρ_b , bulk density of rock tuff (g cm⁻³); ζ , z/H , dimensionless distance in the vertical direction; *Subscripts*: i , any compound of the liquid mixture; a, air; 1, 2, 3, 4, 5, 6, acetone, hexane, heptane, octane, nonane, and decane, respectively; *Superscripts*: o, at $t = 0$; ~, dimensionless variables

^{*} Corresponding author. Tel.: +39 81 7682277; fax: +39 81 2391800; e-mail: gioia@ds.unina.it

model. Finally, the reliability of the physical parameters reported in the literature for an accurate modelling of the process is assessed. Experiments have been conducted with an arrangement of particles of a porous rock tuff in a packed bed geometry covering a liquid mixture of volatile components. The experimental investigation has been extended to liquid mixtures of up to four components which have vapor pressures falling into a two order of magnitude range of values. The effect of the non-ideality of the liquid mixture is investigated, too. The theoretical model, very simple indeed, represents the experimental data with good accuracy, and is a reliable tool for accurately predicting the time required for the complete release of the volatiles and emission fluxes into the atmosphere. © 1998 Elsevier Science B.V.

Keywords: Volatile organic compounds; Porous material; Evaporation

1. Introduction

The release of volatiles into the atmosphere across porous materials is a subject of interest in environmental engineering. In a previous paper, Gioia et al. [1] have investigated the role of natural convection on the emissions from a bed of porous particles saturated with volatile organic compounds. In the present paper the emission of volatiles, resulting from the evaporation of multicomponent liquid mixtures covered by a layer of porous material, is studied theoretically and experimentally. This subject has been frequently dealt with in the literature. Recently a model for the multiphase multicomponent transport in porous media has been presented by Wang and Cheng [2]. It is a complex model not immediate or simple to use. We aim at a more direct and simple approach to the specific mass transfer problem dealt with in this paper. This approach has been frequently followed by previous authors [3–6], but under a number of simplifying hypotheses. In fact, in some cases the bulk flow induced by diffusion is neglected. In others the change of the liquid composition during the evaporation process is considered, but in an approximate manner.

The specific problem dealt with in the present paper is of interest in itself or as a part of a more complex emission problem. However, the main purpose of the paper is to demonstrate that a good knowledge of the basic physical phenomena involved and the use of the general results and methods of transport phenomena permit a very accurate modelling of the emission problem, without the need to resort to strong simplifying assumptions. The most appropriate simplifications are directly suggested by the physics of the problem. It will be proved that neglecting the bulk flow induced by diffusion does not significantly influence the release model. In particular it is possible to calculate beforehand an indicator (the Peclet number) which can effectively monitor the importance of this flow on the overall diffusion process. On the contrary, the change of the composition in the liquid phase during the evaporation must be properly accounted for, inasmuch as it plays a fundamental role in the predictive capability of the release model. Finally, it will be shown that among the few parameters to be estimated for making use of the model, the most critical ones are the activity coefficients which cannot be estimated with the same degree of accuracy as the others (i.e. diffusivities, vapour pressures, etc.).

2. Theory

We describe the covering layer as a bed of unconsolidated particles and use a one-dimensional model that accounts only for vertical variation in the variables. We set the z -axis along the bed (perpendicular to the top and bottom face of the bed), with the origin at the bottom. The top of the bed is at $z = H$. Below the bed there is a liquid mixture which evaporates.

2.1. Mass balance on the liquid mixture

Let $L(t)$ be the moles of liquid present at any time in the system, then for a mixture of n components the mass balance equations are:

$$\frac{dL}{dt} = -S \sum_{i=1}^n N_i|_{z=0} \quad (1)$$

$$\frac{dLx_i}{dt} = -SN_i|_{z=0} \quad (i = 1, \dots, n) \quad (2)$$

Substituting Eq. (1) into Eq. (2) we obtain:

$$\frac{dx_i}{dt} = \frac{x_i S \sum_{j=1}^n N_j|_{z=0}}{L} - \frac{SN_i|_{z=0}}{L} \quad (3)$$

in which S is the total cross-sectional area of the bed and N_i is the flux through the free cross-section of the porous bed.

2.2. Diffusion in the gas phase

For a n -component ideal-gas mixture (low-density gases) the constitutive equations for the molar fluxes are given by the Stefan–Maxwell equations [7]. For systems in which the n components are diffusing through a porous medium and are diluted in air which is stagnant, the molar flux relative to stationary coordinates of any component i through the free cross-section of the porous bed may be approximated by the following equation, which is a form of Fick's law of diffusion:

$$N_i = -\frac{c\theta\mathcal{D}_{ia}}{q} \nabla y_i + y_i \sum_{i=1}^n N_i; \quad i = 1, 2, \dots, n \quad (4)$$

We will briefly name Eq. (4) as Fick's equation. The last term of Eq. (4) is the flux resulting from the bulk flow induced by diffusion. \mathcal{D}_{ia} is the free diffusivity of i in air, θ is the free cross-section fraction of the porous bed, and q is the tortuosity factor. Correspondingly, with the further assumption of constant temperature and pressure ($c = \text{constant}$) and constant \mathcal{D}_{ia} , the local mass balance on the gas phase is:

$$\varepsilon \frac{\partial c_i}{\partial t} + (v^* \cdot \nabla c_i) = \frac{\theta\mathcal{D}_{ia}}{q} \nabla^2 c_i \quad (5)$$

in which ε is the porosity of the porous bed. The local molar average velocity v^* (bulk flow velocity) is defined as:

$$v^* = \frac{\sum_{i=1}^n N_i}{c} \quad (6)$$

In writing Eq. (5) it has been considered that for a fluid of constant molar density c (in absence of reactions), it is:

$$\nabla \cdot v^* = 0 \quad (7)$$

i.e. v^* does not depend on the space coordinates.

It is useful to make a dimensional analysis of Eq. (5). We select as characteristic length the diffusion distance H and as characteristic molar velocity $\nu = v^*|_{t=0}$. Then the characteristic time is $\tau = H/\nu$. The dimensionless form of Eq. (5) is:

$$\varepsilon \frac{\partial y_i}{\partial \tilde{t}} + \frac{\nu \tau}{H} (\tilde{v}^* \cdot \nabla y_i) = \frac{\tau D_{ia}}{H^2} \tilde{\nabla}^2 y_i \quad (8)$$

in which D_{ia} is the effective diffusivity in air:

$$D_{ia} = \frac{\theta \mathcal{D}_{ia}}{q} \quad (9)$$

The following dimensionless variables have been introduced in Eq. (8):

$$\tilde{v}^* = v^*/\nu; \tilde{t} = t/\tau; \tilde{\nabla} = H\nabla \quad (10)$$

It is:

$$\frac{\nu \tau}{H} = 1 \quad (11)$$

and

$$\frac{\tau D_{ia}}{H^2} = \frac{D_{ia}}{H\nu} = \frac{1}{\text{Pe}_i^0} \quad (12)$$

Pe_i^0 is the Peclet number evaluated at $t = 0$. Finally Eq. (8) may be written as:

$$\varepsilon \frac{\partial y_i}{\partial \tilde{t}} + (\tilde{v}^* \cdot \tilde{\nabla} y_i) = \frac{1}{\text{Pe}_i^0} \tilde{\nabla}^2 y_i \quad (13)$$

The Peclet number is the indicator of the importance of the convective flux on the diffusion process. For the case at hand it cannot be $\text{Pe}_i^0 \gg 1$ because the molar average velocity v^* is induced by the diffusion process. If it were $\text{Pe}_i^0 \gg 1$ the diffusion term in Eq. (13) would become negligible and the equation itself would lose meaning. Therefore it must be $\text{Pe}_i^0 \leq 1$.

The overall release problem is described by the solution of the set of coupled differential equations (Eq. (1), Eqs. (3)–(6)). In order to reduce the mathematical complexity of the problem, we assume that the quasi-steady-state condition [8] holds true for the gas-phase profiles. In fact, the characteristic diffusion time in the bed:

$$t_c = \frac{H^2}{16D_{ia}} \quad (14)$$

is of the order of two minutes which is much smaller than the time for a significant composition change in the liquid phase. With this assumption Eq. (13) reduces to:

$$(\tilde{v}^* \cdot \tilde{\nabla} y_i) = \frac{1}{Pe_i^0} \tilde{\nabla}^2 y_i \tag{15}$$

and it is:

$$\nabla \cdot N_i = 0 \tag{16}$$

At this stage we will examine the difference obtained in the solution to the mass transfer problem by neglecting, or not, the bulk flow term in the constitutive Eq. (4); i.e. by using the incomplete vs. the complete Fick’s Eq. (4).

2.3. Incomplete Fick’s equation

We neglect the bulk flow term in Eq. (4) that is equivalent to set $\tilde{v}^* \cdot \tilde{\nabla} y_i = 0$ in Eq. (15). Therefore, the concentration in the bed of any compound varies linearly in the z direction. We assume that the air at the top of the bed is free of component i . Thus, the evaporation flux of i is:

$$N_i(t)|_{z=0} = cD_{ia} \frac{y_i|_{z=0}}{H} = \frac{PD_{ia}}{\mathfrak{RT}} \frac{y_i|_{z=0}}{H} \tag{17}$$

Assuming that $z = 0$ coincides with the liquid–gas interface and that equilibrium exists at this interface, it is:

$$y_i|_{z=0} = \frac{p_i^v \gamma_i x_i}{P} \tag{18}$$

which may be substituted into Eq. (17) to obtain:

$$N_i(t)|_{z=0} = \frac{D_{ia}}{\mathfrak{RT}} \frac{p_i^v \gamma_i x_i}{H} \tag{19}$$

in which γ_i is the activity coefficient, which is a function of the pressure, temperature, and composition of the liquid phase. Substituting Eq. (19) into Eqs. (1) and (3) we obtain:

$$\frac{dL}{dt} = \sum_{i=1}^{n-1} (k_n - k_i) x_i - k_n \tag{20}$$

$$\frac{dx_i}{dt} = - \frac{x_i \left[\left(\sum_{i=1}^{n-1} (k_n - k_i) x_i \right) + k_i - k_n \right]}{L} \tag{21}$$

where it is:

$$k_i = \frac{SD_{ia}}{\mathfrak{RT}} \frac{p_i^v \gamma_i x_i}{H} \tag{22}$$

The solution to the diffusion problem for ideal mixtures ($\gamma_i = 1$) is obtained by numerically solving the set of coupled equations (Eqs. (20)–(22)) to obtain L and x_i vs. t . Then (recalling Eq. (16)) the flux released to the atmosphere of any component i may be calculated vs. t by means of Eq. (19). The procedure is somewhat more involved

when the mixture is not ideal, because the above equations must be coupled with the equations $\gamma_i = \gamma_i(T, P, x_1, \dots, x_n)$.

2.4. Complete Fick's equation

In this case, for the geometry under consideration, Eq. (15) may be written as:

$$\tilde{v}^* \frac{dy_i}{d\zeta} = \frac{1}{Pe_i^0} \frac{d^2 y_i}{d\zeta^2} \quad (23)$$

Recalling Eq. (7) that v^* does not depend on z , Eq. (23) may be integrated with the boundary conditions:

$$\zeta = 0; y_i = \frac{p_i^v \gamma_i x_i}{P} \quad (24)$$

$$\zeta = 1; y_i = 0 \quad (25)$$

to obtain:

$$y_i(\zeta, t) = \frac{p_i^v \gamma_i x_i}{P} \left(\frac{e^{\tilde{v}^* Pe_i^0 \zeta} - e^{\tilde{v}^* Pe_i^0}}{1 - e^{\tilde{v}^* Pe_i^0}} \right) \quad (26)$$

Then, the evaporation flux of compound i is given by:

$$N_i(t)|_{z=0} = -cD_{ia} \left. \frac{dy_i}{dz} \right|_{z=0} + cv^* y_i|_{z=0} \quad (27)$$

Introducing Eqs. (24) and (26) into Eq. (27) we finally obtain:

$$N_i(t)|_{z=0} = \frac{D_{ia}}{\Re T} \frac{p_i^v \gamma_i x_i}{H} \left(\frac{\tilde{v}^* Pe_i^0 e^{\tilde{v}^* Pe_i^0}}{e^{\tilde{v}^* Pe_i^0} - 1} \right) \quad (28)$$

Eq. (28), due to Eq. (16), gives the flux of any compound i even at any other z ($0 < z < H$). The solution of the set of differential equations (Eqs. (1), (3) and (28)) is more involved than for the previous case of incomplete Fick's equation. In fact, Eq. (28) is implicit in the sum of fluxes through v^* . We have solved the system of equations (Eqs. (1), (3) and (28)) by trial and error, assigning a first trial flux as:

$$N'_i = \frac{PD_{ia}}{H \Re T} \ln \left(\frac{1}{1 - \frac{p_i^v \gamma_i x_i}{P}} \right) \quad (29)$$

which, according to Eq. (28), is the flux of i if it were diffusing alone in stagnant air.

3. Experimental section

3.1. Apparatus and materials

A sketch of the assembly of the experimental apparatus is given in Fig. 1. The lowest part is a glass cylindrical flat bottom vessel (9.3 cm inside diameter and 5 cm height) with a flat flange joint welded at the top. A small glass tube with screw cap and inlet rubber septum, is welded on the side of the vessel and used for loading the liquid by syringe at the beginning of the run. The same port is used for sampling the liquid during

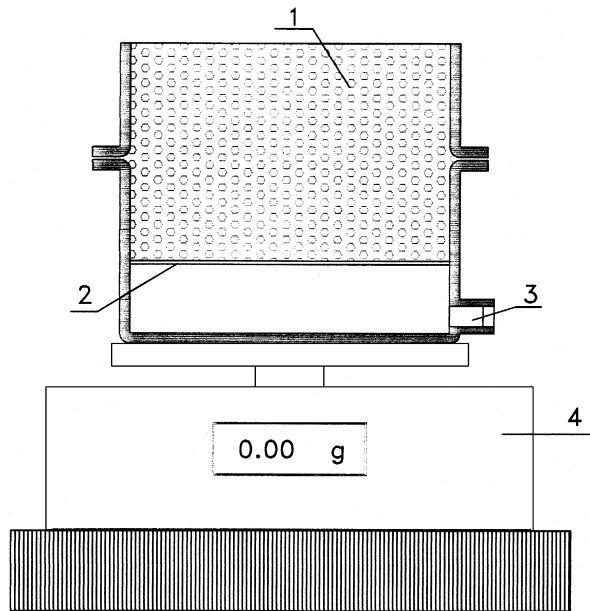


Fig. 1. Sketch of assembly of the experimental apparatus. 1: porous layer; 2: supporting net; 3: syringe loading/sampling port; 4: balance.

the run. In the bottom vessel, a removable stainless steel net for supporting the bed of particles is located 3 cm from the base. The upper part is a glass cylindrical column (inside diameter as that of the vessel) fitted with a flat flange to join it to the bottom vessel. A number of cylinders of different lengths were available for making runs with different bed heights. After a few preliminary runs the most convenient bed height was found to be 5.5 cm. Correspondingly, the length of the upper cylinder was such that the top of the bed was level with the upper border of the cylinder. The amount of liquid loaded in the bottom vessel was such that the thickness of the liquid layer was kept down to between 1 and 2 mm in order to minimize the importance of the concentration profiles which could generate themselves in the liquid phase. A gap of about 3 cm existed between the free surface of the liquid and the bottom of the bed of particles, thus preventing the liquid wetting the particles and impregnating the bed by capillarity. The gas phase concentration gradients in the free space of the gap may be calculated to be about one order of magnitude smaller than those in the bed. Therefore, Eq. (18) is an approximation, even though reasonable. The porous material utilized in all experiments is a natural rock (yellow tuff) whose internal structure characteristics are described in Ref. [9]. This material was ground and sieved to create 1–2 mm size particles. Operating conditions selected for the experimental runs are reported in Table 1.

3.2. Experimental procedure

The bottom vessel, the net and the upper cylinder were assembled, set on a two decimal digit balance and put in a hood. The particles were loaded in the apparatus and

Table 1

Operating conditions for the various runs. $H = 5.5$ cm for all runs. Particle size ranging between 1–2 mm

Run	Operating parameters			Initial mole fractions in the liquid ^a					
	T_m (°C)	ε	m^0 (g)	x_1^0	x_2^0	x_3^0	x_4^0	x_5^0	x_6^0
1	26	0.35	26.85	1	–	–	–	–	–
2	27	0.31	7.02	–	0.498	–	0.502	–	–
3	23	0.30	4.23	–	0.396	0.314	0.290	–	–
4	22	0.31	5.57	–	0.564	0.291	–	0.074	0.071
5	17	0.28	6.39	0.856	0.144	–	–	–	–
6	17	0.29	7.63	–	0.841	–	0.159	–	–

^aFor subscripts see abbreviations.

their weight (W_p) recorded. The bulk density of yellow tuff ρ_b is equal to 1.09 g cm^{-3} . Therefore the volume of the dry particles loaded in the apparatus is $V_p = W_p/\rho_p$. The voidage of the bed (see Table 1) was evaluated using the following relationship:

$$\varepsilon = 1 - \frac{V_p}{V} \quad (30)$$

in which V is the volume of the bed. The liquid was loaded in the bottom vessel by means of a 10-ml syringe, the hood was closed and the fan turned off in order to carry out the experiments in still air. From this moment the weight of the apparatus was recorded and liquid samples were withdrawn (every 15 min during the first hour; then every 30 min) by means of a $1 \mu\text{l}$ syringe and analysed by gas chromatography. Frequently the apparatus was gently shaken in order to break possible concentration gradients in the liquid phase. A continuous stirring was not applicable because it would have warmed up the liquid. On the other hand the Biot number calculated at the liquid–gas interface warned of the possibility that concentration gradients could build up in the liquid phase. Temperature variations in the hood during each run were less than 2°C . Inclusion of this temperature change in the model did not have any effect on the results. Therefore the runs were considered isothermal at the average temperature T_m (see Table 1). Further details on the apparatus and on the experimental procedure may be found in the thesis by Santoro [10].

The direct results obtained from the experimental apparatus are data points of mass of the remaining liquid (m) and molar fractions (x_i) in the liquid phase, vs. time (see Figs. 2 and 3). The relationship between m and L is:

$$m(t) = \sum_{i=1}^n [L(t) x_i M_i] \quad (31)$$

3.3. Interpretation of experimental results

In order to compare the experimental results with the model equations, it is necessary to know the numeric values of a few more parameters. They are:

- free diffusivity of the diffusing chemical in air
- vapor pressures
- activity coefficients
- tortuosity factor

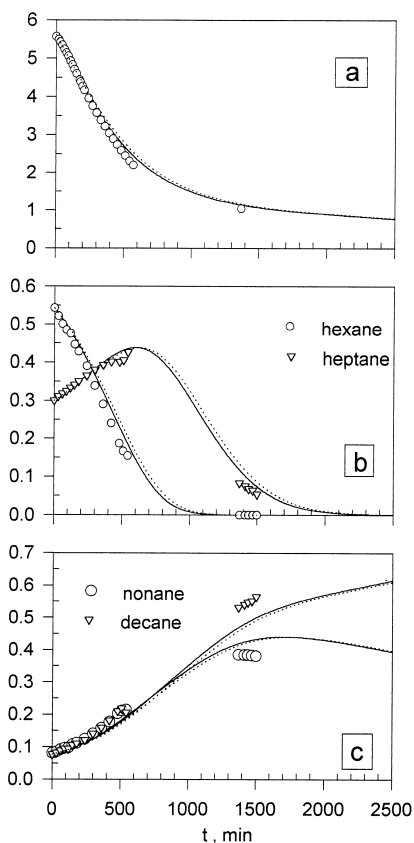


Fig. 2. Experimental results and model prediction for the evaporation of the liquid mixture of hexane, heptane, nonane, and decane. (a) mass of liquid in the system as function of time; (b) mole fractions of hexane and heptane vs. time; (c) mole fractions of nonane and decane vs. time. Curves: solid = model with complete Fick's equation; dotted = model with incomplete Fick's equation.

For evaluating the free diffusivity we used the correlation proposed by Fuller which is reported in p. 587 of Ref. [11]. The calculated values were compared with the few available experimental data reported in the literature (pp. 3–256 of Ref. [12]). The comparison showed that the correlation by Fuller has a difference with experimental data of about $\pm 10\%$. Vapor pressures were obtained from pp. 3–47 of Ref. [12]. The method used for evaluating the activity coefficients will be indicated when run 5 (non-ideal mixture) is discussed.

The values of the diffusivities and of the vapor pressures, for the runs discussed in this paper, estimated at the average temperature of the run, are reported in Table 2. For the other runs of Table 1, see the thesis by Santoro [10].

The most questionable parameter to be determined is the tortuosity. Specific instruments to measure it are not available. Inspection of the many experimental values which have accumulated in the literature [13] shows that the tortuosity of porous catalysts ranges between 0.4 and 7. Therefore, the only possibility of obtaining a closer estimate

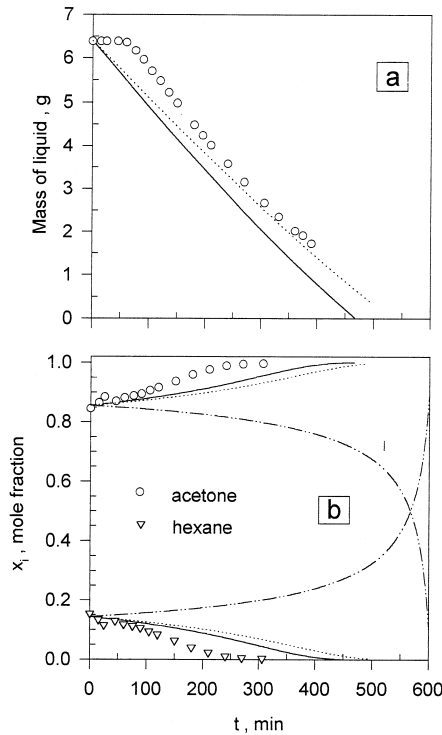


Fig. 3. Experimental results and model prediction for the evaporation of the non-ideal liquid mixture of acetone and hexane. (a) mass of liquid in the system as function of time; (b) mole fractions of acetone and hexane vs. time. Curves: solid = model with complete Fick's equation; dotted = model with incomplete Fick's equation; dashed-dotted = model neglecting the non-ideality of the mixture.

of q is to perform diffusion experiments directly on the porous solid of interest and evaluating the tortuosity as an adjustable parameter. In order to achieve the determination of q , run 1 was carried out. Pure acetone was evaporated through the porous bed. The mass m of acetone remaining in the vessel was recorded vs. time and the evaporation flux of acetone was calculated. After an initial transient, a steady-state was reached. The steady-state flux data points were regressed by means of the equation:

$$N_1 = \frac{c\theta\mathcal{D}_{1a}}{qH} \ln\left(\frac{1 - y_1|_{z=H}}{1 - y_1|_{z=0}}\right) \tag{32}$$

in which $y_1|_{z=H} = 0$, $y_1|_{z=0} = p_1^y/P$, and θ is the free cross-section fraction of the porous bed. In Eq. (32), the only unknown is the adjustable parameter θ/q . We determined $\theta/q = 0.37$. Then assuming that the free cross-section θ is identical with the volume fraction voids $\varepsilon = 0.35$ (evaluated by means of Eq. (30)) we obtained $q = 0.93$. This result indicates either that for the relatively large particle size we have used, the tortuosity of the diffusion paths is negligible or that the surface porosity is somewhat larger than the volume porosity. As a matter of fact it is reported in Ref. [13] that, for unconsolidated particles, q is roughly 1.5 to 2.0.

Table 2
Physical parameters for the runs discussed in this paper^a

Run	Effective diffusivities ^b (cm ² s ⁻¹)					Vapor pressures ^b (mm Hg)					\overline{Pe}	t_f^c (min)
	D_{1a}	D_{2a}	D_{3a}	D_{5a}	D_{6a}	p_1^v	p_2^v	p_3^v	p_5^v	p_6^v		
4	–	2.33×10^{-2}	2.15×10^{-2}	1.88×10^{-2}	1.77×10^{-2}	–	132.4	39.38	3.96	1.44	0.06	6500
5	2.82×10^{-2}	2.04×10^{-2}	–	–	–	154.99	105.69	–	–	–	0.22	470

^aFor the other runs see Santoro [10].

^bAt the average temperature T_m of the run, reported in Table 1.

^cCalculated time for the complete evaporation of the liquid.

In Table 2 the Peclet number for the various runs is reported. Because we will show that the use of the incomplete Fick's equation is a very good approximation for calculating the fluxes, the Peclet number of Table 2 has been obtained by the simple equation:

$$\overline{\text{Pe}} = \frac{\sum_{i=1}^n p_i^v \gamma_i^o x_i^o D_{ia}}{PD_{\text{av}}} \quad (33)$$

in which D_{av} is the average diffusivity defined as:

$$D_{\text{av}} = \frac{\sum_{i=1}^n D_{ia}}{n} \quad (34)$$

In Figs. 2 and 3 the experimental results of the most representative runs (4, 5) among those of Table 1, consisting of m and x_i vs. t , are reported. The curves are the model prediction. The plots and the interpretation of runs 2, 3, and 6 are given in the thesis by Santoro [10].

3.4. Run 4: Liquid mixture of *n*-hexane, *n*-heptane, *n*-nonane, and *n*-decane

This is an ideal liquid mixture (i.e. $\gamma_i = 1$). The four components have vapor pressures which span over a two order of magnitude range (see Table 2). The calculated times for the complete release of the four components are \approx :1100 min for hexane, 2100 min for heptane, 6200 min for nonane, and 6500 min for decane. The results of this run are represented in Fig. 2. The solid lines refer to the model with complete Fick's equation, the dotted ones are for the incomplete equation. It may be observed that the two curves are almost indistinguishable. Therefore in this case the simpler model (Eqs. (20)–(22)) can be safely used. This result is also suggested by the small value of the Peclet number (0.06, see Table 2). In Fig. 2a the measured mass of liquid vs. time is compared with the theoretical curve. A very good agreement between experimental results and theoretical prediction exists. In Fig. 2b and c the molar fractions in the liquid of the four components are plotted vs. time. Again the agreement between data points and theoretical predictions is quite good. It is of interest to interpret the behaviour of the mole fractions. Hexane, which is the most volatile component, has the highest rate of evaporation. Therefore, at the beginning of the process, even though the other three components are evaporated too, the net effect is that liquid mixture enriches in heptane, nonane and decane. When hexane is almost completely depleted, the heptane mole fraction reaches a maximum and then decreases inasmuch as it is now the most volatile among the three components left. Analogous behaviour is shown by the nonane and decane mole fractions. The important role played by the change of liquid concentration during the evaporation process must be considered: the total flux is 1×10^{-4} [g (cm² min)⁻¹] at $t = 0$ and reduces by one order of magnitude at $t = 1500$ min. Therefore, if we did not account for the change of liquid concentration, the flux at $t = 1500$ min would have been overestimated by one order of magnitude.

3.5. Run 5: Liquid mixture of acetone and hexane

This is a non-ideal liquid mixture. Experimental values of the activity coefficients are not available in the literature. Therefore, they have been calculated by the Wilson equation with parameters determined from the MOSCED correlation proposed by Thomas and Eckert, reported in pp. 291–307 of Ref. [11]. The results for this run are plotted in Fig. 3. The two components are both very volatile, thus the time scale of the evaporation process is smaller than that of the previous run. Therefore a singular behaviour around $t=0$ which was barely observable in run 4 (but was clearly observable, even though to a lesser extent, also in runs 1, 2, and 3) is evident in Fig. 3a. Namely, we observe that the mass of liquid does not change for about 60 min. As a matter of fact, according to the experimental procedure, what actually remains unchanged is the mass of the whole system. Therefore, the liquid which evaporates in the initial minutes is not released into the atmosphere. Our interpretation is that the vapours which are produced at the beginning of the process remain adsorbed on the porous particles until the adsorption capacity of the solid is saturated. An estimate of the specific internal area of rock tuff (based on the data reported in Ref. [9]) is $6 \text{ m}^2 \text{ cm}^{-3}$. On the basis of this value we calculated that the amount of acetone which could be adsorbed in order to form a monolayer on the active surface of the rock (0.18 g) is actually of the same order of magnitude as the mass of vapours not released into the atmosphere at the beginning of the run (0.68 g). Notice that the model does not account for this minor phenomenon. Therefore, the theoretical curve in Fig. 3a is shifted to the left with respect to the experimental data. With this proviso the agreement between data and model is satisfactory, even though not as accurate as for the other runs (ideal mixtures). This is due to the activity coefficients which are difficult to estimate with reasonable accuracy in a large range of concentrations. Notice that the activity coefficients play a fundamental role in the correctness of predictions. In fact, the experimental data show that the first compound to be released is the less volatile hexane ($p^v = 121.11 \text{ mm Hg}$ at 20°C) instead of the most volatile acetone ($p^v = 177.47 \text{ mm Hg}$ at 20°C). If we did not consider the non-ideality of the mixture we would have reached completely wrong predictions which are represented in Fig. 3b by the dashed–dotted curves. Finally, it must be observed that the Peclet number (0.22) is larger than that for run 4. Therefore a larger difference exists between the prediction using the incomplete Fick's equation (dotted lines) and that using the complete one (solid lines). Even in this case, however, neglecting the flux resulting from bulk flow gives a very good approximation.

4. Conclusions

The transient evaporation of liquid mixtures of organic volatiles through a layer of unconsolidated particles can be accurately modelled by using well-established methods and equations which are of current use in chemical engineering. For the diffusion problem examined in this paper it is important to account properly for the change of composition in the liquid phase during the evaporation. If one neglects this phenomenon the calculated rate of emission of the volatiles into the atmosphere can be affected by errors of order of magnitude. Furthermore, it has been proved that neglecting the bulk

flow term in Fick's diffusion law does not affect the calculated fluxes to a significant extent. This considerably simplifies the mathematics for solving the equations which describe the diffusion model. An indicator (the Peclet number) has been defined which can monitor the importance of the bulk flow with respect to diffusion. Furthermore it has been shown that the non-ideality of the liquid mixture must be properly accounted for, otherwise the model predictions can be completely wrong. Among the few parameters to be estimated for making use of the model, the most critical are, for non-ideal mixtures, the activity coefficients which cannot be estimated with the same degree of accuracy as the others (i.e. diffusivities, vapour pressures, etc.).

Acknowledgements

This work was financed by a research grant from 'Ministero dell'Università e della Ricerca Scientifica e Tecnologica'.

References

- [1] F. Gioia, F. Murena, V. Esposito, A theoretical and experimental study of the role of natural convection on the emission of volatiles from a bed of contaminated particles, *Environ. Sci. Technol.* 31 (1997) 351–358.
- [2] C.Y. Wang, P. Cheng, A multiphase mixture model for multiphase multicomponent transport in capillary porous media: I. Model development, *Int. J. Heat Mass Transfer* 39 (1996) 3607–3618.
- [3] L.J. Thibodeaux, K.T. Valsaraj, C. Springer, G. Hildebrand, Mathematical models for predicting chemical vapor emission from landfills, *J. Hazard. Mater.* 19 (1988) 119–123.
- [4] R.R. Dupont, Evaluation of air emission release rate model predictions of hazardous organics from land treatment facilities, *Environ. Progr.* 5 (1986) 197–206.
- [5] A.A. Karimi, W.J. Farmer, M.M. Cliath, Vapor-phase diffusion of benzene in soil, *J. Environ. Qual.* 16 (1987) 38–43.
- [6] A. Karimi, V. Ravindran, M. Pirbazari, A laboratory experiment and predictive model for evaluating landfill cover controls of emissions of volatile organic chemicals to air, *Hazard. Waste Hazard. Mater.* 5 (1988) 203–218.
- [7] Bird, R.B., Stewart, W.E., Lightfoot, E.N., *Transport Phenomena*, Wiley, New York, 1960, p. 570.
- [8] K.B. Bischoff, Accuracy of the pseudo-steady-state approximation for moving boundary diffusion problems, *Chem. Eng. Sci.* 18 (1963) 711–713.
- [9] F. Gioia, F. Murena, G. Savino, P. Saha, The release into the atmosphere of hazardous volatiles: Part I. Release from porous solids imbued with a liquid mixture in which the volatiles are dissolved, *J. Hazard. Mater.* 40 (1995) 213–235.
- [10] Santoro, A., Studio teorico e sperimentale sulla evaporazione di una miscela multicomponente attraverso un letto poroso, *Chem. Eng. Thesis*, University of Naples, Italy, 1997.
- [11] Reid, R.C., Prausnitz, J.M., Poling, B.E., *The Properties of Gases and Liquids*, 4th edn., McGraw-Hill, New York, 1988, pp. 587, 291–307.
- [12] Perry, R.H., Green, D.W., *Perry's Chemical Engineers' Handbook*, 6th edn., McGraw-Hill, New York, 1984.
- [13] Satterfield, C.N., Sherwood, T.K., *The Role of Diffusion in Catalysis*, Addison-Wesley Publ., Reading, MA, 1963, pp. 12–23.