Modeling Nonlinear Moisture Diffusion in Inhomogeneous Media

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Abstract

While moisture diffusion in microelectronic device and packaging has been studied for decades, the problems involving complex nonlinear moisture diffusion in multi-material assembly have not been fully studied. This paper has developed a general nonlinear diffusion model by adopting water activity, a continuous state variable, as the field variable. The generalized solubility is introduced, which is temperature- and water activity-dependent. The effective diffusivity is defined and derived in terms of generalized solubility and water activity. By comparing the water activity-based model with the existing various normalized models, the present theory can unify and generalize the current approaches. More importantly, the present model can solve both linear and nonlinear moisture diffusion in inhomogeneous material system without normalization. The commercial finite element software has been applied to solve the nonlinear generalized moisture diffusion problem using the analogy of water activity and temperature. A source code of user-defined subroutines in ABAQUS has been provided in the Appendix of the paper. The mathematical formulation and the numerical implementation method presented in this paper can be applied to any nonlinear sorption or diffusion problems in inhomogeneous material system.

Keywords: Moisture diffusion; Multi-material systems; Microelectronics; Water activity; Nonlinear sorption isotherm; Electronic packaging

Nomenclature

$\mathbf{J}$	water flux vector, kg/s/m^2
C	moisture concentration, kg/m^3
D_0	diffusivity, m^2/s
D_{eff}	effective diffusivity, m^2/s
B	mobility of water molecules, mol×m^2/s/J
γ	activity coefficient, m^3/kg
μ_w	water chemical potential, J/mol
a_w	water activity, dimensionless
p_{amb}	ambient partial pressure of water vapor, Pa
p_g	saturated water vapor pressure, Pa
K, K^H	generalized solubility, and generalized Henry's solubility, kg/m^3

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C_{sat} saturated moisture concentration, kg/m^3
S, S^H solubility coefficient, and Henry solubility coefficient, kg/m^3/Pa
w wetness, C/C_{sat}, dimensionless
p_s normalized pressure term, Pa
φ advanced normalized concentration, dimensionless
M modified solubility, dimensionless
c_T specific heat capacity, J/K/kg
k_T thermal conductivity, W/m/K
r volumetric heat source, W/m^3
E_D activation energy for diffusivity, J/mol
E_S activation energy for solubility, J/mol
E_b activation energy for Langmuir hole affinity constant, J/mol
C_H' Langmuir hole concentration constant, kg/m^3
b Langmuir hole affinity constant, Pa^{-1}
i subscript i refers to the material identification number

1 Introduction

Polymeric materials are widely used to make today's microelectronic devices in wafer processing, packaging, and encapsulations. One undesired characteristic is that polymeric materials inevitably absorb certain amount of moisture from the ambient. The absorbed moisture can lead to many deleterious effects, including material aging [1], hygroscopic swelling [2], electrochemical migration [3], and even popcorn failures [4-9]. Thus, studying moisture diffusion is crucial for the reliability of microelectronics, and has become a major focus of numerous research works [10-14].

To model moisture diffusion, Fick's law has been widely used, assuming that moisture flux is driven by the gradient of moisture concentration. The mathematical equation for Fickian moisture diffusion can be written as

$$\mathbf{J} = -D_0 \nabla (C) \quad \textit{Fick's law}; \qquad (a)$$
$$\frac{\partial C}{\partial t} = -\nabla \cdot \mathbf{J} \quad \textit{Law of mass conversation} \qquad (b)$$

(1)

where $\mathbf{J}$ is water flux, C is moisture concentration and D_0 is moisture diffusivity, which typically is a constant at a given temperature. For multi-material systems like electronic packaging, however, moisture concentration is discontinuous at the material interface due to distinct absorption capabilities of materials, as shown in Fig. 1a. As a result, Eq. (1) cannot be solved directly using field variable moisture concentration C [15-18]. To overcome the limitation, a common practice is to transform Eq. (1) by adopting a continuous field variable through normalization, as shown in Fig. 1b.
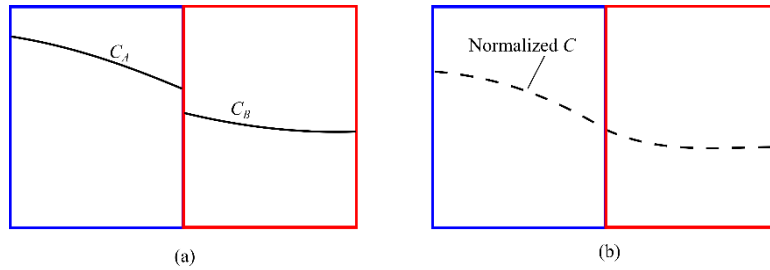
Fig. 1. Illustration of a bi-material system with (a) discontinuous moisture concentration and (b) continuous normalized concentration.

Different approaches have been developed in the literature, including the wetness theory [19], partial pressure technique [20], advanced normalization concentration approach [21], and direct concentration approaches such as Surface Humidity Potential (SHP) method [22]. According to a recent review[23], the wetness theory was considered more general than the other normalized theories. However, it may still encounter discontinuity issue when dissimilar materials have various temperature-dependent saturated moisture concentration. In addition, current normalization schemes are largely based on Henry's law, which is a linear relationship between saturated water concentration and relative humidity. Markus, et al. [22] proposed a Surface Humidity Potential (SHP) method to deal with non-Henry sorption behavior, but the nonlinear sorption relationship was only applied to the material surface or interface in the method.

This paper proposes a nonlinear diffusion model that can be used directly for heterogeneous system without the need of normalization. Water activity, which is a thermodynamic state variable and always continuous, is adopted as field variable. A water activity-based diffusion theory is formulated using the fundamental nonlinear diffusion equation with a generalized sorption isotherm theory. The generalized theory calculates moisture concentration as a product of water activity and generalized solubility. Determination of the generalized solubility and effective moisture diffusivity can be achieved by conducting sorption tests at various humidity and temperature conditions. The paper is organized as follows. The detailed model development is given in Section 2. Section 3 shows the use of the new model can unify the existing normalized models and furthermore serves as nonlinear diffusion model. Section 4 derives the effective diffusivity due to the nonlinearity of moisture diffusion. Section 5 validates the new model and provides a case study with non-Henry sorption isotherm material. The solutions are obtained in commercial finite element analysis package using the activity-temperature analogy.

2 Theory

Generally, mass diffusion could have many driving forces, such as the gradients of chemical potential, temperature and hydrostatic stress [13]. In this paper, we limit our scope to the mass diffusion driven by the gradient of chemical potential for clarity purpose. The consideration of the other driving forces will be reported in future work.

2.1. Fundamental equations

Consider a multi-material system subjected to dynamic humidity and temperature conditions, as shown in Fig. 2. The system contains multiple solid solvents with different chemical compositions and properties, representing a typical electronic assembly. Each solid (solvent) is able to absorb and transport moisture from the ambient. Without losing the generality, the isothermal condition is assumed throughout the system so that thermal diffusion is neglected.
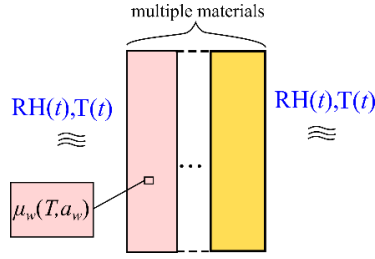
Fig. 2. A multi-material system subjected to dynamic humidity and temperature conditions. The chemical potential of water is a function of water activity and temperature.

As shown in Fig. 2, the thermodynamic state of water in a solid is characterized by the chemical potential μ_w. At a time and location, the chemical potential of water can be expressed in terms of two state variables, temperature T and water activity a_w, as [24-26]

$$\mu_w = \mu_{w0} + RT \ln a_w \tag{2}$$

with μ_{w0} is the standard chemical potential and R is universal gas constant. Water activity a_w is a thermodynamic term for describing the availability of water, a well-adopted concept on food and membrane systems [26-32]. The water activity of a moisture-solid (water-solvent) system *at equilibrium* can be determined by the following equation [26, 28, 33].

$$a_{w,eq} = p_{amb} / p_g \equiv RH \tag{3}$$

where p_{amb} is the partial water vapor pressure of the ambient that contacts with the system, and p_g is saturated water vapor pressure. Therefore, the water activity of an equilibrium system can be directly determined by measuring the RH, except that RH is usually expressed in percentage.

To describe moisture diffusion in multi-material system, the fundamental equation for water flux, $\mathbf{J}$, should be used [24, 25]

$$\mathbf{J} = -C_i \mathbf{v}_i = -C_i \left(B_i \nabla \mu_w \right). \tag{4}$$

Here, the subscript "i", refers to the identification number of material, is used in those discontinuous variables such as C_i (kg/m^3), the moisture concentration, $\mathbf{v}_i$, the solute transport velocity, and B_i, the mobility of water molecules in solvent i. Since $\mathbf{J}$ and μ_w are always continuous, subscript "i" is not used. This rule will be applied throughout the following derivations. Eq. (4) states that zero water flux exists only when the chemical potential of water is the same everywhere.

While the chemical potential is continuous, it is difficult to unitize Eq. (4) for engineering applications. Since water activity is also a continuous state variable, one can replace the chemical potential by water activity in Eq. (4) without losing the continuity requirement. Substituting Eq. (2) into (4) and considering the isothermal condition (i.e., $\nabla T = 0$) yields

$$\mathbf{J} = -C_i B_i \left(\frac{RT}{a_w} \nabla a_w \right) = -\frac{C_i}{a_w} \left(B_i RT \right) \nabla a_w = -K_i D_{0,i} \nabla a_w \tag{5}$$

in which $D_{0,i} = B_i RT$ and K_i is defined as

$$K_i = C_i/a_w \text{ or } C_i = K_i a_w. \tag{6}$$

and it is called the generalized solubility. Eq. (5) indicates that the driving force of water diffusion is, in fact, the gradient of water activity, and the equilibrium is achieved by the movement of water from the regions of high water activity to the regions of low water activity. With Eqs. (5) and (6), both water flux and concentration are expressed in terms of water activity. Therefore, the continuity equation (Eq. (1b)) can be written as

$$\frac{\partial(K_i a_w)}{\partial t} = \nabla \cdot \left(K_i D_{0,i} \nabla a_w\right). \tag{7}$$

As will be shown later, K_i is typically a function of temperature and water activity, so Eq. (7) can be further written as

$$\left(K_i + a_w \frac{\partial K_i}{\partial a_w}\right)\frac{\partial a_w}{\partial t} = \nabla \cdot \left(K_i D_{0,i} \nabla a_w\right) - a_w \frac{\partial K_i}{\partial T}\frac{\partial T}{\partial t} \tag{8}$$

which is a general and nonlinear diffusion equation based on water activity. It is worth noting two key features of the model. First, the model is derived from the fundamental diffusion equation and thus can describe nonlinear diffusion. Second, water activity is a state variable and the continuity at the material interface is warranted. Therefore, no normalization is needed to apply Eq. (8) for multi-material systems.

2.2. Determination of K

To solve Eq. (8), the generalized solubility K_i and its relationship between water activity and temperature must be known for each solid (solvent). Below we show that K_i can be related to the saturated moisture concentration C_{sat}, which can be measured at various RH and temperatures after an equilibrium is established [34]. Notice that at equilibrium water activity $a_{w,eq}$ equals RH and C reaches C_{sat} everywhere. We can apply Eq. (6) for any equilibrium system, yielding

$$K(a_{w,eq}, T) = \frac{C_{sat}(a_{w,eq}, T)}{a_{w,eq}} \tag{9}$$

where $C_{sat}(a_{w,eq}, T)$ is saturated moisture concentration for any $a_{w,eq}$ and T. Note that the relationship between C_{sat} and $a_{w,eq}$ at a fixed temperature is also called moisture sorption isotherm. Therefore, one can use Eq. (9) to determine K by conducting moisture sorption isotherms at various temperatures.

Especially, when C_{sat} has a linear relationship with $a_{w,eq}$, the sorption isotherm follows Henry's law, as

$$C_{sat} = S^H(T)p_{amb} = S^H(T)\left(p_g \times a_{w,eq}\right) \tag{10}$$

where S^H is Henry solubility that depends on temperature. Comparing Eq. (9) and (10) yields the definition of K^H, as

$$K^H(T) = S^H(T)p_g(T) \cdot \tag{11}$$

Eq. (11) indicates that K for Henry's law only depends on temperature. This is not the case for nonlinear sorption isotherm. One example is the Langmuir-type sorption isotherm, as [35]

$$C_{sat} = \frac{C_H'b(T)p_{amb}}{1+b(T)p_{amb}} = \frac{C_H'b(T)p_g(T) \times a_{w,eq}}{1+b(T)p_g(T) \times a_{w,eq}} \quad \text{for Langmuir} \tag{12}$$

where C_H' is hole saturation constant and b is hole affinity constant. Eq. (12) results in the following generalized solubility

$$K(a_{w,eq},T) = \frac{C_H' \times b(T)p_g(T)}{1+b(T)p_g(T) \times a_{w,eq}} \quad \text{for Langmuir.} \tag{13}$$

Eq. (13) shows that K could depend on both water activity and temperature. The problems involving nonlinear sorption isotherms will be studied in Section 5.

3 Water Activity Versus Existing Normalized Concentration Variables

This section explores the relationship between water activity and several existing normalized concentrations. The fundamental differences are pointed out between the activity-based model and the existing normalization schemes.

3.1. Wetness versus water activity

The concept of wetness has been proposed in Eq. (1) to remove the concentration discontinuity at the interface [19, 36]. The wetness in material i or at interface is defined as

$$w_i = C_i / C_{sat,i} \tag{14}$$

where the denominator C_{sat} can be chosen at any *RH* and varies with material types.

To gain insights into the concept of wetness, let the denominator C_{sat} in Eq. (14) be chosen at a reference *RH* (or water activity $a_{w,ref}$, shown in Eq. (3)). Then we can obtain the relationship between water activity and wetness at the same temperature T as follows

$$w_i = \frac{K_i(a_w,T)a_w}{K_i(a_{w,ref},T)a_{w,ref}} \cdot \tag{15}$$

From Eq. (15), the continuity of wetness is met only by satisfying the following condition:

$$\frac{K_i(a_w,T)}{K_i(a_{w,ref},T)} = f(a_w,T) \tag{16}$$

where f must be continuous at the interface and thus has no subscript "i". Assuming all the materials follow

Henry sorption behaviors, we can have a special case with $f=1.0$ for all the materials, so that Eq. (16) holds. However, if we consider a nonlinear isotherm such as Langmuir-type in Eq. (12), f becomes a function that contains material constants and thus Eq. (16) will not be satisfied. This implies that the wetness theory may not be applicable to an inhomogeneous material system involving nonlinear sorption isotherm materials.

3.2. Pressure versus water activity

Another approach to normalizing Eq. (1) is called the pressure technique, which was first proposed by Wadiak [37] for nonlinear diffusion in polymer composites, as

$$p_{s,i} = C_i / S_i(T, p_s) \tag{17}$$

where p_s has the unit of pressure and S is solubility function of p_s and T.

If we define S as Henry's constant of solubility S^H, we have

$$p_{s,i} = K^H a_w / S^H = p_g a_w. \tag{18}$$

Eq. (18) shows a simple relationship between p_s and a_w, proving that p_s is always continuous under the assumption of Henry's law because both p_g and a_w are material-independent.

3.3. Advanced normalized concentration versus water activity

Jang, et al. [21] proposed an "advanced normalized concentration method" that can be practiced only for the polymers that have a temperature-independent linear relationship between C_{sat} and the RH. In the advanced normalized concentration method, the following normalized concentration φ was used:

$$\varphi_i = C_i / M_i = C_i / \left(p_\infty S_{\infty,i} \right) \tag{19}$$

where M_i is called modified solubility, and the constants p_∞ and $S_{\infty,i}$ are used in Eqs. (20) and (21) below to calculate p_g and Henry solubility S_i^H, respectively, as

$$p_g(T) = p_\infty \exp\left(-E_p / RT \right) \tag{20}$$

$$S_i^H = S_{\infty,i} \exp\left(E_{s,i} / RT \right) \tag{21}$$

where both E_p and E_s are constants of activity energy. According to Jang *et al.* [21], E_p is approximately equal to E_s so that

$$C_{sat,i} = p_{amb} S_i^H = RH \times M_i \quad \text{with } M_i = p_g S_i^H = p_\infty S_{\infty,i}. \tag{22}$$

Realizing these underlying assumptions, we can find the relationship between φ_i and water activity as

$$\varphi_i = \frac{\left(K_i^{\,H} a_w\right)}{M_i} = \frac{(p_g S_i^H) a_w}{\left(p_\infty S_{\infty,i}\right)} \approx a_w \quad \text{with } E_p \approx E_{s,i}. \tag{23}$$

Therefore, the advanced normalized concentration is a special case of water activity under two particular assumptions: the isotherm follows Henry's law, and the product of p_g and S^H is a constant.

3.4. A summary

Generally, Henry's law is a common assumption in the existing normalized schemes. This assumption makes them special cases of the activity-based model. The governing equation solved by the current normalized schemes can be obtained by substituting K^H into Eq. (8). Note that K^H is independent of water activity, the activity-based model in Eq. (8) simplifies into

$$K_i \frac{\partial a_w}{\partial t} = \nabla \cdot \left(K_i D_{0,i} \nabla a_w\right) - a_w \frac{\partial K_i}{\partial T} \dot{T} \quad \text{with } K_i = K_i^{\,H}(T). \tag{24}$$

The source term in Eq. (24) is similar to the source term produced in other normalization technique [13, 23]. For solving the problem with varying temperature with the wetness approach, special and complex numerical treatments must be introduced in order to solve the problem correctly [23]. As to be shown in the example in Section 5, the activity-based model is able to solve complex problems involving Henry's material with varying temperature more effectively based on Eq. (24).

The source term disappears when K^H is independent of temperature or there is no temperature change ($\dot{T} = 0$), yielding the following simplest case of water activity-based model, as

$$\partial a_w / \partial t = \nabla \cdot \left(D_{0,i} \nabla a_w\right) \quad \text{when } K_i = const \text{ or } (K_i = K_i^{\,H}(T) \, \& \dot{T} = 0). \tag{25}$$

which resembles the model used in the advanced normalization technique [21].

Another case derived from the activity-based model is given below

$$\left(K_i + a_w \frac{\partial K_i}{\partial a_w}\right) \frac{\partial a_w}{\partial t} = \nabla \cdot \left(K_i D_{0,i} \nabla a_w\right) \quad \text{with } K_i = K_i\,(a_w) \text{ or } \dot{T} = 0. \tag{26}$$

where the source term vanishes but the nonlinear term $\partial K_i / \partial a_w$ remains. The case in Eq. (26) occurs when nonlinear sorption isotherm is considered, and it cannot be solved correctly by the existing normalization schemes.

4 Effective Diffusivity for Nonlinear Diffusion Model

Since the activity-based model can handle nonlinear moisture diffusion, it becomes important to understand the effective diffusivity due to the nonlinearity. The concept of effective diffusivity was initially developed for nonlinear moisture concentration-based diffusion model [24, 38, 39]. Similar to the activity-based model, the nonlinear concentration-based model also adopts the same fundamental equation for diffusion given Eq. (4). The activity coefficient γ_i is used to calculate water activity from moisture concentration, as

$$a_w = \gamma_i(C_i, T)C_i.$$ (27)

With Eq. (27), the general diffusion flux in Eq. (5) can be written as

$$
\begin{aligned}
\mathbf{J} &= -\frac{1}{\gamma_i} D_{0,i} \nabla(\gamma_i C_i) = -\frac{1}{\gamma_i} D_{0,i} [\gamma_i \nabla C_i + C_i \nabla \gamma_i] \\
&= -D_{0,i}\left(\nabla C_i + \frac{C_i}{\gamma_i} \frac{\partial \gamma_i}{\partial C_i} \nabla C_i \right) = \underbrace{-D_{0,i}\left(1 + \frac{\partial \ln \gamma_i}{\partial \ln C_i} \right)}_{D_{eff}} \nabla C_i
\end{aligned}
$$ (28)

where D_{eff} is the effective diffusivity. Eq. (28) is the nonlinear concentration-based diffusion model given in the literature [24, 38, 39]. With Eq. (28), a nonlinear concentration-based model can be obtained. In the literature, concentration-dependent diffusivity has been discussed [40]. However, the nonlinear concentration-based model with concentration-dependent diffusivity is not suitable for heterogeneous systems due to the discontinuity of moisture concentration at the material interface. Also, Eq. (28) may not be directly normalized by the existing normalized schemes discussed in Section 3.

By comparing Eq. (27) with the definition of K in Eq. (6), one can find that the activity coefficient γ is, in fact, the reciprocal of generalized solubility K. This relationship allows us to evaluate the effective diffusivity based on K. According to the derivation in Appendix A, the normalized effective diffusivity in terms of K is

$$\frac{D_{eff,i}}{D_{0,i}} = \left(1 + \frac{\partial \ln \gamma_i}{\partial \ln C_i} \right) = K_i \left(a_w \frac{\partial K_i}{\partial a_w} + K_i \right)^{-1}.$$ (29)

A simple calculation shows that the normalized effective diffusivity becomes 1.0 for the case of Henry's law. For nonlinear sorption isotherm, the normalized effective diffusivity will become dependent on water activity. To determine the concentration-dependent diffusivity, the following steps can be used. First, K is determined by the procedures described in Section 2.2. Second, D_0 is measured by fitting the dynamic weight gain data for a given temperature. The fitting model will be the activity-based equation in Eq. (26) with K as a known property. Note that K and D_0 are determined from the same moisture sorption tests. With both K and D_0 determined, D_{eff} can be evaluated using Eq. (29).

5 Validation and Case Study

5.1. Numerical implementation in FEA software package

Since water activity is a continuous state variable like temperature, the activity-based model can be solved using the activity-temperature analogy. A typical heat transfer equation can be written as

$$\rho c_T \partial T / \partial t = \nabla \cdot (k_T \nabla T) + r$$ (30)

where ρ is density, c_T is specific heat capacity, k_T is thermal conductivity, and r is volumetric heat source.

Table 1 provides the analogy between the activity-based model in Eq. (8) and the heat transfer equation in Eq. (30). Using the analogy, the activity-based model has been implemented in commercial finite-element-analysis (FEA) package ABAQUS. As the source term is solution-dependent, ABAQUS User Subroutines

UMATH is required, see Appendix B for the script of an example. In the subroutine, both moisture concentration and effective diffusivity are calculated by considering them as solution-dependent state variables based on Eq. (6) and Eq. (29), respectively.

Table 1. The analogy between activity-based moisture diffusion and thermal diffusion.

Equation	Analogy			
	Field Variable	Material Properties		Source Term
Eq. (8)	a_w	$\left(K_i + a_w \dfrac{\partial K_i}{\partial a_w} \right)$	$K \cdot D_0$	$- a_w \dfrac{\partial K_i}{\partial T} \dfrac{\partial T}{\partial t}$
Eq. (30)	T	ρC_T	k_T	r

5.2. Benchmarking problem based on Henry sorption isotherms

Fig. 3 shows a benchmarking problem for studying diffusion in a heterogeneous system. A bi-material system subjected to a dynamic humidity and temperature condition is studied. In the previous studies, the diffusion mechanism was assumed to be governed by the linear Fickian diffusion model [18]. Due to dissimilar properties, moisture concentration is discontinuous and normalization was thus required.
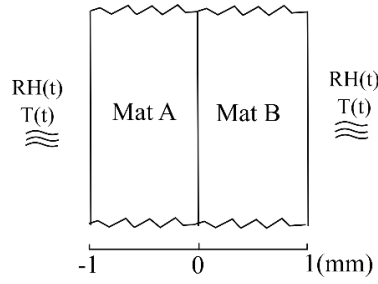

Fig. 3. A benchmarking problem for moisture diffusion in a bi-material system with dynamic humidity and temperature conditions.

To apply the water activity-based model, the initial and boundary conditions are given as

$$a_w(t=0) = RH_0; \quad a_w \big|_{bc}(t) = RH(t) = p_{amb} / p_g(T); \quad T = 25 + t/60\,^oC \tag{31}$$

where initial relative humidity RH_0=0% and the ambient pressure p_{amb}=3207 Pa based on the literature [18].

Each material in the benchmarking problem has a thickness of 1 mm. To use the activity-based model, the generalized Henry solubility K^H is calculated using Eq. (11), where saturated water vapor pressure p_g and Henry solubility S_i^H can be calculated from Eq. (20) and Eq. (21), respectively. Water diffusivity is assumed to follow the Arrhenius equation, as

$$D_{0,i}(T) = D_{\infty,i} \exp\left(- E_{D,i} / RT \right) \tag{32}$$

where D_∞ and E_D are material constants. The required material constants are summarized in Table 2.

Table 2. Material properties for benchmarking the activity-based model[18].

Properties	Materials	
	A	B
D_∞(m2/s)	5.0×10^{-3}	4.0×10^{-3}
E_D (J/mol)	5.0×10^4	5.0×10^4
S_∞(kg/m/ Pa)	6.0×10^{-10}	2.0×10^{-10}
E_s(J/mol)	4.0×10^4	4.0×10^4

The results of moisture distribution at two different times are presented in Fig. 4. The solutions in the previous study are also plotted for comparison. It can be seen that the FEA results agree well with the literature, validating the activity-based model as well as the implementation of activity-thermal analogy in ABAQUS.
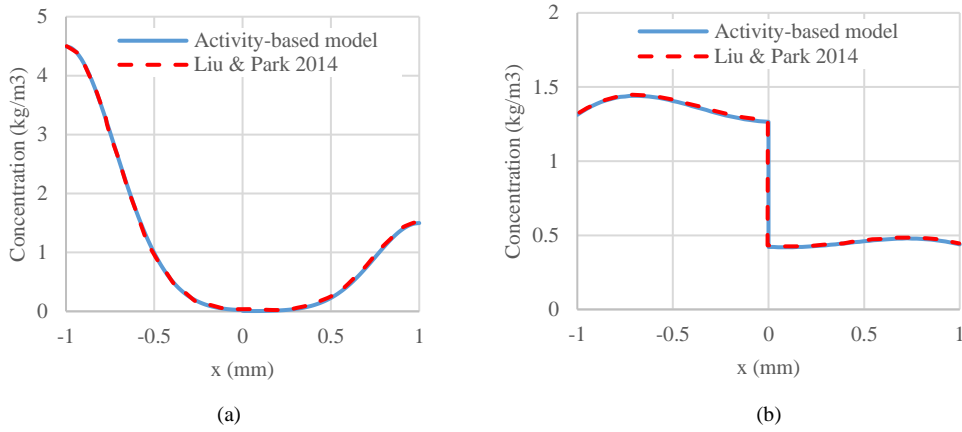

(a)

(b)

Fig. 4. Results of benchmarking the activity-based model based on Liu and Park [18]. (a) t=1800 s (b) at t=3600 s.

5.3. Case study with nonlinear sorption isotherms

For further demonstration, we design a diffusion problem involving with nonlinear sorption isotherm. Langmuir-type sorption isotherm described in Section 3 is applied. To consider the temperature effect, we assume that Langmuir affinity constant b follows Arrhenius equation, as

$$b(T) = b_\infty \exp[E_b /(RT)] \qquad (33)$$

where b_∞ and E_b are material constants. The corresponding K for the Langmuir isotherm becomes

$$K(a_{w,eq}, T) = \frac{C_H' \times b_\infty p_\infty \exp[(E_b - E_p)/(RT)]}{1 + b_\infty p_\infty \exp[(E_b - E_p)/(RT)] \times a_{w,eq}} . \qquad (34)$$

For comparison, two cases were studied,

a) Case I: both Mat-A and Mat-B follow Henry's law with the parameters given in Table 2, except that $E_{s,A} = E_{s,B} = 3.8 \times 10^4$ J/mol;

b) Case II: The isotherm for Mat-A follows Henry's law, whereas the isotherm of Mat-B is devised to become the Langmuir isotherm with $C_H' = 4.14$ kg/m^3, $b_\infty = 6 \times 10^{-9}$ Pa^{-1}, and $E_b = 3.01 \times 10^4$ J/mol.

Fig. 5 compares the sorption isotherms of Mat-B given in Case-I and Case-II. For Case I, C_{sat} has a linear relationship with a_w for a given temperature. In Case II, the relationship is nonlinear. Note that C_{sat} at $RH=100\%$ and 25 °C are devised to be similar for both cases. In the case study, the initial and boundary conditions are the same as Eq. (31), except that the initial condition is set to 100% to simulate a desorption process.
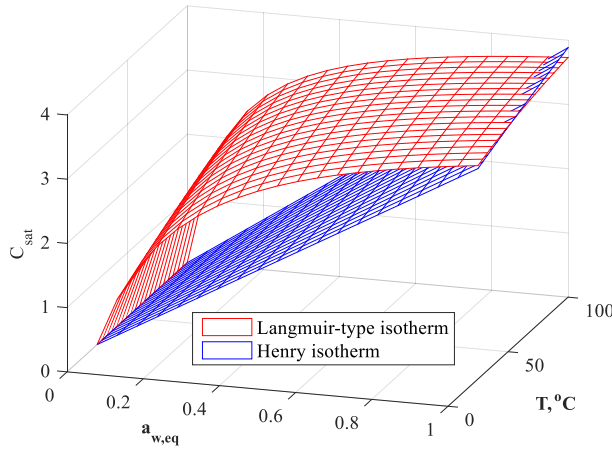

Fig. 5. Two sorption isotherms are adopted for material *B*: Henry isotherm in Case I and Langmuir-type isotherm in Case II. Both cases are temperature-dependent.

5.4. Results

The calculated distributions of water activity and moisture concentration at $t=60$ minutes are plotted in Fig. 6. To verify the FEA results, finite difference method (FDM) is also applied to solve the same equation (8) with MATLAB programming. The numerical results from both FDM and FEA are in excellent agreement, as shown in Fig. 6. This confirms that the FEA implement using commercial finite element software is correct. From Fig. 6, it can be seen that water activity is always continuous despite isotherm type. However, moisture concentration is discontinuous at the interface. The results show that two different isotherms make a great impact on the redistribution of moisture. In Fig. 6a, much lower water activity is obtained in Case II with temperature-dependent Langmuir isotherm compared to Case I with Henry isotherm. In Fig. 6b, Case II yields very different moisture redistribution in comparison to Case I. Note that Case-II cannot be solved by the existing normalized schemes.
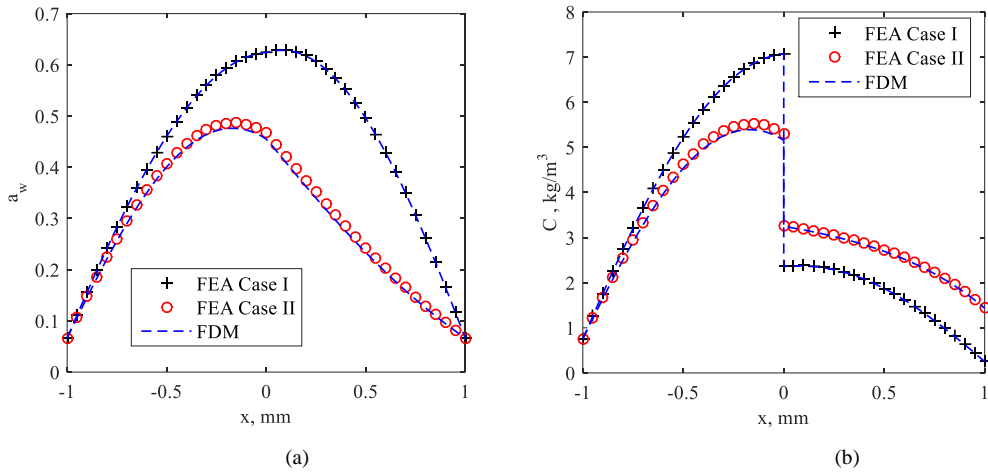
Fig. 6. Calculated profiles of (a) water activty and(b) concentration at t=3600 s.

Fig. 7 compares interfacial moisture concentration for Case-I and Case-II, respectively. Generally, moisture concentration of material A decays much faster than material B in both cases. However, with Langmuir-type isotherm used in Case II, the moisture concentration in material B has a slight increase first and starts to drop at $t\approx$45 minutes. The increase in moisture concentration is also called "over-shooting" reported in the literature [16, 41]. The results indicate that there is net moisture flux from material-A to material-B in Case II, despite the applied desorption condition.
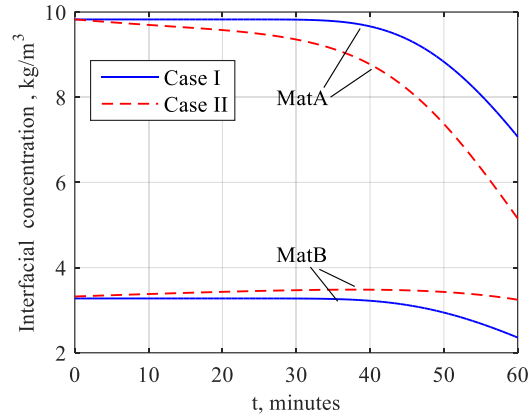

Fig. 7. The effect of nonlinear sorption isotherms (Case II) on the history of water concentration at the material interface.

Fig. 8 plots the profiles of normalized effective diffusivity for Case-II at different times. The normalized diffusivity for material *A* is always equal to 1.0 because it has linear sorption isotherm. In comparison, for material B, the normalized effective diffusivity is not uniform and generally higher than 1.0, especially near the material interface.
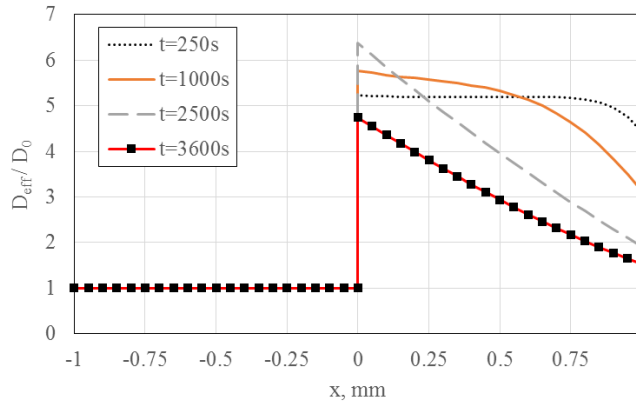
Fig. 8. Plots of the normalized effective diffusivity calculated by Eq. (29). The isotherm for material-B is temperature-dependent Langmuir isotherm (Case II).

Fig. 9 compares the concentration profile in material *B* between Case I and Case II at different times. Generally, Case II yields "flatter" moisture concentration profile or smaller gradients than Case I.
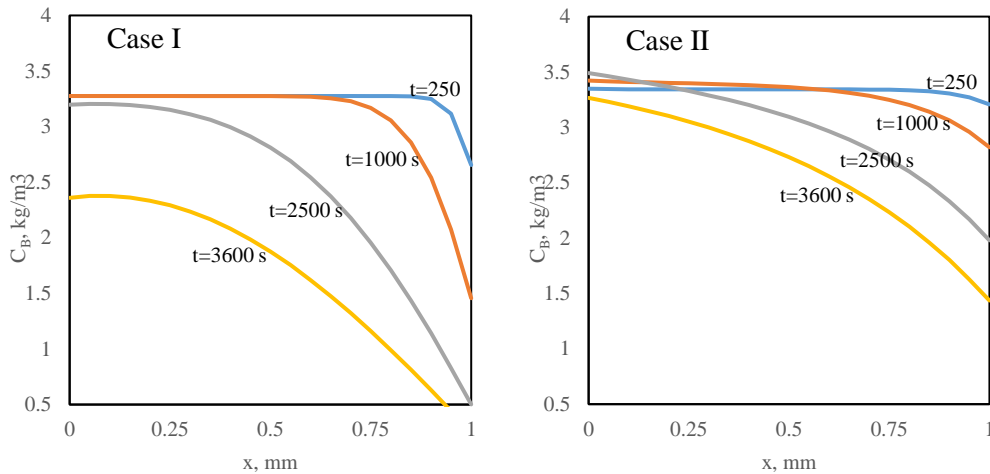

Fig. 9. Profiles of water concentration in Material-B. (a) Case I with temperature-dependent Henry isotherm; (b) Case II with temperature-dependent Langmuir isotherm.

Fig. 10 compares the total moisture loss of the whole material system (material A and material B) as a function of time for two cases. Interestingly, the difference in total moisture loss is insignificant in spite of two different isotherms used for material B. From Fig. 8 Case II yields higher diffusivity but smaller concentration gradients from Fig. 9. Therefore, the effective moisture flux, which is the product of effective diffusivity and concentration gradient, does not change much. We may conclude that, for the specific case study, different

isotherms may greatly affect the redistribution of moisture but might have limited effect on the total moisture desorption behaviors.
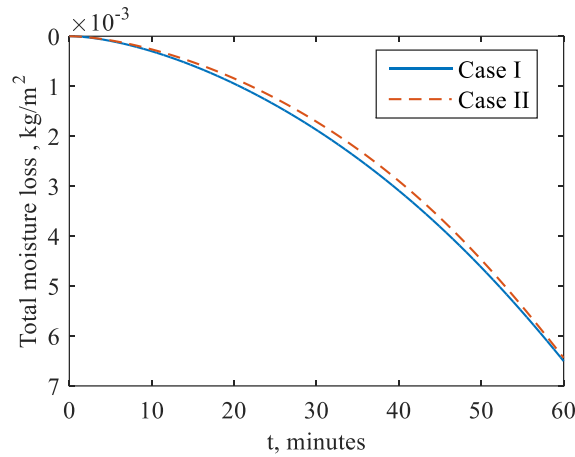

Fig. 10. Total moisture loss for Case I and Case II.

6 Discussions and Conclusions

In this paper, a mathematical formulation for nonlinear moisture diffusion based on water activity has been developed. The proposed model can be directly applied to multi-material systems without normalization. Water activity, a state field variable, warrants the continuity along the interface of dissimilar materials. The governing equation features its theoretical basis on the very fundamental moisture transport mechanism, which is that water transports from the regions of high water activity to the regions of low one, regardless of material discontinuity or inhomogeneity. A generalized solubility K is introduced, which is temperature- and water activity- dependent. The effective diffusivity is defined and derived in terms of K and water activity. Under the assumption of Henry's law, K becomes independent of water activity, and therefore, the governing equation can be reduced to the conventional Fickian-based moisture diffusion equation. By comparing the water activity-based theory with the existing various normalized theories, the present model can unify and generalize the current approaches, and more importantly, can solve the nonlinear moisture diffusion in an inhomogeneous material system with nonlinear moisture sorption isotherms.

When considering dynamic boundary condition that is temperature-dependent, even for the materials with Henry's isotherm, special treatment and care must be taken with the previous normalization approaches to satisfy certain continuity conditions. However, using the mathematical formulation developed in this paper, the existing commercial finite element software can be applied to solve such problems using a user-defined subroutine without additional special numerical treatment. This paper first applied a benchmarking problem to validate the implementation of using commercial finite element software and results through the literature results. Then the problem has been extended to a nonlinear diffusion involving with material with nonlinear sorption isotherm. It is found that nonlinear sorption isotherm resulted in very different distribution of water activity and moisture concentration compared to the linear sorption isotherm or Henry's law. The effective diffusivity was also evaluated. The effective diffusivity evolves with both water activity and temperature, and can only return to the conventional diffusivity under the assumption of Henry's law. The capability to evaluate the effective diffusivity of nonlinear diffusion in multi-material systems makes the activity-based model unique.

The mathematical formulation and the numerical implementation method presented in this paper can also be applied to any nonlinear sorption or diffusion problems in inhomogeneous material system.

Appendix A. Derivation of Effective Diffusivity

The effective diffusivity can be calculated from the generalized solubility K and the solution of a_w. From the following basic equations:

$$C = Ka_w = C(a_w, T)$$
$$a_w = \gamma C = a_w(C, T)$$
(A.1)

we have

$$\gamma = a_w / C$$
(A.2)

To calculate the effective diffusivity in Eq. (29), we first write

$$\frac{\partial \ln \gamma}{\partial \ln C} = \frac{C}{\gamma} \frac{\partial \gamma}{\partial C}$$
(A.3)

where the derivative of γ over C can be evaluated as

$$\frac{\partial \gamma}{\partial C} = \frac{\partial (a_w / C)}{\partial C} = \frac{1}{C} \frac{\partial a_w}{\partial C} - \frac{a_w}{C^2}.$$
(A.4)

Note that

$$\frac{\partial a_w}{\partial C} = \lim_{\Delta C \to 0} \frac{\Delta a_w}{\Delta C} = \lim_{da_w \to 0} \frac{1}{\Delta C / \Delta a_w} = \left(\frac{\partial C}{\partial a_w} \right)^{-1} = \left[\frac{\partial (Ka_w)}{\partial a_w} \right]^{-1} = \left(a_w \frac{\partial K}{\partial a_w} + K \right)^{-1}$$
(A.5)

Substituting A.5 into Eq. A.4 and applying the basic equations in Eq. A.1 yields

$$\frac{\partial \gamma}{\partial C} = \frac{1}{Ka_w} \left(a_w \frac{\partial K}{\partial a_w} + K \right)^{-1} - \frac{1}{K^2 a_w}$$
(A.6)

Finally, the effective diffusivity can be calculated as

$$D_{eff} / D_0 = 1 + \frac{\partial \ln \gamma}{\partial \ln C} = 1 + \frac{Ka_w}{1/K} \left[\frac{1}{Ka_w} \left(a_w \frac{\partial K}{\partial a_w} + K \right)^{-1} - \frac{1}{K^2 a_w} \right] = K \left(a_w \frac{\partial K}{\partial a_w} + K \right)^{-1}.$$
(A.7)

Appendix B. User Subroutines for Solving Nonlinear Activity-Based Model

The activity-based model includes a solution-dependent source term, which cannot be solved by the commercial software directly. A User Subroutine UMATHT is developed for the case study shown in Section 5, as follows (all the codes should be placed in a single file with extension .for):

```
c define mat-a as Henry and mat-b as Langmuir
      subroutine umatht(u,dudt,dudg,flux,dfdt,dfdg,statev,temp,
     1           dtemp,dtemdx,time,dtime,predef,dpred,cmname,ntgrd,nstatv,
     2           props,nprops,coords,pnewdt,noel,npt,layer,kspt,kstep,kinc)

c
      include 'aba_param.inc'

      character*80 cmname
      dimension dudg(ntgrd),flux(ntgrd),dfdt(ntgrd),dfdg(ntgrd,ntgrd),statev(nstatv),
     *          dtemdx(ntgrd),time(2),predef(1),dpred(1),props(nprops),coords(3)

         if (cmname(1:4) == 'MATB') then
              call umathtB(u,dudt,dudg,flux,dfdt,dfdg,statev,temp,
     1           dtemp,dtemdx,time,dtime,predef,dpred,cmname,ntgrd,nstatv,
     2           props,nprops,coords,pnewdt,noel,npt,layer,kspt,kstep,kinc)
         else if (cmname(1:4) == 'MATA') then
              call umathtA(u,dudt,dudg,flux,dfdt,dfdg,statev,temp,
     1           dtemp,dtemdx,time,dtime,predef,dpred,cmname,ntgrd,nstatv,
     2           props,nprops,coords,pnewdt,noel,npt,layer,kspt,kstep,kinc)
         end if


      return
      end


c Actual definition of material laws for material B using Langmuir isotherm

      subroutine umathtB(u,dudt,dudg,flux,dfdt,dfdg,statev,temp,
     1           dtemp,dtemdx,time,dtime,predef,dpred,cmname,ntgrd,nstatv,
     2           props,nprops,coords,pnewdt,noel,npt,layer,kspt,kstep,kinc)
c
      include 'aba_param.inc'
c
      character*80 cmname
      dimension dudg(ntgrd),flux(ntgrd),dfdt(ntgrd),dfdg(ntgrd,ntgrd),statev(nstatv),
     *          dtemdx(ntgrd),time(2),predef(1),dpred(1),props(nprops),coords(3)

c current time tc, current temperature Tc and Tck in Kelvin, and temperature increment dT
      tc=time(2)
```

```
      Tc=25.+tc/60.
      Tck=Tc+273.15
      dT=dtime/60.

c constants for Langmuir type isotherm
      pinf=3.8208e10
      R=8.3145
      binf=6e-9
      CH=4.14
      Ep=4.01e4
      Eb=3.01e4

c define aw, K, dK/daw, dK/dT, Diffusivity, cT and conductivity
      aw=temp
      dER=(Eb-Ep)/R
      bp=binf*pinf*exp(dER/Tck)
      f_K=CH*bp/(1.0+bp*aw)
      f_dKdaw=-(CH*bp*bp)/(bp*aw + 1.0)**2.0
              f_dKdT=(CH*aw*bp**2*dER*exp((2*dER)/Tck))/(Tck**2*(aw*bp*exp(dER/Tck)
     1        + 1.0)**2) - (CH*bp*dER*exp(dER/Tck))/(Tck**2*(aw*bp*exp(dER/Tck) + 1.0))
      Diff=4.e-3*exp(-5.e4/R/(Tc+273.15))
      cT=f_K+aw*f_dKdaw
      cond=Diff*f_K

c store normalized effective Diffusivity and water concentration
      statev(1)=f_K/cT
      statev(2)=f_K*aw
c

      dudt = cT

c add solution-dependent source term
      du = dudt*dtemp+aw*f_dKdT*dT

      u = u+du

      do i=1, ntgrd
              flux(i)=-cond*dtemdx(i)
              dfdg(i,i)=-cond
      end do

    return
    end

c Actual definition of material laws for material A using Henry isotherm

    subroutine umathtA(u,dudt,dudg,flux,dfdt,dfdg,statev,temp,
     1          dtemp,dtemdx,time,dtime,predef,dpred,cmname,ntgrd,nstatv,
```

```
     2                props,nprops,coords,pnewdt,noel,npt,layer,kspt,kstep,kinc)
c
      include 'aba_param.inc'
c
     character*80 cmname
     dimension dudg(ntgrd),flux(ntgrd),dfdt(ntgrd),dfdg(ntgrd,ntgrd),statev(nstatv),
     *          dtemdx(ntgrd),time(2),predef(1),dpred(1),props(nprops),coords(3)

c current time, temperature, and temperature increment

      tc=time(2)
      Tc=25.+tc/60.
      dT=dtime/60.
      Tck=Tc+273.15
c define K, dK/dT, D, cT, and conductivity
      R=8.314
      pinf=3.8208e10
      Ep=4.01e4
      Sinf=6.e-10
      Es=3.8e4
      dE=Es-Ep
      f_K=pinf*Sinf*exp(dE/R/Tck)
      dKdT=-pinf*Sinf*exp(dE/R/Tck)*dE/R/Tck/Tck
      Diff=5.e-3*exp(-5.e4/R/Tck)
      cT=f_K
      cond=f_K*Diff

c store normalized Diff and water concentration
      statev(1)=1.0
      statev(2)=f_K*temp
c
      dudt = cT

c add solution-dependent source term
      du = dudt*dtemp+temp*dKdT*dT

      u = u+du

c
      do i=1, ntgrd
        flux(i)=-cond*dtemdx(i)
        dfdg(i,i)=-cond
      end do
      return
      end
```

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