Int. J. Heat Mass Transfer. Vol. 34, No. 6, pp. 1572–1575, 1991
Printed in Great Britain

0017-9310/91 $3.00 + 0.00

Discussion of the effect of convection during solute transfer between stationary and partially miscible phases†

FERNANDO J. AGUIRRE and BAINIAN LIU
Chemical and Metallurgical Engineering Department, University of Nevada–Reno, Reno, NV 89557, U.S.A.

(*Received* 30 *January* 1990 *and in final form* 24 *July* 1990)

INTRODUCTION

INTERFACIAL activity generated between partially miscible liquids in some industrial systems can be responsible for significant enhancements in mass transfer rates. Considering that thermal effects can be important in the generation of interfacial activity, Perez de Ortiz and Sawistowski [1] proposed a diffusion model for obtaining temperature and concentration profiles as a function of time when partially miscible binary liquids are contacted at a planar interface. They obtained an analytical solution for temperature and concentration profiles in both phases when considering a linear variation of the heat of solution with concentration. This coupled diffusion model for mass and heat transfer was improved upon in ref. [2] by considering a non-linear relationship between the heat of solution and concentration. This note discusses the addition of a convection mechanism to the model. The presence of a heat source/sink due to the heat of solution for solute transfer between stationary and partially miscible phases is also considered. Experimental data obtained by Yang [3] are used to test the pure diffusion and convection/diffusion models.

Since interfacial activity is generally present in the systems under study, this phenomenon can be characterized by the velocity of the fluid in each phase. In this note, a simple approach is considered for the convective mechanism. This approach involves finding a fluid velocity, in both phases, that produces the best fit of the temperature changes predicted by the model when compared to experimental data. This modeling work allows us to significantly improve our understanding of the phenomena of interfacial activity and how it affects the mass and heat transfer rates in such systems. This improved understanding will ultimately permit a better estimation of mass and heat transfer coefficients in liquid extraction systems.

BASIC MODEL

The pure diffusion model for partially miscible binary systems [2] was extended to consider the transfer of a solute between two partially miscible phases. A convective mechanism was also incorporated into the model. The geometrical configuration of the experimental conditions consists of a cylindrical transfer cell in which two stationary liquid phases are placed in contact [2]. This is shown in Fig. 1. The lighter phase is in the top half of the cell and the heavier phase is in the bottom half. These two phases are separated by an interface defined at $z = 0$, and they are contacted by smoothly and slowly rotating the upper half of the transfer cell. The overall system contains three components, 1, 2, and 3, which form two phases A and B. Components 1 and 2 are the solvents, and component 3 the solute which is completely miscible in both solvents. After contacting of the two phases, components 1 and 3 will transfer from phase A to phase B, and component 2 will transfer from phase B to phase A.

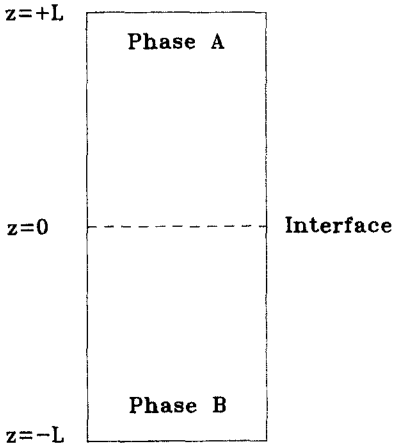

FIG. 1. Geometrical configuration.

The convection/diffusion model can be described by the following PDEs for mass and heat transfer in each phase:

$$\frac{\partial C_{2A}}{\partial t} = D_{2A}\frac{\partial^2 C_{2A}}{\partial z^2} - V_A\frac{\partial C_{2A}}{\partial z} \quad (t > 0, z \geqslant 0) \qquad (1)$$

$$\frac{\partial C_{3A}}{\partial t} = D_{3A}\frac{\partial^2 C_{3A}}{\partial z^2} - V_A\frac{\partial C_{3A}}{\partial z} \quad (t > 0, z \geqslant 0) \qquad (2)$$

$$\frac{\partial C_{1B}}{\partial t} = D_{1B}\frac{\partial^2 C_{1B}}{\partial z^2} - V_B\frac{\partial C_{1B}}{\partial z} \quad (t > 0, z \leqslant 0) \qquad (3)$$

$$\frac{\partial C_{3B}}{\partial t} = D_{3B}\frac{\partial^2 C_{3B}}{\partial z^2} - V_B\frac{\partial C_{3B}}{\partial z} \quad (t > 0, z \leqslant 0) \qquad (4)$$

$$\frac{\partial T_A}{\partial t} = \alpha_A\frac{\partial^2 T_A}{\partial z^2} - \left(\frac{\partial H_A^E}{\partial X_{2A}}\frac{\partial C_{2A}}{\partial t} + \frac{\partial H_A^E}{\partial X_{3A}}\frac{\partial C_{3A}}{\partial t}\right)\frac{1}{\rho_A C_{pA}} - V_A\frac{\partial T_A}{\partial z} \quad (t > 0, z \geqslant 0) \qquad (5)$$

$$\frac{\partial T_B}{\partial t} = \alpha_B\frac{\partial^2 T_B}{\partial z^2} - \left(\frac{\partial H_B^E}{\partial X_{1B}}\frac{\partial C_{1B}}{\partial t} + \frac{\partial H_B^E}{\partial X_{3B}}\frac{\partial C_{3B}}{\partial t}\right)\frac{1}{\rho_B C_{pB}} - V_B\frac{\partial T_B}{\partial z} \quad (t > 0, z \leqslant 0). \qquad (6)$$

Derivation of this model is described in more detail elsewhere [4]. C_{2A}, C_{3A}, C_{1B}, and C_{3B} represent the molar concentrations of components 2 and 3 in phase A, and components 1 and 3 in phase B, respectively. C_{1A} and C_{2B} can be obtained from the condition that the sum of mole fractions in each phase is equal to one. V_A and V_B represent the net fluid velocities in the axial direction due to convection in phases A and B, respectively. Velocity fields in other directions are neglected in this initial work. T represents the

---

† Paper presented at the 1988 AIChE Annual Meeting, Washington, DC, 27 November–2 December 1988.

temperature difference between the actual value and the initial condition; H^E the heat of solution of the ternary system; and X_{ij} the mole fraction of component i in phase j.

Initial condition

$$t = 0, \quad C_{2A} = C_{2AE}, \quad z \geqslant 0 \tag{7}$$

$$t = 0, \quad C_{3A} = C_{3AE}, \quad z \geqslant 0 \tag{8}$$

$$t = 0, \quad C_{1B} = C_{1BE}, \quad z \leqslant 0 \tag{9}$$

$$t = 0, \quad C_{3B} = C_{3BE}, \quad z \leqslant 0 \tag{10}$$

$$t = 0, \quad T_A = 0, \quad z \geqslant 0 \tag{11}$$

$$t = 0, \quad T_B = 0, \quad z \leqslant 0. \tag{12}$$

Boundary conditions

$$z = L, \quad T_A = 0, \quad t > 0 \tag{13}$$

$$z = L, \quad C_{2A} = C_{2AE}, \quad t > 0 \tag{14}$$

$$z = L, \quad C_{3A} = C_{3AE}, \quad t > 0 \tag{15}$$

$$z = -L, \quad T_B = 0, \quad t > 0 \tag{16}$$

$$z = -L, \quad C_{1B} = C_{1BE}, \quad t > 0 \tag{17}$$

$$z = -L, \quad C_{3B} = C_{3BE}, \quad t > 0 \tag{18}$$

$$z = 0, \quad T_A = T_B, \quad t > 0. \tag{19}$$

The liquids in a very thin layer close to the interface are assumed to be very well mixed immediately after the contacting takes place. Therefore, instantaneous equilibrium is assumed at the interface. Interfacial concentrations can be determined from the equilibrium phase diagram of the ternary systems [5]. In this preliminary work the equilibrium concentrations are assumed independent of temperature

$$z = 0, \quad C_{2A} = C_{2AI}, \quad t > 0 \tag{20}$$

$$z = 0, \quad C_{3A} = C_{3AI}, \quad t > 0 \tag{21}$$

$$z = 0, \quad C_{1B} = C_{1BI}, \quad t > 0 \tag{22}$$

$$z = 0, \quad C_{3B} = C_{3BI}, \quad t > 0. \tag{23}$$

The total length or depth of each liquid phase is represented by L. The concentrations with a subscript I represent a condition at the interface, and those with a subscript E represent a condition at a distance L from the interface. The last boundary condition represents the condition of equality of energy fluxes at the interface

$z = 0, \quad t > 0$

$$-k_A \frac{\partial T_A}{\partial z} + D_{2A} \frac{\partial H_A^E}{\partial X_{2A}} \frac{\partial C_{2A}}{\partial z} + D_{3A} \frac{\partial H_A^E}{\partial X_{3A}} \frac{\partial C_{3A}}{\partial z} - V_A C_{2A} \frac{\partial H_A^E}{\partial X_{2A}}$$
$$- V_A C_{3A} \frac{\partial H_A^E}{\partial X_{3A}} + \rho_A C_{pA} V_A T_A = -k_B \frac{\partial T_B}{\partial z} + D_{1B} \frac{\partial H_B^E}{\partial X_{1B}} \frac{\partial C_{1B}}{\partial z}$$
$$+ D_{3B} \frac{\partial H_B^E}{\partial X_{3B}} \frac{\partial C_{3B}}{\partial z} - V_B C_{1B} \frac{\partial H_B^E}{\partial X_{1B}} - V_B C_{3B} \frac{\partial H_B^E}{\partial X_{3B}} + \rho_B C_{pB} V_B T_B. \tag{24}$$

The pure diffusion and heat conduction model is a special case of the above model when both V_A and V_B are equal to zero.

The following velocity profiles were used:

$$V_A = V_{A\max}(1 - 100z) \quad (0 < z \leqslant 0.01 \text{ m}) \tag{25}$$

$$V_A = 0 \quad (0.01 \text{ m} \leqslant z \leqslant L) \tag{26}$$

$$V_B = -V_{B\max}(1 + 100z) \quad (-0.01 \text{ m} \leqslant z < 0) \tag{27}$$

$$V_B = 0 \quad (-L \leqslant z \leqslant -0.01 \text{ m}). \tag{28}$$

The expressions used for the velocity profiles indicate that convection effects are confined to an area very close to the interface. This is consistent with experimental results [3]. The maximum velocities for each phase, $V_{A\max}$ and $V_{B\max}$, are considered equal in magnitude and will be denoted as $V_{\max}$. The interfacial movements generated near the interface are assumed to propagate towards the bulk, with a resulting net velocity of zero at the interface. Therefore, for $z = 0$ the convection/diffusion and pure diffusion models become identical.

METHOD OF SOLUTION

This mathematical model was numerically solved for various ternary liquid systems using the DSS/2 differential equation solver [6]. The PDE differentiator used [7] computes derivatives by five-point centered and non-centered approximations based on the fourth-order Lagrange interpolation polynomial. The work described in this note was performed on an IBM PS/2 Model 80 microcomputer.

A total of 51 grid points were used in each phase for implementing the Numerical Method of Lines, with points closer together near the interface [4]. The error tolerance used for all runs was 10^{-5}. An efficient method for applying the boundary conditions [8] was used in the solution of this model.

Due to the lack of concentration-dependent physical property data, the properties of the pure solvent were considered representative of each phase.

SYSTEMS STUDIED

Three partially miscible ternary liquid systems were used for the analysis with the pure diffusion model: (AA system) ethyl acetate(1)–water(2)–acetic acid(3); (EE system) ethyl acetate(1)–water(2)–ethanol(3); and (IS system) isobutanol(1)–water(2)–ethanol(3). These systems were selected because of the availability of experimental data for temperature changes as a function of time and position in one of the phases [3]. In all cases, component 3 is the solute which is miscible in the other two components and is transferred between the two partially miscible phases. Temperature and concentration profiles were calculated for initial volume percentages of component 3 in phase A of 5, 10, and 33%. In addition, for each of these cases both the initially saturated and unsaturated conditions were considered.

When solving the convection/diffusion model, temperature and concentration profiles were obtained for the EE system.

RESULTS AND ANALYSIS

Both the pure diffusion and convection/diffusion models were solved with the following initial conditions. For the unsaturated cases, $C_{2AE} = C_{1BE} = 0$. For the saturated cases the values of C_{2AE} and C_{1BE} were determined by the mutual solubilities of the binary system 12. The value for C_{3BE} was always zero and C_{3AE} varied from case to case. The total length of each phase was $L = 0.02$ m.

Pure diffusion model

When a value of zero is used for both velocities V_A and V_B, this model represents a pure diffusion mechanism for mass transfer and pure conduction for heat transfer. A total of 18 cases were evaluated (six for each ternary system). These included initial volume percentages for component 3 in phase A of 5, 10, and 33% for both saturated and unsaturated cases. The temperature changes predicted by the pure diffusion model were in qualitative agreement with the experimental data for the EE and IS systems. The predictions for the AA system were less successful due to the density inversion mechanism taking place during transfer of acetic acid from an ethyl acetate to a water-rich phase. The model-generated values are normally lower than the experimental temperature differences, with the ratio between the two varying from 0.1 to 0.8. Quantitative results and a comparison between model-generated temperature profiles and experimental data are reported in detail in ref. [5]. From the results for these three ternary systems and those obtained for binary systems [2] it appears that the disagreement between the model-generated values and the experimental data is mainly due to the lack of a convective mechanism in the model.

Convection/diffusion model

In an effort to improve the prediction of temperature changes generated upon contact of partially miscible ternary systems, a convective mechanism was added to the pure diffusion model. Since interfacial activity has been noted in such systems, the fluid circulation close to the interface was characterized by a fluid velocity in the axial direction. Linear velocity profiles were used as described by equations (25)–(28). The maximum fluid velocity, $V_{\max}$, was treated as an adjustable parameter by finding the best fit to the available experimental heat transfer data for ternary liquid systems [3]. This is a simple approach which proved very useful in improving the model-generated temperature changes. Due to differences in the physical properties of both phases the magnitudes of the fluid velocities are not expected to be equal. However, this assumption was used due to the unavailability of experimental heat transfer data in one of the phases. Future work will consider relaxing some of these assumptions to make further improvements in the model and make it more realistic.

The convection/diffusion model was numerically solved for the ethyl acetate(1)–water(2)–ethanol(3) system using several values for $V_{\max}$. The optimum value for $V_{\max}$ was determined by minimizing the average deviation between the experimental and model-predicted temperature profiles. The objective function used was the following:

$$\text{Avg. deviation} = \sqrt{\left(\frac{1}{n}\sum_{i=0}^{n}(T_{\mathrm{calc},i} - T_{\mathrm{exp},i})^2\right)}. \qquad (29)$$

This objective function was evaluated for the temperature changes measured by the thermocouple closest to the interface (1.4 mm). The calculated and experimental values used in the evaluation were sampled at 5 s intervals between 0 and 2 min after the contacting of the phases ($n = 24$). The average deviation is very sensitive to the value of $V_{\max}$. The effect of the fluid velocity on the prediction of temperature changes, in the aqueous phase of the EE system at 1.4 mm from the interface, is presented in Fig. 2. The conditions used are an initial volume percent of ethanol in an ethyl acetate-rich phase of 5% with the two phases mutually saturated before the contacting. The case for $V_{\max} = 0.0$ corresponds to the pure diffusion model. It is evident that the improvements in the prediction of temperature changes are significant when adding a simple convective mechanism.

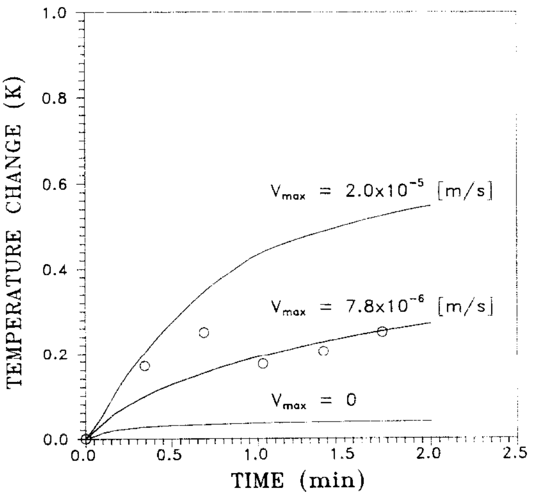

FIG. 2. Effect of fluid velocity on the prediction of temperature changes (EE system): ○, experimental data [3]; ——, model predictions.

CONCLUSIONS

A convection/diffusion model was developed for the prediction of temperature and concentration profiles when a solute is transferred between two partially miscible phases. A linear velocity profile was selected in the region close to the interface, considering that the net fluid movements are due to interfacial activity propagated from the interface to the bulk. This mathematical model was solved using the DSS/2 differential equation solver. The results for temperature changes with a pure diffusion model were in qualitative agreement with available experimental data. Solution of the convection/diffusion model involved the use of an adjustable parameter in the velocity profile equation. In this case the agreement between the experimental data and predicted values was significantly improved. This confirms the existence of both diffusion and convection mechanisms during transfer of a solute in interfacially active liquid systems.

In order to improve the model, future work in this area should concentrate on eliminating some of the major assumptions. Improvements are required in the following areas: (a) use of a time-dependent two-dimensional velocity profile which takes into account circulation of the fluid; (b) consider that equilibrium of the phases is not reached instantaneously at the interface; (c) consider equilibrium concentrations to be functions of time due to temperature dependence; (d) use of experimental heat of mixing data or better predictive methods; and (e) consider concentration and temperature dependence of liquid diffusion coefficients and other physical properties. For an effective verification of the improved mathematical model, experimental data in both phases should be acquired.

The present results provide useful information for the understanding of the effect of convection during solute transfer between partially miscible phases. Guidelines have been provided for future directions of this work so that the results can significantly enhance our understanding of the phenomena of interfacial activity and how it affects mass and heat transfer rates in such systems.

Acknowledgement—The financial support provided by the Mackay Mineral Resources and Research Institute to Bainian Liu is gratefully acknowledged.

REFERENCES

1. E. S. Perez de Ortiz and H. Sawistowski, Interfacial stability of binary liquid–liquid systems—II. Stability behaviour of selected systems. *Chem. Engng Sci.* **28**, 2063–2069 (1973).
2. F. J. Aguirre, G. E. Klinzing, S. H. Chiang, G. K. Leaf and M. Minkoff, Diffusion model for simultaneous mass and heat transfer in partially miscible liquid systems: experimental findings and numerical simulation. *Chem. Engng Sci.* **40**, 1449–1456 (1985).
3. Y. T. Yang, Heat transfer in partially miscible ternary systems. M.S. Thesis, University of Pittsburgh, Pittsburgh, Pennsylvania (1985).
4. B. Liu and F. J. Aguirre, Modeling transfer processes in partially miscible ternary liquid systems, presented at AIChE Annual Meeting, Washington, DC, Paper No. 21z (1988).
5. B. Liu, Use of DSS/2 software for the solution of a

coupled mass and heat transfer problem, M.S. Thesis, University of Nevada, Reno, Nevada (1988).

6. W. Schiesser, DSS/2—An introduction to the numerical method of lines integration of partial differential equations, Lehigh University, Bethlehem, Pennsylvania (1976).
7. W. Schiesser, Variable-grid spatial differentiator in the numerical method of lines, Lehigh University, Bethlehem, Pennsylvania (1984).
8. B. Liu and F. J. Aguirre, An efficient method for handling time-dependent boundary conditions with the DSS/2 differential equation solver, *Simulation* **54,** 274–279 (1990).

Int. J. Heat Mass Transfer. Vol. 34, No. 6, pp. 1575–1576, 1991
Printed in Great Britain

0017–9310/91 $3.00+0.00

Estimation of the stagnant thermal conductivity of saturated porous media

D. A. Nield

Department of Engineering Science, University of Auckland, Auckland, New Zealand

(*Received* 13 *March* 1990 *and in final form* 24 *July* 1990)

INTRODUCTION

Prasad *et al.* [1] recently reported new experimental data for the thermal conductivity of liquid-saturated porous beds of spheres. They compared their data with three correlation formulas proposed by Kunii and Smith [2], Krupiczka [3] and Zehner and Schlünder [4], respectively. Each of these formulas is quite complicated and contains at least two numerical constants which either have been determined empirically or are specific to a particular geometry. The purpose of this note is to demonstrate a simple correlation formula which contains no empirical constants and which gives a useful prediction of the thermal conductivity, given the values of the porosity ε, the fluid conductivity k_f and the solid conductivity k_s. Some other aspects of the results of Prasad *et al.* are also discussed.

The weighted arithmetic, harmonic and geometric means of k_f and k_s, with weighting factors ε and $1-\varepsilon$, are denoted here by k_A, k_H and k_G, respectively, and are given by

$$k_A = \varepsilon k_f + (1-\varepsilon)k_s \quad (1)$$

$$1/k_H = \varepsilon/k_f + (1-\varepsilon)/k_s \quad (2)$$

$$k_G = k_f^{\varepsilon} k_s^{(1-\varepsilon)}. \quad (3)$$

Equation (1) gives the appropriate overall conductivity if the heat conduction in the fluid and solid phases is entirely 'in parallel'. Equation (2) is appropriate if the conduction in the fluid and solid phases is entirely 'in series'. One would expect on physical grounds that k_A and k_H should be upper and lower bounds on the overall conductivity k_m of the medium, since a parallel arrangement should offer the least resistance to heat flow and a series arrangement the greatest resistance. The geometric mean of two quantities is always intermediate in value between the arithmetic and harmonic means of those quantities. This suggests that k_G may well be a good candidate for a correlation formula for a general porous medium.

To test this suggestion, these formulas have been applied to the data given in Table 1 of ref. [1], and the results are given in our Table 1. For comparison, we have listed in the last column the values predicted from the formula of Kunii and Smith [2], namely

$$k_{KS} = k_f\left[\varepsilon + \frac{a_1(1-\varepsilon)}{a_3 + a_2\lambda}\right] \quad (4)$$

where $\lambda = k_f/k_s$, $a_1 = 1$, $a_2 = 2/3$, $a_3 = \varphi_2 + 4.63(\varepsilon - 0.26) \times (\varphi_1 - \varphi_2)$, and the quantities φ_1 and φ_2, which depend on ε, can be obtained from a plot in ref. [2]. On the criterion of smallest root mean square relative error, the Kunii–Smith formula is slightly more successful in predicting the data of Prasad *et al.* [1] than the other correlation formulas mentioned above, namely those of Krupiczka [3] and Zehner and Schlünder [4].

We see from Table 1 that k_G is reasonably competitive with k_{KS} as a predictor of the measured data. Prediction becomes difficult when the values of k_f and k_s are greatly different from each other. The root mean square relative error for the k_G values is 2.8 times that for the k_{KS} values, but to balance this disadvantage formula (3) is clearly much less complicated than equation (4), so if a quick estimate of k_m is required then k_G should serve the purpose. Formula (3) is not specific to beds of spheres (as are the other correlation formulas). It is suggested that formula (3) should be useful in estimating the conductivity of general isotropic porous media.

It is true that equation (3) has its limitations, especially when λ is small. In this situation we see from Tables 1 and 2 of ref. [1] that the three correlations represented in ref. [1] are capable of predicting the thermal conductivity quite accurately, whereas our equation (3) leads to an overprediction for each of the systems glycol/steel (Medium 5 in our Table 1), water/steel (for which Table 3 of ref. [1] lists a measured value of 4.653 whereas equation (3) gives 7.61) and water/

Table 1. Data based on Table 1 of ref. [1]. The values of ε, k_s, λ and k_{KS}, and the measured values of conductivity, are those given in that table. The values for k_f have been computed from the two previous columns. The values of k_A, k_H and k_G have been computed from equations (1), (2) and (3), respectively

	Medium	ε	k_s	$\lambda = k_f/k_s$	k_f	k_A	k_H	k_G	Measured	k_{KS}
1	water/glass	0.396	1.10	0.560	0.616	0.908	0.839	0.874	0.837	0.831
2	water/glass	0.425	1.10	0.562	0.618	0.894	0.824	0.860	0.842	0.810
3	glycol/glass	0.349	1.10	0.235	0.259	0.806	0.515	0.664	0.559	0.656
4	glycol/glass	0.427	1.10	0.235	0.259	0.741	0.460	0.593	0.597	0.555
5	glycol/steel	0.416	37.39	0.007	0.262	21.940	0.623	4.746	2.584	2.167
6	glycol/acrylic	0.402	0.16	1.630	0.261	0.201	0.189	0.195	0.221	0.206
7	water/acrylic	0.427	0.16	3.937	0.630	0.361	0.235	0.287	0.479	0.371