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A multiphase mixture model for multiphase, multicomponent transport in capillary porous media—I. Model development

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Abstract—A new model for multiphase, multicomponent transport in capillary porous media is developed, in which the multiple phases are considered as constituents of a multiphase mixture. This multiphase mixture model consists only of the conservation equations for the multiphase mixture and is derived from the classic multiphase flow formulation without making any approximations. In addition, algebraic relations are found which can be used to back out the individual phase flow fields from the mixture velocity in a post-processing fashion. While being mathematically exactly equivalent to the traditional multiphase flow model, the present formulation significantly reduces the number of model equations, thus offering an efficient alternative for the theoretical analysis and numerical simulation of multiphase transport phenomena in porous media. A detailed application to two-phase, binary systems shows that the complex transport problems become more tractable within the framework of this new formulation. Copyright © 1996 Elsevier Science Ltd.

1. INTRODUCTION

Problems involving multiphase flow and multicomponent transport in porous media arise in a number of scientific and engineering disciplines. Important technological applications can be found in petroleum engineering, where multiple flowing phases are present in natural oil reservoirs and when various enhanced exploitation techniques such as water and steam flooding are employed. A recent major environmental concern, i.e. groundwater contamination by organic compounds, is also related to the transport of immiscible nonaqueous phase liquids in groundwater systems [1, 2]. Restoration of contaminated groundwater systems may involve even more phases, thereby warranting studies of multiphase transport behaviors. Other industrial examples of multiphase flow and transport in porous media include heat pipe technology using binary mixtures [3], drying processes [4], multiphase trickle bed reactors [5, 6], and geothermal reservoirs with brine mixtures [7, 8].

A number of complex, interacting transport phenomena may take place in a multiphase, multicomponent system. Multiphase flows are, in general, driven by gravitational, capillary and viscous forces. Gravity causes phase migration in the direction of the gravitational field. A common example is gravity override of steam as encountered in steam injection for enhanced oil recovery and subsurface remediation, where the injected steam tends to rise to the top of the formation thus leading to a premature breakthrough of steam into production wells. The detrimental outcome of steam override is a large reduction in the recovery of oil or contaminant and a significant waste of latent-heat thermal energy. Another example of the influence of gravity is thermosolutal convection in the gas phase as a result of density variations due to combined temperature and concentration gradients typically present in a multiphase, multicomponent system. Thermosolutal convection greatly enhances the vapor phase transport of contaminants in subsurface environment and in remediation processes (e.g. during soil vapor extraction). Capillary forces play fundamental roles in controlling the phase distribution in heterogeneous porous media. In the context of groundwater contamination, the capillary forces due to interfacial tension are largely responsible for the extent of lateral spreading of a contaminant as it encounters a low-permeability zone. Viscous forces influence relative phase motion; fluids with lower viscosity tend to migrate more rapidly due to their reduced resistance to flow. When a denser, less viscous fluid displaces another fluid of lower density and higher viscosity, the process is inherently unstable, leading to fingering of phase interfaces [9]. Laboratory experiments have shown that unstable finger-like infiltration of an organic contaminant can significantly alter the transport and dilute characteristics of the contaminant [10, 11].

Traditionally, complex problems of multiphase flow and transport in porous media are tackled by a multiphase approach [12], in which various phases are regarded as distinct fluids with individual thermodynamic and transport properties and with different flow velocities. The transport phenomena are mathematically described by the basic principles of

NOMENCLATURE

c	specific heat
C	mass species concentration
Ca	capillary coefficient
Cs	solutal-capillary coefficient
Ct	thermo-capillary coefficient
D	diffusion coefficient
$\mathbf{g}$	gravity vector
h	enthalpy
$\mathbf{j}$	diffusive mass flux
J	interfacial species transfer rate
$J(\mathrm{s})$	capillary pressure function
k_r	relative permeability
k_{eff}	effective thermal conductivity
K	absolute permeability
K_{kg}	partition coefficient between phase k and the gas phase
m	interfacial mass transfer rate
$\mathbf{n}$	unit vector normal to boundaries
p	pressure
q	heat flux
$\dot{q}$	volumetric heat generation rate
s	phase saturation
t	time
T	temperature
$\mathbf{u}$	superficial or Darcian velocity vector.

Greek symbols

γ	multi-phase correction factor
ε	porosity
γ	relative mobility
μ	viscosity
v	kinematic viscosity
ρ	density
σ	interfacial tension.

Subscripts

c	capillary
g	gas phase
h	pertinent to enthalpy
i	phase i
k	phase k
kj	interface between phases k and j
j	phase j
l	liquid phase
n	normal
s	solid matrix or solutal
sat	saturated state
t	thermo-capillary
α	pertinent to species α
ρ	pertinent to density.

Superscripts

e	equilibrium
o	reference
α	species α
–	interfacial.

conservation for each phase separately and by appropriate interfacial conditions between various phases. The generalized Darcy's law is employed to represent momentum conservation in each phase, with the relative permeabilities of each phase introduced to account for a decrease in the effective flow cross-section due to the presence of other fluids.

Due to the inherent nonlinearities of multiphase flow problems, exact solutions are limited to a small class of problems in one dimension and with numerous simplifying assumptions, e.g. the Buckely–Leverett case [13]. Solving practical problems, which usually involve multi-dimensional effects, gravity, capillarity and phase change, requires sophisticated numerical procedures and represents a challenging task, since multiple coupled sets of differential equations must be solved. For this reason, there has been a great number of studies to develop robust numerical algorithms [14] and approximate models such as the unsaturated flow theory [15]. Another obstacle to numerical simulations of multiphase flow and transport in porous media lies in the presence of moving and irregular phase interfaces separating the single- and multi-phase regions. The locations of these interfaces are not known *a priori*, but must be determined by the coupled flows in adjacent regions. A numerical procedure for such a multi-region problem based on the multiphase approach needs to explicitly track the moving interfaces, thus calling for complex coordinate mapping or numerical remeshing [16]. Alternatively, in the water resources literature [17] the procedure of switching the primary variables and governing equations in various regions is usually adopted, which can severely affect numerical stability and convergence.

Recently, an alternative approach was developed to the modeling of two-phase flow and heat transfer in porous media [18]. In this so-called two-phase mixture model, the two-phase system is viewed as being a binary chemical mixture. Hence, two-phase flow can be described by a mass-averaged mixture velocity and a diffusive flux representing the difference between the mixture velocity and an individual phase velocity. Through a rigorous derivation, an explicit relation for the diffusive flux was found, and a new set of transport equations for the two-phase mixture was obtained. Compared to the multiphase flow formulation, the new model offers the following advantages: (i) it strongly resembles the single-phase transport theory, thus facilitating both theoretical and numerical analyses; (ii) it requires much fewer nonlinear and coupled differential equations to be solved; and (iii) it is a mixture formulation, thus eliminating the need to handle phase appearance or disappearance and the need to track interfaces separating single- from two-phase regions. Nevertheless, the two-phase mixture model still offers the same predictive capabilities as the conventional multiphase flow model because it is a mathematically equivalent, but reformulated, version of the multiphase flow model (i.e. without making any additional assumptions). In addition, the new model embodies simple algebraic relations describing the relative motion between the two-phase mixture and an individual phase, so that the intrinsic characteristics of the phase dynamics (e.g. the phase velocity fields) can be calculated after a converged solution to the governing equations for the two-phase mixture is obtained. Several sample calculations and model validation against experimental data have shown that the two-phase mixture model provides an attractive alternative to the conventional multiphase approach for problems involving phase change heat transfer [19–22].

Recognizing the advantages and computational merits of the two-phase mixture model, the present study aims at extending this previous model for *single-component, two-phase* systems to generally *multiphase, multicomponent* situations. Efforts are focused on developing a multiphase mixture formulation for multiphase, multicomponent transport through capillary porous media that is both physically meaningful and numerically amenable to solutions by standard numerical procedures for single-phase flow and transport problems.

In Section 2, Abriola and Pinder's multiphase flow model [12] is used to derive a consistent set of conservation equations of mass, momentum, species and energy for a multiphase mixture. As in a classical multicomponent mixture, all physical properties of the multiphase mixture are consequences of the properties of its constituents; however, their functional forms are not assumed *a priori*, but are derived strictly from the multiphase flow formulation. Hence, mathematically, the present multiphase mixture model is exactly equivalent to the existing multiphase flow formulation which enjoys widespread applications in the current literature. The differences between these two models lie solely in the number and form of the governing equations, their physical meanings and amenability to numerical implementation.

In Section 3, application of the present model to two-phase, binary systems is demonstrated in order to provide a specific example for further elaboration. In a companion paper [23], the capabilities of the multiphase mixture model are demonstrated through numerically simulating the transport of several nonaqueous phase liquids into the unsaturated subsurface after a hypothetical spill.

2. MODEL FORMULATION

In the present multiphase mixture model, the multiple phases are regarded as constituents of a multiphase mixture. So as to distinguish this mixture from a conventional *multicomponent* mixture [24], it is referred to as a *multiphase* mixture in this work. In this definition, phases are assumed to be distinct and separable components with nonzero interfacial areas, and their mixture represents a single fluid with smoothly varying phasic compositions. In contrast, a multicomponent mixture is defined as consisting of different chemical components. The development of the present formulation is based on the classical multiphase approach, which is briefly reviewed below; for more details, the reader is referred to Abriola and Pinder [12]. A complete list of symbols is given in the Nomenclature.

2.1. *Multiphase approach*

As shown in Abriola and Pinder [12], the multiphase approach results in the following equations which govern multiphase, multicomponent transport in a porous medium:

(*i*) *Mass conservation in phase* k.

$$\varepsilon\frac{\partial(\rho_k s_k)}{\partial t}+\nabla\cdot(\rho_k\mathbf{u}_k)=\dot{m}_k, \qquad (1)$$

where ε is the porosity of the porous medium, s_k is the phase saturation denoting the volumetric fraction of the void space occupied by phase k, and $\mathbf{u}_k$ is the superficial (or Darcian) velocity vector based on the total cross-sectional area of multiple fluids and porous medium. The term $\dot{m}_k$ represents an interfacial mass transfer rate from all other phases to phase k. In the absence of any external mass source or sink, it follows that

$$\sum_k \dot{m}_k = 0. \qquad (2)$$

Equations (1) and (2) assume that the porous medium is not deformable.

(*ii*) *Momentum conservation in phase* k *in the form of the generalized Darcy's law.*

$$\mathbf{u}_k=-K\frac{k_{rk}}{\mu_k}(\nabla p_k-\rho_k\mathbf{g}), \qquad (3)$$

where the presence of the gravitational force has been taken into account. In equation (3), K is the absolute permeability of the porous medium, and k_r denotes the relative permeability of a phase and is a function of phase saturations alone. The difference between the pressures for two adjacent phases k and j is called a capillary pressure

$$p_{ckj}=p_k-p_j. \qquad (4)$$

The capillary pressure, p_{ckj}, depends only on the pore geometry, fluid physical properties and phase saturations [2], i.e.

$$p_{ckj}=fn(\varepsilon,\sigma_{kj},s_1,s_2,\ldots s_k,\ldots), \qquad (5)$$

where σ_{kj} is the interfacial tension at the k–j interface.

(*iii*) *Mass conservation of species* α *in phase* k.

$$\frac{\partial}{\partial t}(\varepsilon\rho_k s_k C_k^\alpha)+\nabla\cdot(\rho_k\mathbf{u}_k C_k^\alpha) = -\nabla\cdot\mathbf{j}_k^\alpha+\bar{J}_k^\alpha, \quad (6)$$

where C_k^α stands for the mass concentration of species α in phase k, and $\mathbf{j}_k^\alpha$ is a diffusive flux of species α in phase k due to molecular diffusion and/or hydrodynamic dispersion. The latter is usually expressed in Fickian form

$$\mathbf{j}_k^\alpha = -\varepsilon\rho s_k\mathbf{D}_k^\alpha\nabla C_k^\alpha, \quad (7)$$

where $\mathbf{D}_k^\alpha$ is a macroscopic second-order tensor which is a function of molecular diffusion coefficient and fluid velocity. A discussion on how to evaluate this coefficient will be briefly presented in Section 2.3. Nonetheless, it should be noted that a great deal of research is presently being directed to this area; see, for example, Brenner and Edwards [25].

The last term $\bar{J}_k^\alpha$ in equation (6) denotes the interphase species transfer rate caused by chemical nonequilibrium and/or phase change at the interfaces between phase k and all other phases. Recognizing that the production of species α in phase k must be accompanied by destruction of species α in other phases, it follows that

$$\sum_k \bar{J}_k^\alpha = 0. \quad (8)$$

No external species generation due to chemical or biological reactions is considered in the present paper.

(*iv*) *Energy conservation in phase* k.

$$\frac{\partial}{\partial t}(\varepsilon\rho_k s_k h_k)+\nabla\cdot(\rho_k\mathbf{u}_k h_k) = \nabla\cdot(s_k k_k\nabla T)+\bar{q}_k, \quad (9)$$

where local thermal equilibrium among phases has been assumed ($T_k = T$), and k_k and $\bar{q}_k$ represent the effective thermal conductivity of phase k and the interphase heat flux associated with phase k, respectively. Hence,

$$\sum_k \bar{q}_k = \dot{q}, \quad (10)$$

where $\dot{q}$ stands for an external volumetric heat source or sink. The phase enthalpy h_k is related to the common temperature T via

$$h_k = \int_0^T c_k\,\mathrm{d}T+h_k^0, \quad (11)$$

where c_k represents an effective specific heat of phase k.

The above basic conservation laws provide a full system of governing equations for the unknown vector velocities $\mathbf{u}_k$, scalar pressures p_k, scalar liquid saturations, s_k, mass concentrations, C_k^α, and the common temperature, T.

2.2. *Multiphase mixture model*

The key idea in the multiphase mixture model to be developed is to focus on the level of a multiphase mixture, rather than on the levels of separate phases. Concepts and definitions of the multiphase mixture are thus introduced. This is then followed by the derivation of conservation equations for the multiphase mixture, which constitute the governing equations for the present model. Finally, this section will establish algebraic relations to determine the individual phase variables from the mixture variables that can be obtained by solving the developed governing equations. Therefore, no phase characteristics would be lost. Notice also that no additional assumptions will be made in the following model derivation.

2.2.1. *Concepts and definitions.* Similar to the classical multicomponent mixture, a multiphase mixture can be considered as a fluid consisting of diffusing constituents (phases). As a result, the mixture density and velocity can be defined, respectively, as

$$\rho = \sum_k \rho_k s_k \quad (12)$$

$$\rho\mathbf{u} = \sum_k \rho_k\mathbf{u}_k. \quad (13)$$

Noting that the superficial velocity of a phase, $\mathbf{u}_k$, is related to its intrinsic velocity by the phase volume fraction, equation (13) implies that the mixture velocity is a mass-weighted average of the intrinsic phase velocities.

The mixture kinematic viscosity is given by

$$\nu = \left(\sum_k \frac{k_{rk}}{\nu_k}\right)^{-1} \quad (14)$$

and the mobility of each phase in the multiphase mixture is defined as

$$\lambda_k = \frac{k_{rk}}{\nu_k}\nu;\quad \sum_k \lambda_k = 1. \quad (15)$$

Specification of the mixture pressure is a little more involved because of the differences between various phase pressures owing to the capillary forces. For the reasons that will become apparent shortly, the mixture pressure is so defined that the following differential equation holds:

$$\nabla p = \sum_j \lambda_j\nabla p_j = \nabla p_k+\sum_j \lambda_j\nabla p_{cjk}. \quad (16)$$

Notice that the capillary pressure between each pair of phases (k and j), as defined in equation (5), is dependent upon phase saturations and the interfacial tension, σ_{jk}, the latter of which is, in turn, a function of concentration and temperature. Therefore, taking the gradient over equation (5) yields

$$\nabla p_{cjk} = \sum_i \frac{\partial p_{cjk}}{\partial s_i}\nabla s_i+\frac{\partial p_{cjk}}{\partial\sigma_{jk}}\left[\sum_\alpha \frac{\partial\sigma_{jk}}{\partial C^\alpha}\nabla C^\alpha+\frac{\partial\sigma_{jk}}{\partial T}\nabla T\right]. \quad (17)$$

Substituting the above into equation (16) results in

$$\nabla p = \nabla p_k + \sum_i Ca_{ik}\,\nabla s_i + \sum_\alpha Cs_{\alpha k}\,\nabla C^\alpha + Ct_k\,\nabla T, \tag{18}$$

where Ca_{ik}, $Cs_{\alpha k}$ and Ct_k, called the capillary, solutal-capillary and thermocapillary factors respectively, can be expressed as

$$Ca_{ik} = \sum_j \lambda_j \frac{\partial p_{cjk}}{\partial s_i} \tag{19}$$

$$Cs_{\alpha k} = \sum_j \lambda_j \frac{\partial p_{cjk}}{\partial \sigma_{jk}} \frac{\partial \sigma_{jk}}{\partial C^\alpha} \tag{20}$$

$$Ct_k = \sum_j \lambda_j \frac{\partial p_{cjk}}{\partial \sigma_{jk}} \frac{\partial \sigma_{jk}}{\partial T}. \tag{21}$$

Integration of equation (18) leads to the following explicit definition of the mixture pressure:

$$p = p_k + \sum_i \int_0^{s_i} Ca_{ik}\,\mathrm{d}s_i + \sum_\alpha \int_0^{C^\alpha} Cs_{\alpha k}\,\mathrm{d}C^\alpha + \int_0^T Ct_k\,\mathrm{d}T. \tag{22}$$

Obviously, when the capillary forces are negligibly small, the last three terms in equation (22) vanish so that $p = p_k$. Moreover, as the saturation of phase k, s_k, approaches unity (i.e. all other phase saturations are identically zero), the three factors defined in equations (19)–(21) become zero (since $\lambda_j = 0$ for $j \neq k$), so that the mixture pressure defined in equation (22) reduces to the appropriate single-phase pressure p_k. These observations show that the definition in equation (22) is indeed consistent with a mixture theory. Later, we shall show how this definition can simplify the momentum conservation equation for a bulk mixture.

2.2.2. *Conservation of mass.* The mass conservation equation for a multiphase mixture can readily be obtained by the addition of the phase conservation equations as represented by equation (1). Note that the production of phase k, $\dot{m}_k$, must come at the expense of the other phases [equation (2)]. Hence,

$$\varepsilon \frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = 0. \tag{23}$$

It is clear that this continuity equation is just a duplicate of the corresponding equation for a single-phase mixture flow. Since the mixture density ρ is strongly variable, the multiphase mixture flow should be categorized as highly compressible.

2.2.3. *Conservation of momentum.* Before deriving the mixture momentum equation, the phase momentum equation, equation (3), is first cast into

$$\rho_k \mathbf{u}_k = -\frac{Kk_{rk}}{\nu_k}(\nabla p_k - \rho_k \boldsymbol{g}) = -\frac{K}{\nu}(\lambda_k\,\nabla p_k - \lambda_k \rho_k \boldsymbol{g}), \tag{24}$$

where use has been made of the definition of the relative mobility, equation (15). The momentum equation for the multiphase mixture is then obtained by summing up the above equations for each phase. Utilizing the definitions of the mixture velocity and pressure given by equations (13) and (16), one arrives at

$$\rho \mathbf{u} = -\frac{K}{\nu}(\nabla p - \gamma_\rho \rho \boldsymbol{g}), \tag{25}$$

where γ_ρ is called the density correction factor and is defined as

$$\gamma_\rho = \frac{\sum_k \rho_k \lambda_k}{\sum_k \rho_k s_k}. \tag{26}$$

It should be noted that this correction factor is a sole function of the phase saturations and, thus, can be regarded as a property of the multiphase mixture. The physical reason that a correction factor arises in the body force term for a multiphase mixture is the relative motion among phases, so that the effective mixture density for the gravitational force contains certain dynamic properties of phases (i.e. λ_k and hence ν_k). Only when $\gamma_\rho = 1$, the body force for the multiphase mixture can be represented by the mixture density defined in equation (12). This is the case of multicomponent mixtures.

As in a traditional mixture theory, one can define a diffusive mass flux of phase k within the multiphase mixture, such that

$$\mathbf{j}_k = \rho_k \mathbf{u}_k - \lambda_k \rho \mathbf{u}; \quad \sum_k \mathbf{j}_k = 0 \tag{27}$$

or rearranging,

$$\rho_k \mathbf{u}_k = \mathbf{j}_k + \lambda_k \rho \mathbf{u}. \tag{28}$$

Substituting the momentum equations for phase k and for the mixture given by equations (24) and (25) into equation (27), the diffusive mass flux, $\mathbf{j}_k$, can be expressed as follows:

$$\mathbf{j}_k = K\frac{\lambda_k}{\nu}(\nabla p - \nabla p_k) + K\frac{\lambda_k}{\nu}(\rho_k - \gamma_\rho \rho)\boldsymbol{g}. \tag{29}$$

In lieu of equation (18) and utilizing the identity

$$\rho_k - \gamma_\rho \rho = \sum_i \lambda_i(\rho_k - \rho_i) \tag{30}$$

equation (29) becomes

$$\mathbf{j}_k = \sum_i \left[-\rho_k D_{cik}\,\nabla s_i + \frac{\lambda_k \lambda_i K(\rho_k - \rho_i)}{\nu}\boldsymbol{g} \right] + \sum_\alpha [-\rho_k D_{s\alpha k}\,\nabla C^\alpha] + (-\rho_k D_{tk})\,\nabla T, \tag{31}$$

where the capillary diffusion coefficient, D_{cik}, the solutal-capillary diffusion coefficient, $D_{s\alpha k}$, and the thermocapillary diffusion coefficient, D_{tk}, are given by

$$D_{cik} = \frac{K}{\rho_k \nu} \lambda_k \sum_j \lambda_j \left[-\frac{\partial p_{cjk}}{\partial s_i} \right] \tag{32}$$

$$D_{s\alpha k} = \frac{K}{\rho_k \nu} \lambda_k \sum_j \lambda_j \left[-\frac{\partial p_{cjk}}{\partial \sigma_{jk}} \frac{\partial \sigma_{jk}}{\partial C^\alpha} \right] \tag{33}$$

$$D_{tk} = \frac{K}{\rho_k \nu} \lambda_k \sum_j \lambda_j \left[-\frac{\partial p_{cjk}}{\partial \sigma_{jk}} \frac{\partial \sigma_{jk}}{\partial T} \right]. \tag{34}$$

Physically, equation (31) implies that the diffusive flux of phase k within the multiphase mixture results from the capillary forces due to saturation gradients, as well as concentration and temperature gradients through their effects on the interfacial tensions. In addition, the second term on the right hand side (RHS) of equation (31) reflects the gravitational separation due to the difference between phase densities. Note also that the diffusion coefficients defined by equations (32)–(34) depend only on phase saturations and, hence, are properties of the multiphase mixture.

Now, with the aid of equations (28) and (31)–(34), the flow dynamics of individual phases can readily be obtained, once the flow problem of the bulk mixture has been solved. Thus, the detailed flow characteristics of each phase are not smeared out in the present model; they are still accessible wherever they are needed. This is why the model is called the *multiphase mixture model*, rather than simply a mixture model, implying that, in the latter, the intrinsic multiphase characteristics are usually lost.

2.2.4. *Conservation of species*. To derive the species conservation equation for the multiphase mixture, a mass-averaged mixture concentration of species α over all phases is defined as

$$\rho C^\alpha = \sum_k \rho_k s_k C_k^\alpha. \tag{35}$$

To construct a transport equation for C^α, equation (6) is summed over all phases to yield

$$\varepsilon \frac{\partial}{\partial t} \left\{ \sum_k \rho_k s_k C_k^\alpha \right\} + \nabla \cdot \left\{ \sum_k \rho_k \mathbf{u}_k C_k^\alpha \right\} = -\nabla \cdot \left\{ \sum_k \mathbf{j}_k^\alpha \right\}, \tag{36}$$

where use has been made of the constraint, equation (8). By definition of the mixture concentration given by equation (35) and using equation (28) to decompose the phase velocity, the phase-summed species conservation equation can be recast into

$$\varepsilon \frac{\partial}{\partial t}(\rho C^\alpha) + \nabla \cdot \left[\left(\sum_k \lambda_k C_k^\alpha \right) \rho \mathbf{u} \right] = -\nabla \cdot \left\{ \sum_k C_k^\alpha \mathbf{j}_k \right\} - \nabla \cdot \left\{ \sum_k \mathbf{j}_k^\alpha \right\}, \tag{37}$$

where the species diffusion flux, $\mathbf{j}_k^\alpha$, is given by equation (7). To further cast equation (37) into a form similar to a traditional species transport equation in a single-phase flow, one can define a correction factor for species advection as

$$\gamma_\alpha = \frac{\rho \sum_k \lambda_k C_k^\alpha}{\sum_k \rho_k s_k C_k^\alpha}. \tag{38}$$

As a result, equation (37) can be finally rewritten as

$$\varepsilon \frac{\partial}{\partial t}(\rho C^\alpha) + \nabla \cdot (\gamma_\alpha \rho \mathbf{u} C^\alpha) = \nabla \cdot [\varepsilon \rho D \nabla C^\alpha] + \nabla \cdot \left\{ \varepsilon \sum_k [\rho_k s_k D_k^\alpha (\nabla C_k^\alpha - \nabla C^\alpha)] \right\} - \nabla \cdot \left(\sum_k C_k^\alpha \mathbf{j}_k \right), \tag{39}$$

where the effective diffusion coefficient for the multiphase mixture is defined as

$$\rho D = \sum_k \rho_k s_k D_k^\alpha. \tag{40}$$

The first two terms on the RHS of equation (39) combine to represent the net Fickian diffusion flux within various phases, while the last term on the RHS represents the diffusive flux across phases. In addition, the second term on the LHS of equation (39) indicates that species α is advected, on the mixture level, by a modified velocity field $\gamma_\alpha \mathbf{u}$ rather than the original mixture velocity field. This peculiar feature resembles the one related to the gravitational term in the momentum equation, equation (25).

A particular case of equation (39) for multiphase flows without interphase mass transfer is worth exploring. In this situation, the concentration of species α in phase k, C_k^α, is equal to zero for $\alpha \neq k$, but unity for $\alpha = k$. Hence, we have that $\rho C^\alpha = \rho_k s_k$ and $\rho C^\alpha \gamma_\alpha = \rho \lambda_k$ by the definitions, equations (37) and (38). Subsequently, equation (39) is simplified as follows:

$$\varepsilon \frac{\partial(\rho_k s_k)}{\partial t} + \nabla \cdot (\rho \mathbf{u} \lambda_k) = -\nabla \cdot \mathbf{j}_k, \tag{39a}$$

where the species diffusion terms vanish due to uniform concentrations in all phases. Equation (39a) can be used to solve for the phase saturations in multiphase flows without interphase mass transfer where species concentrations become trivial. Note also that equation (39a) is a generalized form of the liquid mass balance equation derived earlier for two-phase systems [18].

2.2.5. *Conservation of energy*. The conservation equation for energy in the multiphase mixture is

$$\frac{\partial}{\partial t} \left[(1-\varepsilon)\rho_s h_s + \varepsilon \sum_k \rho_k s_k h_k \right] + \nabla \cdot \left(\sum_k \rho_k \mathbf{u}_k h_k \right) = \nabla \cdot (k_{\text{eff}} \nabla T) + \dot{q} \tag{41}$$

which results from the summation of phase energy equations represented by equation (9) and the constraint given by equation (10). The term k_{eff} stands for an effective thermal conductivity of the multiple flowing phases combined with the solid matrix phase, and $\dot{q}$ is a volumetric heat source.

The advective term in the energy equation, equation (41), can be further decomposed, with the help of equation (28), into contributions due to the bulk mixture motion and intrinsic relative phase motion, i.e.

$$\sum_k \rho_k \mathbf{u}_k h_k = \rho \mathbf{u} \sum_k \lambda_k h_k + \sum_k h_k \mathbf{j}_k. \qquad (42)$$

Defining the mixture enthalpy h as

$$\rho h = \sum_k \rho_k s_k h_k \qquad (43)$$

and the correction factor for energy advection, γ_{h}, as

$$\gamma_{\mathrm{h}} = \frac{\rho \sum_k \lambda_k h_k}{\sum_k \rho_k s_k h_k} \qquad (44)$$

the energy equation can be simplified to the following form in which only mixture variables are involved:

$$\frac{\partial}{\partial t}[(1-\varepsilon)\rho_{\mathrm{s}} h_{\mathrm{s}} + \varepsilon \rho h] + \nabla \cdot (\gamma_{\mathrm{h}} \rho \mathbf{u} h) = \nabla \cdot (k_{\mathrm{eff}} \nabla T) + \nabla \cdot \left[\sum_k (h_k \mathbf{j}_k)\right] + \dot{q}. \qquad (45)$$

To further eliminate the temperature as an explicit dependent variable, we note the following identity obtained from the enthalpy definition:

$$\nabla T = \frac{1}{c_j} \nabla h_j = \frac{1}{c_j} \nabla h + \frac{1}{c_j} \nabla (h_j - h), \qquad (46)$$

where j denotes an arbitrary phase. Substituting equation (46) into equation (45) yields

$$\frac{\partial}{\partial t}[(1-\varepsilon)\rho_{\mathrm{s}} h_{\mathrm{s}} + \varepsilon \rho h] + \nabla \cdot (\gamma_{\mathrm{h}} \rho \mathbf{u} h) = \nabla \cdot \left(\frac{k_{\mathrm{eff}}}{c_j} \nabla h\right) + \nabla \cdot \left[\frac{k_{\mathrm{eff}}}{c_j} \nabla (h_j - h)\right] + \nabla \cdot \left[\sum_k (h_k \mathbf{j}_k)\right] + \dot{q}. \qquad (47)$$

The physical meanings of all the terms appearing in equation (47) are apparent, since the equation strongly resembles the classical formulation describing heat transfer of a single-phase multicomponent mixture inside porous media. Nevertheless, several salient features are worth outlining. First, equation (47) is a variable-property equation, in which all physical properties are strongly dependent on phase saturations. Also, we include a source term to account for possible volumetric heating. Secondly, the third term on the RHS describes the energy flux due to relative phase motions, including both sensible and latent heat transport. Lastly, equation (47) is valid throughout an entire problem domain which may simultaneously involve single- and multi-phase subregions.

2.3. *Supplementary relationships*

The system of conservation equations obtained above for a multiphase mixture requires constitutive equations for relative permeabilities, $k_{\mathrm{r}k}$, capillary pressure functions, p_{cjk}, the effective mass diffusivity, $\mathbf{D}_k^{\alpha}$, and the thermal conductivity, k_{eff}.

In general, the relative permeabilities are assumed to be known functions of the phase saturations, which must be empirically determined. The capillary pressure functions are dependent upon both phase saturations and interfacial tensions. They are generally multi-valued, and exhibit hysteretic behaviors. The capillary pressure function for a liquid–gas two-phase system can be evaluated from Udell's correlation [26], while three-phase capillary pressure functions can be developed from two-phase relationships, as discussed by Parker *et al.* [27].

The effective mass diffusivity, $\mathbf{D}_k^{\alpha}$, and the thermal conductivity, k_{eff}, for a system consisting of a solid matrix and the flowing multiphase mixture are usually complicated functions of the thermophysical properties of the fluids and solid matrix, phase velocities, pore microstructure and phase saturations. While there is no general formula used to evaluate these parameters, correlations for specialized situations are abundant in the existing literature [28].

Finally, to close the mathematical system, expressions are needed to determine phase saturations s_k and compositions C_k^{α} within all the phases. For a wide range of practical applications, a multiphase system can be closely approximated by the assumption of local chemical equilibrium at phase interfaces. This assumption of interfacial equilibrium does not rule out the possibility of phase composition gradients on a macroscopic scale, but rather implies that within some short time scale (essentially instantaneously) contiguous phases reach a thermodynamic equilibrium. Thus, the mass concentration in the gas phase can be related to temperature and pressure through equilibrium phase diagrams, i.e.

$$C_{\mathrm{g}}^{\alpha} = C_{\mathrm{g}}^{\alpha}(T, p). \qquad (48)$$

The concentrations of this same species in other phases can be related to the above one in the gas phase through the partitioning concept

$$C_k^{\alpha} = K_{k\mathrm{g}}^{\alpha} C_{\mathrm{g}}^{\alpha}, \qquad (49)$$

where $K_{k\mathrm{g}}^{\alpha}$ is called the partition coefficient of species α between the phases k and g. In general, partition coefficients are represented by functions of phase compositions and pressures. These coefficients may be determined from Henry's law constants and solubility relations.

The phase saturations s_k can be determined by solving equation (39) for the mixture concentrations. For an m-phase, n-component system, equation (39) represents $(n-1)$ equations for $(m-1)$ unknown phase saturations. The other phase saturation can be obtained from the constraint that the summation of all phase saturations is equal to unity. According to Gibbs phase rule, n is always equal to or greater than m when the multiphase, multicomponent system has two or more degrees of freedom (i.e. one for the temperature and others for phase saturations); therefore, equation (39) provides a sufficient number of equations to solve for all phase saturations. A specific example is given in Section 3.

It is important to recognize that the assumption of local thermal and chemical equilibrium does not preclude the existence of nonequilibrium conditions on a larger macroscopic scale. Macroscopic redistribution of species by both advective and diffusive transport is accommodated in equation (39). If local equilibrium is unlikely, as in some rapid spread processes of chemical compounds [29], alternative means of relating the mixture concentration with the phase compositions would be required. This nonequilibrium case will be studied in a future publication.

2.4. *Initial/boundary conditions*

In order to make problems well-posed, appropriate boundary and initial conditions are required for the present multiphase mixture formulation. Initial conditions are usually known or taken from a steady-state solution. Various types of hydrodynamic boundary conditions are possible. The first and most common type is the impermeable condition, which requires no mass exchange through the wall. If the wall is at rest in the chosen frame of reference, this implies that the normal component of the mixture velocity must vanish; i.e.

$$\mathbf{u}\cdot\mathbf{n} = 0. \tag{50}$$

However, a slip condition is allowed at the impermeable surface, since Darcy's law is used here to formulate the momentum equation for the multiphase mixture. Other important types of hydrodynamic boundary conditions include constant mass flow rates of the multiphase mixture and constant pressures along permeable surfaces; both can be directly implemented in the present formulation. Boundary conditions for concentration and temperature fields are analogous to those for two-phase systems as discussed in Wang and Beckermann [18].

3. APPLICATION TO TWO-PHASE, BINARY SYSTEMS

In the preceding section, a general multiphase mixture model has been rigorously derived from the classical multiphase approach, without invoking additional approximations. In other words, the new model is an alternative, but equivalent, version of the original multiphase flow formulation. In this section we proceed to consider an application to liquid–gas, binary systems. Examples of such systems include organic liquid–air during groundwater contamination, water–air in drying processes, and binary mixtures in heat pipes. For binary systems, species concentration equations need only be considered for one species, since the overall species conservation requires $\Sigma_\alpha C^\alpha = 1$. In the remainder of this paper, the symbol C without superscript is reserved for the mass concentration of the more volatile component, while the concentration of the less volatile component is simply equal to $(1-C)$. The liquid and gas saturations are denoted by s_l and s_g (i.e. $1-s_l$, respectively).

3.1. *Governing equations*

The basic conservation laws for the multiphase mixture derived in the preceding section reduce to the following for a two-phase, binary system:

mass conservation

$$\varepsilon\frac{\partial\rho}{\partial t}+\nabla\cdot(\rho\mathbf{u}) = 0; \tag{51}$$

momentum conservation

$$\rho\mathbf{u} = -\frac{K}{\nu}(\nabla p-\gamma_\rho\rho\boldsymbol{g}); \tag{52}$$

species conservation

$$\begin{aligned}\varepsilon\frac{\partial}{\partial t}(\rho C)+\nabla\cdot(\gamma_s\rho\mathbf{u}C) &= \nabla\cdot(\varepsilon\rho D\nabla C)\\ &\quad+\nabla\cdot[\varepsilon(\rho_l s_l D_l\nabla C_l+\rho_g s_g D_g\nabla C_g-\rho D\nabla C)]\\ &\quad-\nabla\cdot[(C_l-C_g)\mathbf{j}_l]; \end{aligned}\tag{53}$$

conservation of energy

$$\begin{aligned}\frac{\partial}{\partial t}[(1-\varepsilon)\rho_s h_s+\varepsilon\rho h]+\nabla\cdot(\gamma_h\rho\mathbf{u}h)\\ = \nabla\cdot\left(\frac{k_{\mathrm{eff}}}{c_l}\nabla h\right)+\nabla\cdot\left[\frac{k_{\mathrm{eff}}}{c_l}\nabla(h_l-h)\right]\\ +\nabla\cdot[(h_l-h_g)\mathbf{j}_l]+\dot{q}, \end{aligned}\tag{54a}$$

where the liquid specific heat is chosen for the first two terms on the RHS for the special case of a two-phase, liquid–gas system. Noting that

$$h_l-h_g = h_{fg}+\int_0^T(c_l-c_g)\,\mathrm{d}T \tag{54b}$$

the third term on the RHS of equation (54a) physically implies that migration of phases is accompanied by the transport of both latent and sensible heats. Equations (51)–(54) represent the governing equations for the mixture unknowns: $\mathbf{u}$, p, h and C.

In addition to the above basic conservation equations, the present formulation embodies the following important relation for calculating the individual phase velocities from the mixture flow field:

$$\mathbf{j}_l = \rho_l(-D_c\nabla s_l-D_s\nabla C-D_t\nabla T)+\frac{\lambda_l\lambda_g K(\rho_l-\rho_g)}{\nu}\boldsymbol{g}. \tag{55}$$

Physically, the first three terms represent the capillary diffusion due to meniscus curvature, solutal- and thermo-capillary effects. The last term accounts for gravity-induced phase migration. The various capillary diffusion coefficients are simplified as

$$D_c = \frac{K}{\rho_l \nu}\lambda_l\lambda_g\left[-\frac{\partial p_c}{\partial s_l}\right] \tag{56}$$

$$D_s = \frac{K}{\rho_l \nu}\lambda_l\lambda_g\left[-\frac{\partial p_c}{\partial \sigma}\frac{\partial \sigma}{\partial C}\right] \tag{57}$$

$$D_t = \frac{K}{\rho_l \nu}\lambda_l\lambda_g\left[-\frac{\partial p_c}{\partial \sigma}\frac{\partial \sigma}{\partial T}\right]. \tag{58}$$

The individual phase velocities are then calculated from

$$\rho_l \mathbf{u}_l = \mathbf{j}_l + \lambda_l \rho \mathbf{u} \tag{59}$$

and

$$\rho_g \mathbf{u}_g = -\mathbf{j}_l + \lambda_g \rho \mathbf{u}. \tag{60}$$

3.2. *Constitutive relations*

The relative permeabilities for liquid and gas phases are well represented by [30]

$$k_{rl} = s_l^n \tag{61}$$

$$k_{rg} = (1-s_l)^n, \tag{62}$$

where the power index may vary between 1 and 3. The two-phase capillary pressure can be expressed in terms of a Leverett function $J(s_l)$ [26], namely

$$p_c = p_g - p_l = \sigma\left(\frac{\varepsilon}{K}\right)^{1/2} J(s_l), \tag{63}$$

where

$$J(s_l) = 1.417(1-s_l) - 2.120(1-s_l)^2 + 1.263(1-s_l)^3. \tag{64}$$

Substituting equation (63) into equations (56)–(58), all the capillary diffusion coefficients can further be expressed as explicit functions of the liquid saturation s_l; i.e.

$$D_c = \frac{K}{\rho_l \nu}\lambda_l\lambda_g\sigma\left(\frac{\varepsilon}{K}\right)^{1/2}[-J'(s_l)] \tag{65}$$

$$D_s = \frac{K}{\rho_l \nu}\lambda_l\lambda_g\left(\frac{\varepsilon}{K}\right)^{1/2}\left[-J(s_l)\frac{\partial \sigma}{\partial C}\right] \tag{66}$$

$$D_t = \frac{K}{\rho_l \nu}\lambda_l\lambda_g\left(\frac{\varepsilon}{K}\right)^{1/2}\left[-J(s_l)\frac{\partial \sigma}{\partial T}\right]. \tag{67}$$

The mass diffusivities of species within each phase include both molecular and hydrodynamic dispersion parts; i.e.

$$D_k = \tau_k D_k^m + D_k^d, \tag{68}$$

where D_k^m and D_k^d denote the molecular binary diffusion coefficient and species dispersion coefficient, respectively. The phase tortuosity τ_k can usually be determined empirically. For a single-phase flow in porous media, Koch and Brady [31] obtained an expression for the species dispersion coefficient. However, in view of the fact that the species dispersion coefficient for a two-phase binary mixture in porous media is not fully understood, we shall neglect this effect as a first approximation.

The effective thermal conductivity for the solid matrix and two-phase mixture system can be obtained in a similar fashion [32],

$$k_{\text{eff}} = k_{\text{eff}}^m + k_{\text{eff}}^d, \tag{69}$$

where k_{eff}^m and k_{eff}^d again denote the molecular thermal conductivity and thermal dispersion coefficient, respectively. These parameters can be calculated, for example, from

$$k_{\text{eff}}^m = k(s_l = 0) + s_l^{1/2}[k(s_l = 1) - k(s_l = 0)], \tag{70}$$

where the single-phase stagnant thermal conductivity k can be obtained from the following expression due to Zehner and Schlünder [33]:

$$\frac{k}{k_f} = [1-\sqrt{1-\varepsilon}] - \frac{2\sqrt{1-\varepsilon}}{1-\lambda B}\left[\frac{(1-\lambda)B}{(1-\lambda B)^2}\ln(\lambda B) + \frac{B+1}{2} + \frac{B-1}{1-\lambda B}\right], \tag{71}$$

where

$$\lambda = \frac{k_f}{k_s};\quad B = 1.25\left[\frac{1-\varepsilon}{\varepsilon}\right]^{10/9} \tag{72}$$

for packed-sphere beds. An expression for the thermal dispersion conductivity of a single-phase flow in a porous medium is given by Hsu and Cheng [32]. However, the thermal dispersion theory for two-phase systems in a porous medium is still in its infancy; thus, this effect will be neglected in the present work as a first approximation.

3.3. *Phase diagram*

A typical binary phase diagram at constant system pressure is schematically shown in Fig. 1. In the diagram, the dew-point curve represents the locus of points at which condensation is first observed, as the binary mixture of a certain concentration is cooled at constant pressure. Similarly, the bubble-point curve is the locus of points at which vaporization begins as the binary mixture is heated at constant pressure. It is seen from Fig. 1 that for a system with fixed temperature and pressure, the saturated concentration of the more volatile component in the vapor is higher than that in the liquid.

In a functional form, the phase diagram can be represented by

$$C_l = C_l^e(T,p) \quad\text{and}\quad C_g = C_g^e(T,p). \tag{73}$$

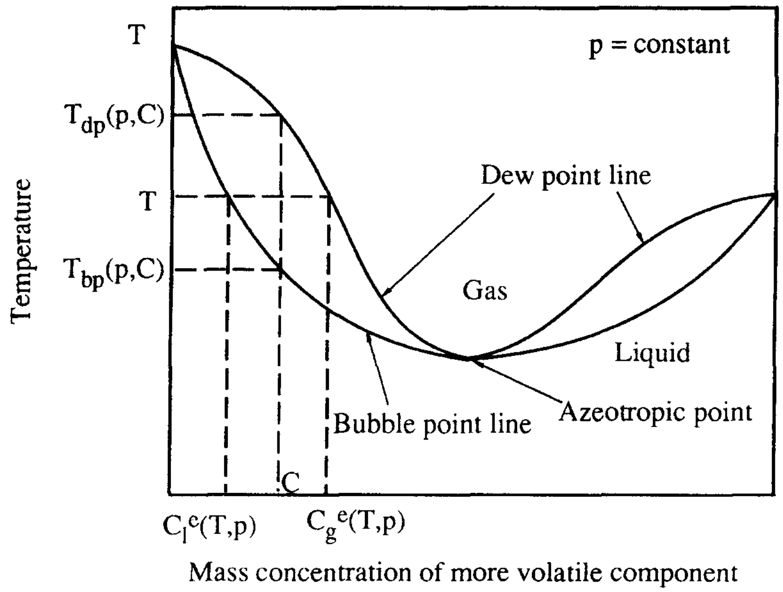

Fig. 1. Schematic of equilibrium binary phase diagram.

Two particular cases of binary phase diagrams may be noted. In a system containing a noncondensible gas, C denotes the mass concentration of the noncondensible gas according to our convention. Hence, one has

$$C_l = 0 \quad \text{and} \quad C_g^e = 1 - \frac{p_v(T)M_v}{R_g\rho_g T}, \tag{74}$$

where p_v is the vapor partial pressure in the gas phase and can be calculated from the saturated vapor table.

In the other situation where one component is present only in the liquid phase, for example, for a brine mixture consisting of water and salt in the liquid and only water vapor in the gas phase, one then has

$$C_g = 1 \quad \text{and} \quad C_l = C_l^e(T,p), \tag{75}$$

where the symbol C denotes the mass concentration of water vapor, and C_l^e is the maximum solubility of water in the liquid phase.

As mentioned in Section 2, the phase saturations are obtained from the definition of the mixture concentration; namely,

$$\rho C = \rho_l s_l C_l + \rho_g s_g C_g. \tag{76}$$

Since $C_l = C_l^e$, $C_g = C_g^e$ and $s_l + s_g = 1$ in the liquid–gas coexisting zone, equation (76) can be rearranged to yield

$$s_l = \frac{\rho_g(C - C_g^e)}{\rho_l(C_l^e - C) + \rho_g(C - C_g^e)}, \tag{77}$$

where the mixture concentration C is determined from the species transport equation, equation (53), and must be bounded by C_g^e and C_l^e. For situations where $C > C_g^e$, then the thermodynamic state of the system is in the pure gas phase, so that $s_l = 0$ and $C_g = C$. In the other limit where $C < C_l^e$, the system consists of the pure liquid phase, so that $s_l = 1$ and $C_l = C$.

In summary, from the mixture concentration, temperature and pressure as determined from the governing equations presented in Section 3.1, various thermodynamic states can be identified according to the conditions summarized in Table 1, and the phase saturations and concentrations are determined accordingly. As can be noted, a salient feature of the present formulation is that the principal equations governing the two-phase transport are valid throughout a problem domain involving various thermodynamic states. A specific thermodynamic state will only affect the auxiliary relations.

4. SUMMARY AND DISCUSSION

A multiphase mixture formulation for analyzing multiphase flow and transport in capillary porous media has been developed. The classical multiphase flow descriptions have been employed to obtain a consistent set of equations governing the conservation of mass, momentum, species and energy for the multiphase mixture. The solution sequence is as follows: (1) from the transport equations for the multiphase mixture, the mixture pressure, velocity, concentration and temperature fields are determined; (2) from the mixture pressure, concentration and temperature at a nodal point, the thermodynamic state of this cell is identified as in Table 1; (3) phase concentrations are then calculated from equilibrium phase diagrams and the phase saturations are determined from the mixture concentration solved from the species transport equation; (4) effective thermophysical properties of the multiphase mixture are then evaluated with the knowl-

Table 1. Thermodynamic states in two-phase, binary systems

Conditions	$C < C_l^e(T,p)$	$C_l^e(T,p) < C < C_g^e(T,p)$	$C > C_g^e(T,p)$
Thermodynamic state	liquid	two-phase	gas
Liquid saturation, s_l	1	$\dfrac{\rho_g(C-C_g^e)}{\rho_l(C_l^e-C)+\rho_g(C-C_g^e)}$	0
Concentration in the liquid phase, C_l	C	$C_l^e(T,p)$	0
Concentration in the gas phase, C_g	0	$C_g^e(T,p)$	C

edge of phase saturations, and finally these properties are substituted back into the transport equations for updating. The entire procedure is iteratively repeated until convergence is achieved. Several salient features of the present formulation become evident from this solution procedure and are discussed in detail below.

In contrast to the existing multiphase approach which is a multi-domain formulation, the present multiphase mixture model represents a single-domain formulation, since all governing equations are valid throughout a problem domain including single- and multi-phase regions. Therefore, the present formulation eliminates the need to track moving phase interfaces and uses of the variable or equation switching technique [17, 34] or numerical remeshing and coordinate mapping [16]. Furthermore, the present formulation strongly resembles the single-phase transport equations, making it possible to take full advantage of well established single-phase computational fluid dynamics (CFD) algorithms.

More importantly, the present formulation does not smear out intrinsic characteristics of the individual phases, despite the fact that the differential governing equations deal solely with the bulk behavior of the mixture. This is because the formulation embodies simple algebraic relations between the motions of the multiphase mixture as a whole and its separable phases, namely equations (28) and (31) for multiphase systems, and equations (59) and (60) for two-phase systems. The diffusive fluxes contained in these relations can readily be calculated from equation (31), once a converged solution to the governing equations for the multiphase mixture is obtained. Similarly, the phase pressures p_k can be obtained from equation (22) after the mixture pressure, temperature, concentration and phase saturation fields are determined. Moreover, this type of calculation, if needed, can be done in a post-processing manner.

Another attractive feature of the present formulation is that the transport equations need not be modified when a phase appears or disappears. The thermodynamic state of a multiphase system is adaptively recognized through, for example, Table 1. Therefore, no additional implementation or programming is required during phase transitions. In contrast, the conventional multiphase approach has to rely on the minimum saturation criterion [34–36]. The drawback of the latter method may be quite significant in applications of environmental contamination and restoration. For example, the minimum saturation of a toxic organic at a small value of 10^{-4} in a porous medium with porosity of 0.4 would represent 40 ml per cubic meter of the porous medium, which is a significant level of contamination.

Finally, the multiphase mixture model reduces the differential governing equations almost by half when compared to the existing multiphase flow formulation. For example, for a three-phase isothermal flow, the multiphase flow model requires a total of 12 primary variables: two phase saturations, nine velocity components (for three phases in three dimensions) and any one phase pressure. In contrast, the present multiphase mixture model contains only six primary variables: two mixture concentrations or equivalently two phase saturations, three mixture velocity components and the mixture pressure. This unique feature renders the new model suitable for numerical simulations with even moderate computer resources. It is expected that the model opens new prospects for understanding complicated multiphase flows in porous media.

In the present work, special efforts have been made to coach the conservation equations in a convenient form for numerical implementation. In addition, some degree of generality has been sacrificed for the sake of the model's utility in a widely encountered class of multiphase, multicomponent systems. Interfacial thermal and chemical equilibrium has been introduced in the model development for convenience. It should be noted, however, that the multiphase mixture model is not inherently an equilibrium model; in fact, the present model has accounted for dynamic nonequilibrium because it allows for different phase velocities. Similarly, the assumptions of interfacial thermal and chemical equilibrium can be relaxed. Under such circumstances, the differential equations derived in the work remain valid, whereas the supplementary relationships for determining phase saturations, phase temperatures and compositions need to be revised. Under thermal and chemical nonequilibrium, the bulk phase temperature and concentration depart from their interfacial counterparts as determined from equilibrium phase diagrams, depending upon the interfacial heat and mass transfer coefficients. Efforts are presently underway to develop a generalized formulation to cover these special cases. Future work will also consist of applying the present multiphase mixture model to a variety of practical problems as well as providing thorough experimental validation. Numerical solutions of a two-phase, binary mixture problem using the present formulation are fully described in a companion paper [23].

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