Brazilian Journal
of Chemical
Engineering

ISSN 0104-6632
Printed in Brazil

Vol. 20, No. 04, pp. 445 - 453, October - December 2003

THE MODELLING OF A TEXTILE DYEING PROCESS UTILIZING THE METHOD OF VOLUME AVERAGING

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(Received: October 25, 2001 ; Accepted: July 3, 2003)

Abstract - In this work the modelling of a process of textile dyeing of a single cotton thread is presented. This thread moves at a constant velocity within a homogeneous dye solution under steady state conditions. The method of volume averaging is applied to obtain the mass transfer equations related to the diffusion and adsorption process inside the cotton thread on a small scale. The one-equation model is developed for the fiber and dye solution system, assuming the principle of local mass equilibrium to be valid. On a large scale, the governing equations for the cotton thread, including the expression for effective diffusivity tensor, are obtained. Solution of these equations permits the dye concentration profile for inside the cotton thread and in the dyeing batch to be obtained and the best conditions for the dyeing process to be chosen.

Keywords: textile, dyeing, modeling.

INTRODUCTION

The problem under study is illustrated in Figure 1, which shows a uniform cotton thread (ω-region), moving at a constant velocity, u_o, within a homogeneous dye solution. The ω-region is composed of fibers (σ-region) and the dye solution inside the thread (β-phase). The concentration of dye in the thread at $x = 0$ is $C_{A\omega}^{o}$, and the concentration in the η-region at $y \sim \infty$ is a constant value, C_A^{∞}.

A small scale can be identified inside the σ-region as shown in Figure 1. On this small scale, two phases can be characterized: liquid in the microfibers, γ-phase, and solid, κ-phase (Plumb and Whitaker, 1988a, b, 1990). The κ-phase refers to the cotton microfibers (Trotman, 1975; Holme, 1986), where the adsorption process occurs.

γ - κ SYSTEM AVERAGING

The governing differential equations and boundary conditions for the mass transfer process in both the γ-phase and the κ-phase, illustrated in Figure 1, are given by

$$\frac{\partial C_{A\gamma}}{\partial t} = \nabla.\left(D_\gamma \nabla C_{A\gamma}\right) \qquad \text{in the } \gamma\text{-phase} \qquad (1)$$

$$\text{B.C.1:} \qquad -n_{\gamma\kappa}.D_\gamma \nabla C_{A\gamma} = \frac{\partial C_{As}}{\partial t} \quad \text{at } \mathscr{A}_{\gamma\kappa} \qquad (2)$$

$$\text{B.C.2:} \quad C_{A\gamma} = f(r,t) \quad \text{at } \mathcal{A}_{\gamma e} \tag{3}$$

$$\text{I.C.:} \quad C_{A\gamma} = g(r) \quad \text{at } t = 0 \tag{4}$$

It is assumed that in the interface the diffusive flux from the γ-phase to the κ-phase is equal to the adsorption rate.

The κ-phase is assumed to be a rigid phase and the adsorption isotherm is a linear function expressed as

$$C_{As} = K_{eq} C_{A\gamma} \quad \text{at } \mathcal{A}_{\gamma\kappa} \tag{5}$$

Here $C_{A\gamma}$ represents the molar concentration of chemical species under study (mol/m^3), C_{As} represents the surface concentration (mol/m^2), and D_γ is the γ-phase molecular diffusivity of species A (Whitaker, 1992). The entrances and exits of the γ-phase at the boundary of the σ-region are represented by variable $\mathcal{A}_{\gamma e}$. Variable $\mathcal{A}_{\gamma\kappa}$ is used to represent the entire interfacial area within that region. The γ-phase and the κ-phase and the σ–β system move at the same velocity in relation to the coordinate system; these two scales are confined to within the cotton fibers.

The intrinsic average concentration is defined by

$$\langle C_{A\gamma}\rangle^\gamma = \frac{1}{V_\gamma}\int_{V_\gamma} C_{A\gamma}\, dV \tag{6}$$

The spatial averaging theorem (Howes and Whitaker, 1985) for volume $\mathcal{V}_\sigma$ can be expressed as

$$\langle \nabla\psi_\gamma\rangle = \nabla\langle\psi_\gamma\rangle + \frac{1}{\mathcal{V}_\sigma}\int_{A_{\gamma\kappa}} n_{\gamma\kappa}\psi_\gamma \; dA \tag{7}$$

in which $A_{\gamma\kappa}$ represents the interfacial area γ-κ contained within averaging volume $\mathcal{V}_\sigma$.

The integration of Eqs. (1) through (4) in volume $\mathcal{V}_\sigma$, using the spatial averaging theorem as presented by Ochoa-Tapia et al. (1993) and Whitaker (1999), results in the volume-averaged form of Eq. (1), given by

$$\varepsilon_\gamma \frac{\partial}{\partial t}\langle C_{A\gamma}\rangle^\gamma =$$

$$= \nabla.\left[\varepsilon_\gamma D_\gamma\left(\nabla\langle C_{A\gamma}\rangle^\gamma + \frac{1}{V_\gamma}\int_{A_{\gamma\kappa}} n_{\gamma\kappa}\tilde{C}_{A\gamma}\, dA\right)\right] - \tag{8}$$

$$-av_{\gamma\kappa} K_{eq}\frac{\partial\langle C_{A\gamma}\rangle^\gamma}{\partial t}\bigg|_{A_{\gamma\kappa}}$$

A key aspect of the process of spatial smoothing is that the boundary condition given by Eq. (2) is combined with the governing equation. The area average concentration can be replaced by the intrinsic average concentration, $\langle C_{A\gamma}\rangle^\gamma \approx \frac{1}{A_{\gamma\kappa}}\int_{A_{\gamma\kappa}} C_{A\gamma}\; dA$ when the following length-scale constraints, $l_\gamma << r_\sigma$ and $\left[\frac{r_\sigma}{l_\sigma}\right]^2 << 1$, are satisfied (Ochoa-Tapia et al., 1993; Whitaker, 1999).

Here $av_{\gamma\kappa}$ represents the surface area per unit volume, given by

$$av_{\gamma\kappa} = \frac{A_{\gamma\kappa}}{\mathcal{V}_\sigma} \tag{9}$$

and the spatial deviation concentration can be expressed as

$$\tilde{C}_{A\gamma} = C_{A\gamma} - \langle C_{A\gamma}\rangle^\gamma \tag{10}$$

The Closure Problem

At this point a representation for the spatial deviation concentration needs to be developed.

Subtracting Eq. (8) divided by ε_γ from Eq. (1), one can obtain

$$\begin{aligned}
\underbrace{\frac{\partial\tilde{C}_{A\gamma}}{\partial t}}_{\text{accumulation}} &= \underbrace{\nabla.\left(D_\gamma\nabla\tilde{C}_{A\gamma}\right)}_{\text{diffusion}}. - \\
&\underbrace{-\varepsilon_\gamma^{-1}\nabla\varepsilon_\gamma.D_\gamma\nabla\langle\tilde{C}_{A\gamma}\rangle^\gamma}_{\text{diffusive source}} - \\
&\underbrace{-\varepsilon_\gamma^{-1}\,\nabla.\left(\frac{D_\gamma}{\mathcal{V}_\sigma}\int_{A_{\gamma\kappa}} n_{\gamma\kappa}\tilde{C}_{A\gamma}\; dA\right)}_{\text{nonlocal term}} + \\
&\underbrace{+\varepsilon_\gamma^{-1} av_{\gamma\kappa} K_{eq}\frac{\partial\langle C_{A\gamma}\rangle^\gamma}{\partial t}}_{\text{adsorptive source}}
\end{aligned} \tag{11}$$

The interfacial boundary condition for the deviation concentration can be expressed as

$$\text{B.C.1}: -n_{\gamma\kappa}.D_\gamma\nabla\tilde{C}_{A\gamma} - Keq\frac{\partial\tilde{C}_{A\gamma}}{\partial t} = \qquad \text{at } \mathscr{A}_{\gamma\kappa} \tag{12}$$

$$= n_{\gamma\kappa}.D_\gamma\nabla\left\langle C_{A\gamma}\right\rangle^\gamma + Keq\frac{\partial\left\langle C_{A\gamma}\right\rangle^\gamma}{\partial t}$$

$$\text{B.C.2}: \qquad \tilde{C}_{A\gamma} = \mathscr{H}(r,t) \qquad \text{at } \mathscr{A}_{\gamma e} \tag{13}$$

$$\text{I.C.}: \qquad \tilde{C}_{A\gamma} = \mathscr{Z}(r) \qquad \text{at } t = 0 \tag{14}$$

Since the source $\mathscr{H}(r,t)$ only influences the $\tilde{C}_A$ field over a distance on the order of l_y, we can generally replace the boundary condition imposed at $\mathscr{A}_{\gamma e}$ with a spatially periodic condition for $\tilde{C}_A$ (Whitaker, 1999). So, when the spatially periodic model is used and $\frac{D_\gamma t^*}{l_\gamma^2}$ is much greater than one, the boundary value problem can be rewritten as

$$\nabla.\nabla\tilde{C}_{A\gamma} = -\left(\frac{av_{\gamma\kappa}Keq}{\varepsilon_\gamma D_\gamma}\right)\frac{\partial\left\langle C_{A\gamma}\right\rangle^\gamma}{\partial t}\Big|_x \tag{15}$$

$$\text{B.C.1}: -n_{\gamma\kappa}.D_\gamma\nabla\tilde{C}_{A\gamma} =$$

$$= n_{\gamma\kappa}.D_\gamma\nabla\left\langle C_{A\gamma}\right\rangle^\gamma\Big|_x + \qquad \text{at } A_{\gamma\kappa} \tag{16}$$

$$+ Keq\frac{\partial\left\langle C_{A\gamma}\right\rangle^\gamma}{\partial t}\Big|_x$$

$$\text{B.C.2}: \qquad \tilde{C}_{A\gamma}(r + \mathit{l}i) = \tilde{C}_{A\gamma}(r), \; i = 1, \; 2, \; 3 \tag{17}$$

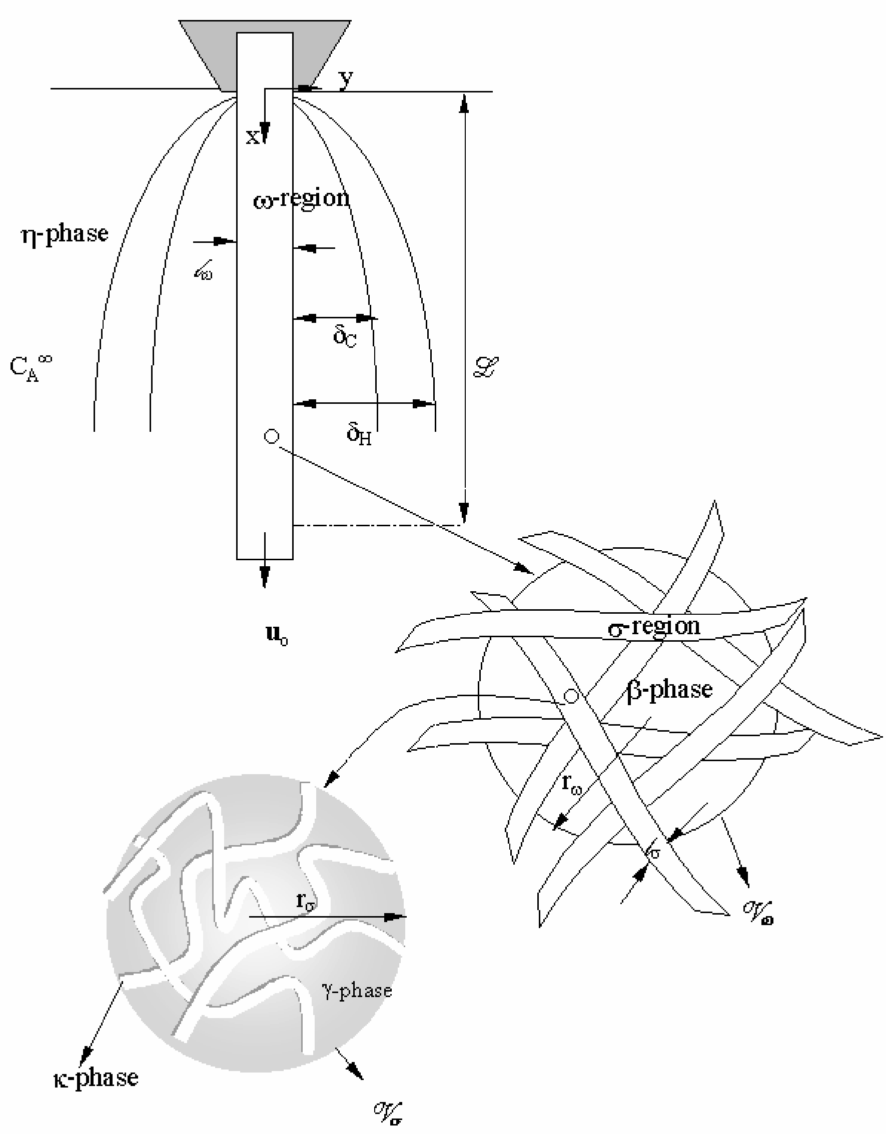

Figure 1: Averaging volumes for diffusion and adsorption within the cotton thread.

Closure Variables

The boundary value problem for deviation concentration is solved by the method of superposition, where a proposed solution is given by

$$\tilde{C}_{A\gamma} = \mathbf{b}.\nabla\langle C_{A\gamma}\rangle^{\gamma} + s\left(\frac{\partial\langle C_{A\gamma}\rangle^{\gamma}}{\partial t}\right) + \psi \tag{18}$$

Whitaker (1999) proves that $\psi = \text{constant}$ is the only solution. Since this additive constant will not pass through the filter, the value of ψ plays no role in the closed form of the volume averaged diffusion equation.

Here b and the scalar s are the closure variables and ψ is an arbitrary function (Whitaker, 1999). The two closure variables can be determined according to the following two boundary value problems:

Problem I

$$\nabla^2 \mathbf{b} = 0 \tag{19}$$

$$\text{B.C.1:} \qquad -\mathbf{n}_{\gamma\kappa}.\nabla\mathbf{b} = \mathbf{n}_{\gamma\kappa} \quad \text{at } A_{\gamma\kappa} \tag{20}$$

$$\text{B.C.2:} \qquad \mathbf{b}(\mathbf{r}+l_i) = \mathbf{b}(\mathbf{r}), \; i = 1,\; 2,\; 3 \tag{21}$$

Problem II

$$\nabla^2 s = -\left(\frac{a_v{}_{\gamma\kappa}K_{eq}}{\varepsilon_\gamma D_\gamma}\right) \tag{22}$$

$$\text{B.C.1:} \qquad -\mathbf{n}_{\gamma\kappa}.\nabla s = \frac{K_{eq}}{D_\gamma} \quad \text{at } A_{\gamma\kappa} \tag{23}$$

$$\text{B.C.2:} \qquad s(\mathbf{r}+l_i) = s(\mathbf{r}), \; i = 1, 2, 3 \tag{24}$$

Closed Form

The closed form of the governing equation for the intrinsic average concentration, $<C_{A\gamma}>^{\gamma}$, can be obtained by substitution of Eq. (18) into Eq. (8). The resulting equation can be expressed as

$$\varepsilon_\gamma\left(1+\frac{a_{v\gamma\kappa}K_{eq}}{\varepsilon_\gamma}\right)\frac{\partial\langle C_{A\gamma}\rangle^{\gamma}}{\partial t} = \nabla.\varepsilon_\gamma \mathbf{D}_{eff}.\nabla\langle C_{A\gamma}\rangle^{\gamma} + \nabla.\left[(\varepsilon_\gamma \mathbf{u})\frac{\partial\langle C_{A\gamma}\rangle^{\gamma}}{\partial t}\right] \tag{25}$$

where the effective diffusivity tensor is defined by

$$\mathbf{D}_{eff} = D_\gamma\left[\mathbf{I} + \frac{1}{V_\gamma}\int_{A_{\gamma\kappa}} \mathbf{n}_{\gamma\kappa}\; \mathbf{b}\, dA\right] \tag{26}$$

and vector **u** is defined by

$$\mathbf{u} = \frac{1}{V_\gamma}\int_{A_{\gamma\kappa}} \mathbf{n}_{\gamma\kappa}\left(D_\gamma\; s\right) dA \tag{27}$$

Here the diffusive tensor, D_{eff}, depends only on the geometry of the porous medium (Whitaker, 1999).

One can use Eq. (23) and Eq. (27) for estimating the order of s and u. Using these results in Eq. (25), Whitaker (1999) demonstrated that the advective term can be neglected for the case of diffusion in porous solids. The final form of the local average diffusion and transport equation is given by

$$\varepsilon_\gamma\left(1+\frac{a_{v\gamma\kappa}K_{eq}}{\varepsilon_\gamma}\right)\frac{\partial\langle C_{A\gamma}\rangle^{\gamma}}{\partial t} = \nabla.\varepsilon_\gamma \mathbf{D}_{eff}.\nabla\langle C_{A\gamma}\rangle^{\gamma} \tag{28}$$

σ–β SYSTEM AVERAGING

In this section we will develop the spatially smoothed equations associated with volume $\mathscr{V}_\omega$, shown in Figure 1. The length scales related to this averaging volume are identified in Figure 1. The boundary value problem associated with the local volume averaging procedure is given by

$$\varepsilon_\gamma\left(1+\frac{a_{v\gamma\kappa}K_{eq}}{\varepsilon_\gamma}\right)\frac{\partial\langle C_{A\gamma}\rangle^{\gamma}}{\partial t} = \nabla.\varepsilon_\gamma \mathbf{D}_{eff}.\nabla\langle C_{A\gamma}\rangle^{\gamma} \tag{29}$$

in the σ-region

$$\text{B.C.1:} \qquad -\mathbf{n}_{\sigma\beta}.\varepsilon_\gamma \mathbf{D}_{eff}.\nabla\langle C_{A\gamma}\rangle^{\gamma} = -\mathbf{n}_{\sigma\beta}.D_\beta\nabla C_{A\beta} \quad \text{at } \mathscr{A}_{\sigma\beta} \tag{30}$$

$$\text{B.C.2:} \qquad \langle C_{A\gamma}\rangle^{\gamma} = C_{A\beta} \qquad \text{at } \mathscr{A}_{\sigma\beta} \tag{31}$$

$$\text{B.C.3:} \qquad C_{A\beta} = \mathscr{G}_1(\mathbf{r},t) \qquad \text{at } \mathscr{A}_{\beta e} \tag{32a}$$

$$\text{B.C.4:} \qquad \langle C_{A\gamma}\rangle^{\gamma} = \mathscr{G}_2(\mathbf{r},t) \qquad \text{at } \mathscr{A}_{\sigma e} \tag{32b}$$

$$\frac{\partial C_{A\beta}}{\partial t} = \nabla.\left(D_\beta \nabla C_{A\beta}\right) \quad \text{in the } \beta\text{-phase} \tag{33}$$

The σ-Region

Integration of Eq. (29) over $\mathcal{V}_\varpi$, illustrated in Figure 1, results in

$$\varepsilon_\gamma\left(1+\frac{a v_{\gamma\kappa} K eq}{\varepsilon_\gamma}\right)\frac{\partial\left\langle C_\sigma\right\rangle}{\partial t} = \left\langle \nabla.\varepsilon_\gamma \mathit{Deff}.\nabla C_\sigma\right\rangle \tag{34}$$

in which the nomenclature for the σ-region has been simplified by using the relationship $\left\langle C_{A\gamma}\right\rangle^\gamma = C_\sigma$, where

$$\left\langle C_\sigma\right\rangle = \varphi_\sigma\left\langle C_\sigma\right\rangle^\sigma \text{ and}$$

$$\left\langle C_\sigma\right\rangle = \frac{1}{\mathcal{V}_\varpi}\int_{V_\sigma} C_\sigma \; dV \tag{35}$$

By using the averaging theorem and following the same procedure as that adopted previously and assuming that the restriction $l_\sigma \ll r_\varpi$ is satisfied, Eq. (34) can be expressed as

$$\varphi_\sigma\varepsilon_\gamma\left(1+\frac{a v_{\gamma\kappa} K eq}{\varepsilon_\gamma}\right)\frac{\partial\left\langle C_\sigma\right\rangle^\sigma}{\partial t} =$$

$$= \nabla.\left[\varepsilon_\gamma \mathit{Deff}\left(\varphi_\sigma\nabla\left\langle C_\sigma\right\rangle^\sigma + \frac{1}{\mathcal{V}_\varpi}\int_{A_{\sigma\beta}} n_{\sigma\beta}\tilde{C}_\sigma \, dA\right)\right] + \tag{36}$$

$$+\frac{1}{\mathcal{V}_\varpi}\int_{A_{\sigma\beta}} n_{\sigma\beta}.\varepsilon_\gamma \mathit{Deff}.\nabla C_\sigma \; dA$$

Here φ_σ represents the volume fraction of the σ-region contained in the volume $\mathcal{V}_\omega$.

The Closure Problem

Analogously to the previous procedure, here a representation for the spatial deviation concentration is required. The use of the spatial deviation concentration defined by Gray (1975) and applied to the σ-region results in

$$C_\sigma = \left\langle C_\sigma\right\rangle^\sigma + \tilde{C}_\sigma \tag{37}$$

The spatial deviation concentration equation can be obtained by subtracting Eq. (36) divided by φ_σ from Eq. (29), and the resulting equation can be simplified when the following restrictions are satisfied: $\frac{r_\varpi}{l_\varpi} \ll 1$ and $\frac{\left(l_\varpi\,\varepsilon_\gamma\,\varphi_\sigma\right)}{l_\sigma} \gg 1$. Under these circumstances Eq. (36) can be rewritten as

$$\varepsilon_\gamma\left(1+\frac{a v_{\gamma\kappa} K eq}{\varepsilon_\gamma}\right)\frac{\partial\tilde{C}_\sigma}{\partial t} =$$

$$= \nabla.\left(\varepsilon_\gamma \mathit{Deff}.\nabla\tilde{C}_\sigma\right) - \tag{38}$$

$$-\frac{\varphi_\sigma^{-1}}{\mathcal{V}_\varpi}\int_{A_{\sigma\beta}} n_{\sigma\beta}.\varepsilon_\gamma \mathit{Deff}.\nabla\tilde{C}_\sigma \; dA$$

$$\begin{aligned}&\text{B.C.1}: -n_{\sigma\beta}.\varepsilon_\gamma \mathit{Deff}\nabla\tilde{C}_\sigma = \\ &-n_{\sigma\beta}.D_\beta\nabla C_{A\beta} + n_{\sigma\beta}.\varepsilon_\gamma \mathit{Deff}\nabla\left\langle C_\sigma\right\rangle^\sigma \end{aligned} \quad \text{at } \mathcal{A}_{\sigma\beta} \tag{39}$$

$$\text{B.C.2}: \quad \tilde{C}_\sigma = C_{A\beta} - \left\langle C_\sigma\right\rangle^\sigma \quad \text{at } \mathcal{A}_{\sigma\beta} \tag{40}$$

The β-Phase

The volume averaging form of Eq. (33) in volume $\mathcal{V}_\omega$, using the averaging theorem, is given by

$$\underbrace{\varphi_\beta\frac{\partial\left\langle C_{A\beta}\right\rangle^\beta}{\partial t}}_{\text{accumulation}} =$$

$$\underbrace{= \nabla.\left[\varphi_\beta D_\beta\left(\nabla\left\langle C_{A\beta}\right\rangle^\beta + \frac{1}{V_\beta}\int_{A_{\beta\sigma}} n_{\beta\sigma}\tilde{C}_{A\beta}\, dA\right)\right]}_{\text{diffusive transport}} + \tag{41}$$

$$\underbrace{+\frac{1}{\mathcal{V}_\omega}\int_{A_{\beta\sigma}} n_{\beta\sigma}.D_\beta\nabla C_{A\beta}\; dA}_{\text{boundary flux}}$$

The deviation concentration for the β-phase is given by $\tilde{C}_{A\beta} = C_{A\beta} - \left\langle C_{A\beta}\right\rangle^\beta$.

The Closure Problem

One can see that the subtraction of Eq. (41) divided by φ_β from Eq. (33) results in the governing equation for the deviation concentration, which is given by

$$\underbrace{\frac{\partial \tilde{C}_{A\beta}}{\partial t}}_{\text{accumulation}} = \underbrace{\nabla.\left(D_\beta \nabla \tilde{C}_{A\beta}\right)}_{\text{diffusive term}} - \underbrace{-\varphi_\beta^{-1}\nabla.\left(\frac{D_\beta}{\mathscr{V}_\omega}\int_{A_{\beta\sigma}} n_{\beta\sigma}\tilde{C}_{A\beta}\; dA\right)}_{\text{nonlocal term}} - \underbrace{-\varphi_\beta^{-1}\nabla\varphi_\beta.\left(D_\beta\nabla\langle C_{A\beta}\rangle^\beta\right)}_{\text{diffusive source}} - \underbrace{-\varphi_\beta^{-1}\frac{1}{\mathscr{V}_\omega}\int_{A_{\beta\sigma}} n_{\beta\sigma}.D_\beta\nabla C_{A\beta}\; dA}_{\text{boundary flux}} \qquad (42)$$

By analysis of the order of the terms in Eq. (42), and assuming the length-scale constraints given by $l_\beta << r_\varpi$ and $\frac{D_\beta\ t^*}{l_\beta^2} >> 1$, one can conclude that the nonlocal term can be considered negligible compared to the diffusion term and the closure process can be considered quasi-steady. Under these circumstances, Eq. (42) can be rewritten as

$$\nabla.\left(D_\beta\nabla\tilde{C}_{A\beta}\right) = \varphi_\beta^{-1}\ \frac{1}{\mathscr{V}_\omega}\int_{A_{\beta\sigma}} n_{\beta\sigma}.D_\beta\nabla\tilde{C}_{A\beta}\ dA \qquad (43)$$

One-Equation Model

Making the assumption that the principle of local mass equilibrium (Quintard and Whitaker, 1993; Whitaker, 1986 a, b) is valid, we can write

$$\langle C_{A\beta}\rangle^\beta = \langle C_\sigma\rangle^\sigma = \langle C_A\rangle^* \qquad (44)$$

Here $<C_A>^*$ is the spatial average concentration defined as

$$\langle C_A\rangle^* = \frac{1}{\mathscr{V}_\omega}\int_{\mathscr{V}_\omega} C_A\ dV = \frac{1}{\mathscr{V}_\omega}\int_{V_\sigma} C_\sigma\ dV + \\ + \frac{1}{\mathscr{V}_\omega}\int_{V_\beta} C_{A\beta}\ dV \qquad (45)$$

The following definitions

$$\varphi_\beta + \varphi_\sigma\varepsilon_\gamma = \langle\varepsilon\rangle \qquad (46)$$

$$\varphi_\sigma a v_{\gamma\kappa}\, Keq = \langle K\rangle \qquad (47)$$

can be used with Eqs. (36) and (41) to give

$$\left(\langle\varepsilon\rangle + \langle K\rangle\right)\frac{\partial\langle C_A\rangle^*}{\partial t} = \nabla.\varphi_\beta\mathscr{D}_{eff}.\nabla\langle C_A\rangle^* \qquad (48)$$

Here we have defined the overall effective diffusivity as

$$\nabla.\left(\varphi_\beta\mathscr{D}_{eff}.\nabla\langle C_A\rangle^*\right) = \nabla.\left[\left(\varepsilon_\gamma\varphi_\sigma \mathit{Deff} + \varphi_\beta D_\beta I\right).\nabla\langle C_A\rangle^* + \varepsilon_\gamma \mathit{Deff}.\frac{1}{\mathscr{V}_\omega}\int_{A_{\sigma\beta}} n_{\sigma\beta}\tilde{C}_\sigma\ dA + \frac{D_\beta}{\mathscr{V}_\omega}\int_{A_{\beta\sigma}} n_{\beta\sigma}\tilde{C}_{A\beta}\ dA\right] \qquad (49)$$

Closure Variables

Considering that the local closure problem has a unique nonhomogeneous term proportional to the gradient of the spatial average concentration evaluated on the centroid, one can write

$$\tilde{C}_{A\beta} = b_\beta.\nabla\langle C_A\rangle^* + \psi \qquad (50)$$

$$\tilde{C}_\sigma = b_\sigma.\nabla\langle C_A\rangle^* + \xi \qquad (51)$$

where b_β and b_σ are the closure variables.

The following boundary value problem needs to be solved:

$$\nabla^2 b_\beta = 0 \qquad (52)$$

B.C.1:
$$-n_{\sigma\beta}.D_\beta\nabla b_\beta = -n_{\sigma\beta}.\varepsilon_\gamma \mathit{Deff}\ .\nabla b_\sigma + \\ + n_{\sigma\beta}.\left(D_\beta I - \varepsilon_\gamma \mathit{Deff}\right) \text{ at } A_{\sigma\beta} \qquad (53)$$

B.C.2: $b_\sigma = b_\beta$ at $A_{\sigma\beta}$ (54)

$$\nabla^2 b_\sigma = 0 \tag{55}$$

$$\textit{Periodicity}: \quad \begin{aligned} & b_\sigma(r) = b_\sigma(r + li)\ ,\ b_\beta(r) = \\ & = b_\beta(r + li)\ ,\ i = 1,2,3 \end{aligned} \tag{56}$$

One can show that $\psi = \xi =$ constant. This constant will not pass through the filter represented by area integrals in Eq. (49), as suggested by Whitaker (1999). So the value of this constant plays no role in the closed-form equation.

The Closed Form

Substituting the expressions given by Eq. (50) and Eq. (51) for the spatial deviation concentrations in Eq. (49), taking into consideration solution of the boundary value problem, one can obtain

$$\left(\langle\varepsilon\rangle + \langle K\rangle\right)\frac{\partial\langle C_A\rangle^*}{\partial t} = \nabla.\left(\varphi_\beta \mathscr{D}_{eff}\ .\nabla\langle C_A\rangle^*\right) \tag{57}$$

where

$$\begin{aligned} \varphi_\beta \mathscr{D}_{eff} &= \left(\varepsilon_\gamma \varphi_\sigma D_{eff} + \varphi_\beta D_\beta I\right) + \\ &+ \varepsilon_\gamma D_{eff}.\frac{1}{\mathscr{V}_\omega}\int_{A_{\sigma\beta}} n_{\sigma\beta} b_\sigma \, dA + \frac{D_\beta}{\mathscr{V}_\omega}\int_{A_{\beta\sigma}} n_{\beta\sigma} b_\beta \, dA \end{aligned} \tag{58}$$

THE ω -η SYSTEM

The ω-Region

At this point we need to consider the ω-region motion related to the η-phase and for this circumstance the time derivative of average concentration of species A in the ω-region can be expressed as

$$\left.\frac{d\langle C_A\rangle^*}{dt}\right|_{u_0} = \left.\frac{d\langle C_A\rangle^*}{dt}\right|_{v=0} + u_0.\nabla\langle C_A\rangle^* \tag{59}$$

By simplification Eq. (59), we can write

$$\left.\frac{d\langle C_A\rangle^*}{dt}\right|_{u_0} = \frac{\partial\langle C_A\rangle^*}{\partial t} + u_0.\nabla\langle C_A\rangle^* \tag{60}$$

The subscript on the left side of Eq. (60) does not indicate what is being held constant, but instead indicates the velocity of the observer who is measuring the concentration. On the basis of Eq. (60) the governing equation for the ω-region can be written as

$$\begin{aligned} &\left(\langle\varepsilon\rangle + \langle K\rangle\right)\left[\frac{\partial\langle C_A\rangle^*}{\partial t} + u_0\ .\ \nabla\langle C_A\rangle^*\right] = \\ &= \nabla.\left(\varphi_\beta \mathscr{D}_{eff}\ .\nabla\langle C_A\rangle^*\right) \end{aligned} \tag{61}$$

The η-Phase

The governing equation for the η-phase is given by

$$\frac{\partial C_{A\eta}}{\partial t} + \mathbf{v}_\eta\ .\ \nabla C_{A\eta} = \nabla.\left(D_\eta \nabla C_{A\eta}\right) \tag{62}$$

One can assume that the boundary layer solution for the hydrodynamic problem in the η-phase is acceptable, and in this circumstance the velocity profiles obtained by Sakiadis (1961a, b, c) can be used in Eq. (62).

CONCLUSIONS

The model of a single cylinder cotton thread, developed using the method of volume averaging for the adsorption dyeing process, represents a fundamental approach in this area. Two scales were considered in order to formulate this problem. The κ-phase, inside the σ-region, is composed of microfibers where the adsorption process occurs. The ω-region, containing the σ-β system, moves at a constant velocity. The method of volume averaging is applied to obtain the mass transfer equations related to the adsorption process on the small and the large scale. The one-equation model is developed for the β- σ system, assuming the local mass equilibrium. The simulation results and validation of this model as well as the effective mass diffusivity obtained by solution of closure problems will be presented in a subsequent paper.

ACKNOWLEGEMENTS

This work was done when Antônio Augusto Ulson de Souza was a postdoctoral student at University of California, Davis, with financial support from the Fundação Coordenação de

Aperfeiçoamento de Pessoal de Nível Superior, CAPES, Brazil.

NOMENCLATURE

$\mathcal{A}_{\gamma\kappa}$	Interfacial area of the γ–κ system, m^2
$\mathcal{A}_{\gamma e}$	Area of entrances and exits for the γ–phase, m^2
$\mathcal{A}_{\sigma\beta}$	Interfacial area of the σ–β system, m^2
$\mathcal{A}_{\sigma e}$	Area of entrances and exits for the σ–region, m^2
$\mathcal{A}_{\beta e}$	Area of entrances and exits for the β–phase, m^2
$A_{\gamma\kappa}$	The γ–κ interfacial area contained within the averaging volume, $\mathcal{V}_\sigma$, m^2
$A_{\gamma e}$	Area of entrances and exits for the γ–phase contained within the averaging volume, $\mathcal{V}_\sigma$, m^2
$A_{\sigma\beta}$	The σ–β interfacial area contained within the averaging volume, $\mathcal{V}_\omega$, m^2
$av_{\gamma\kappa}$	The γ–κ interfacial area per unit volume, m^{-1}
C_A^{∞}	Concentration in the η–phase outside the boundary layer, kgmol/ m^3
$C_{A\gamma}$	Point concentration in the γ–phase, kgmol/ m^3
$\langle C_{A\gamma}\rangle^{\gamma}=C_\sigma$	Intrinsic averaged concentration in the γ–phase, kgmol/ m^3
$\tilde{C}_{A\gamma}$	Spatial deviation concentration in the γ–phase, kgmol/ m^3
$C_{A\beta}$	Point concentration in the β–phase, kgmol/ m^3
$C_{A\eta}$	Point concentration in the η–phase, kgmol/ m^3
$\langle C_{A\beta}\rangle^{\beta}$	Intrinsic regional averaged concentration for the β–phase, kgmol/ m^3
$\langle C_\sigma\rangle$	Superficial regional averaged concentration for the σ–region, kgmol/ m^3
$\langle C_\sigma\rangle^{\sigma}$	Intrinsic regional averaged concentration for the σ–region, kgmol/ m^3
$\tilde{C}_\sigma$	Spatial deviation concentration in the σ–region, kgmol/ m^3
$\tilde{C}_{A\beta}$	Spatial deviation concentration in the β–phase, kgmol/ m^3
$\langle C_A\rangle^{*}$	Intrinsic spatial averaged concentration for the σ–β system, kgmol/ m^3
D_γ	The γ–phase molecular diffusivity, m^2/s
D_{eff}	The γ–phase effective diffusivity tensor, m^2/s
D_β	The β–phase molecular diffusivity, m^2/s
D_η	The η–region molecular diffusivity, m^2/s
$\mathcal{D}_{eff}$	Effective diffusivity tensor for the σ–β system , m^2/s
I	Unit tensor
$\langle K\rangle$	The averaged adsorption equilibrium constant, m
Keq	Adsorption equilibrium constant, m
ℓ_ω	Characteristic length of the ω–region, m
ℓ_σ	Characteristic length of the σ–region, m
ℓ_β	Characteristic length of the β–phase, m
ℓ_γ	Characteristic length of the γ–phase, m
l_i	Lattice vectors describing a spatially periodic porous medium, m
$\mathcal{L}$	Long length for volume averaged quantities associated with the ω–η system, m
$n_{\gamma\kappa}$	Outwardly directed unit normal vector pointing from the γ–phase toward the κ–phase
$n_{\sigma\beta}$	Outwardly directed unit normal vector pointing from the σ–region toward the β–phase
r_σ	Radius of the γ–κ system averaging volume, $\mathcal{V}_\sigma$, m
r_ω	Radius of the σ–β system averaging volume, $\mathcal{V}_\omega$, m
t	Time, s
t*	Characteristic time, s
$\mathcal{V}_\sigma$	Small-scale averaging volume, m^3
$\mathcal{V}_\omega$	Large-scale averaging volume, m^3
u_o	The ω–region velocity vector, m/s
v_η	The η–phase velocity vector, m/s
V_γ	Volume of the γ–phase contained within $\mathcal{V}_\sigma$, m^3
V_σ	Volume of the σ–region contained within $\mathcal{V}_\omega$, m^3
δ_C	Mass boundary layer
δ_H	Hydrodynamic boundary layer
ε_γ	The γ–phase volume fraction in the γ–κ system
φ_σ	The σ–region volume fraction in the σ–β system
φ_β	The β–phase volume fraction in the σ–β system
$\langle\varepsilon\rangle$	The averaged porosity

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