Selection of Mass Transfer Correlations for Rate Based Liquid-Liquid Extraction Model

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(*Received 21 October 2002 • acceped 6 February 2003*)

Abstract−A rate-based model for *mass transfer* in liquid-liquid extraction (LLX) has been developed using *three distinct stages* of drop formation, drop fall or rise and drop coalescence. Binary diffusivities in infinite dilution as well as for concentrated multicomponent mixtures were used to estimate the Maxwell-Stefan binary mass transfer coefficients for both the phases. The mass transfer resistances associated with these coefficients have been categorized in four configurations. Because of the very large number of computations associated with repeated calculations of mass transfer coefficients, a *local model* has been incorporated. A *comparative study* between rate-based and non-equilibrium simulator and our bench scale experiments (LLX of toluene-acetone-water system) has been done. The stage-wise composition profiles of acetone in water and toluene phase of the experimental and simulation runs have been compared by using the relative error square analysis. Based on this analysis, best mass transfer combination and mass transfer resistance model has been selected.

Key words: Rate Based LLX Model, Parallel and Series Resistances, Local Mass Transfer Model, Bench Scale Experiment, Error Square Analysis

INTRODUCTION

Most references in literature assume thermodynamic equilibrium and isothermal operation for liquid-liquid extraction. But real extraction operations are non-equilibrium and may be non-isothermal. This non-equilibrium extraction process can be easily modeled by using a rate-based approach [Taylor and Krishna, 1993; Debjit and Khanna, 2000]; that is, the modeling equations should contain mass transfer rate terms. For multicomponent systems the rate of mass transfer can be written in terms of Maxwell-Stefan [Zimmermann et al., 1995] mass transfer coefficients k_{ij}. These mass transfer coefficients are functions both of binary diffusion coefficients D_{ij} of concentrated mixtures and the convective velocities (slip velocity and jet velocity). D_{ij}s in turn are functions of infinite dilution [Taylor and Krishna, 1993] efficient D_{ij}^0. In the extraction process, the mass transfer between continuous and dispersed phases occurs during drop formation, rise/fall and coalescence. Handlos-Baron [Handlos and Baron, 1957], Skelland-Conger [Skelland and Conger, 1973], Seibert-Fair [Seibert and Fair, 1993], Rocha and Fair [Rocha et al., 1986] developed the mass transfer coefficient expressions for the above three hydrodynamic phenomena. Skelland-Conger [Skelland and Conger, 1973] have adopted a resistance in series approach for these three phenomena, whereas Nanoti and co-workers [Nanoti et al., 1989] have used correction factors for the same. Chun and co-workers [Chun et al., 1996] have shown mass transfer in a spray column considering only the droplet travel-up effect and neglecting the other effects drop formation and coalescence. In this work, four new mass transfer resistance models have been proposed based on the resistances in both the continuous and dispersed phases. The possible combinations of the two-phase resistances are parallel-parallel, parallel-series, series-series and series-parallel. These mass

transfer resistance models have been incorporated in the rigorous non-equilibrium rate-based model (modeling equations of the rate-based model are given in references [Debjit and Khanna, 2000]). To make the mass transfer calculations faster, a simplified local mass transfer model has been proposed.

MASS TRANSFER RESISTANCE MODELS

1. Parallel Resistance Model

In the parallel resistance approach for our rate-based (LLXSIM) model [Debjit and Khanna, 2000] of liquid-liquid extraction, the bulk concentration on each tray is assumed constant, i.e., the concentrations of components in both phases do not change within the static and dynamic holdup over the tray. It has been assumed that in the pth phase mass transfer is taking place from inter-phase (I) to bulk phase (b) and all the three mass transfer effects simultaneously. The total diffusive mass transfer rate equation based on drop rise/fall area a_{kr} for the ith component on the kth stage for the pth phase can be written as follows:

$$J_{ikt}^p = a_{kr}(k_{ij}^p)_{kt}(z_{ik}^{Ip} - z_{ik}^{bp})_{av} \tag{1}$$

where $(z_{ik}^{Ip} - z_{ik}^{bp})_{av}$ is the average driving force for the mass transfer on the kth stage and j is the second component. Based on the above assumption, all three phenomena (drop formation, rise/falling and coalescence) have the same driving force on the kth stage; thus

For *drop formation* (f):

$$J_{ikf}^p = a_{kf}(k_{ij}^p)_{kf}(z_{ik}^{Ip} - z_{ik}^{bp})_{av} \tag{2}$$

drop rise or *fall* (r):

$$J_{ikr}^p = a_{kr}(k_{ij}^p)_{kr}(z_{ik}^{Ip} - z_{ik}^{bp})_{av} \tag{3}$$

drop coalescence (c):

$$J_{ikc}^p = a_{kc}(k_{ij}^p)_{kc}(z_{ik}^{Ip} - z_{ik}^{bp})_{av} \tag{4}$$

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Based on the comparison, taking individual transfer rates in Eqs. (2), (3) and (4) with the total diffusive mass transfer in Eq. (1), one can write the following resistance ($\mathfrak{R}^p$) equation:

$$\frac{1}{\mathfrak{R}^p_{kt}} = \frac{1}{\mathfrak{R}^p_{kf}} + \frac{1}{\mathfrak{R}^p_{kr}} + \frac{1}{\mathfrak{R}^p_{kc}} \qquad (5)$$

where

$$\text{Resistance, } \mathfrak{R}^p_{kph} = \frac{\text{concentration gradient}}{\text{mass transfer rate}}$$
$$= (z^{Ip}_{ik} - z^{bp}_{ik})_{av}/J^p_{ikph} = 1/[a_{kph}(k^p_{ij})_{kph}]$$

Putting the appropriate expression for the resistance terms,

$$a_{kr}(k^p_{ij})_{kt} = a_{kf}(k^p_{ij})_{kf} + a_{kr}(k^p_{ij})_{kr} + a_{kc}(k^p_{ij})_{kc} \qquad (6)$$

Thus the net mass transfer coefficient can be calculated as

$$(k^p_{ij})_{kt} = c_{kf}(k^p_{ij})_{kf} + c_r(k^p_{ij})_{kr} + c_{kc}(k^p_{ij})_{kc} \qquad (7)$$

where

$$c_{kf} = \frac{a_{kf}}{a_{kr}}, \ c_r = 1.0, \ c_{kc} = \frac{a_{kc}}{a_{kr}} \qquad (8)$$

Thus the diffusive mass transfer rate equations for the multi-component system for the parallel resistance model in the dispersed and the continuous phase will be as follows:

$$[\check{J}^d]_k = a_{kr}[\check{\kappa}^d]_k \cdot \Delta \check{x}_k \qquad (9)$$

$$[\check{J}^c]_k = a_{kr}[\check{\kappa}^c]_k \cdot \Delta \check{y}_k \qquad (10)$$

where $\Delta \check{x}_k$ and $\Delta \check{y}_k$ are the mass transfer driving forces in both the phases on the kth stage.

The $[\check{\kappa}^p]$ values are a function of the binary mass transfer coefficients and the mole fractions of the components present in the multi-component mixture and for non-ideal system can be expressed as follows:

$$[\check{\kappa}^p]_k = [\check{R}^p]_k[\check{\Gamma}^p]_k \qquad (11)$$

where the elements of $[\check{R}^p]$ in terms of general mole fractions z_i, are:

$$(R^p_{ii})_k = \frac{z_{ik}}{(k^p_{iNC})_k} + \sum_{\substack{j=1 \\ j \neq i}}^{NC} \frac{z_{jk}}{(k^p_{ij})_k} \qquad \text{where } i=1, 2, …, (NC-1)$$

$$(R^p_{ij})_k = -z_{ik}\left[\frac{1}{(k^p_{ij})_k} - \frac{1}{(k^p_{iNC})_k}\right] \qquad \text{where } i \neq j \ i=1, 2, …, (NC-1) \qquad (12)$$

Thus for a three component liquid-liquid (e.g., Toluene-Acetone-Water) system for the continuous phase the combination of Eq. (11) and Eq. (12) will be:

$$\begin{bmatrix} J^c_1 \\ J^c_2 \end{bmatrix}_k = a_{kr}\begin{bmatrix} R^c_{11} & R^c_{12} \\ R^c_{21} & R^c_{22} \end{bmatrix}\begin{bmatrix} y^I_1 - y^b_1 \\ y^I_2 - y^b_2 \end{bmatrix}_k [\check{\Gamma}^c]_k \qquad (13)$$

The term in Eq. (11) and (13) is a (NC−1)X(NC−1) matrix of thermodynamic factors that corrects for non-ideality, when an activity-coefficient model is used:

$$(\Gamma^p_{ij})_k = \delta_{ij} + z^p_{ik}\left(\frac{\partial \ln \nu^p_{ik}}{\partial z^p_{ik}}\right)_{T,P} \qquad (14)$$

The diffusive mass transfer rate for the third component can be calculated as:

$$J^p_{3k} = -(J^p_{1k} + J^p_{2k}) \qquad (15)$$

Now for the three components system, the total mass transfer rate on the kth stage for component 1 and 2 in both the phases can be written as follows:

$$c\text{-phase}: \quad N^c_{ik} = J^c_{ik} + y_{ik}N_{tk} \quad \text{for i=1 and 2} \qquad (16)$$

$$d\text{-phase}: \quad N^d_{ik} = J^d_{ik} + x_{ik}N_{tk} \quad \text{for i=1 and 2} \qquad (17)$$

For the third component, total rate will be,

$$c\text{-phase}: \quad N^c_{3k} = -(N^c_{1k} + N^c_{2k}) \qquad (18)$$

$$d\text{-phase}: \quad N^d_{3k} = -(N^d_{1k} + N^d_{2k}) \qquad (19)$$

2. Series Resistance Model

In this approach, the concentrations of components in both the phases change within the static and dynamic holdup over the tray. The three mass transfer effects are in series, i.e., drop formation, drop fall/rise and then drop coalescence. Assuming mass transfer rate is taking place from the inter-phase (I) to the bulk phase (b), net mass transfer rate equation based on drop area a_{kr} for the ith component on the kth stage for the pth phase can be written same as Eq. (1). As the three phenomena (drop formation, rise/falling and coalescence) are occurring one after another on the kth stage, it is assumed as a series resistance model, for the pth phase the total diffusive mass transfer rate (J^p_{ikt}) is same for all the three phenomena; thus

For *drop formation*:

$$J^p_{ik} = a_{kf}(k^p_{ij})_{kf}(z^{Ip}_{ik} - z^p_{ikf}) \qquad (20)$$

drop rise or *fall*:

$$J^p_{ik} = a_{kr}(k^p_{ij})_{kr}(z^p_{ikf} - z^p_{ikr}) \qquad (21)$$

drop coalescence:

$$J^p_{ik} = a_{kc}(k^p_{ij})_{kc}(z^p_{ikr} - z^{bp}_{ik}) \qquad (22)$$

z^p_{ikf}, z^p_{ikr} and z^p_{ikc} or z^{bp}_{ik} are the concentrations of the pth phase for the ith component on the kth stage after drop formation, drop rise/fall and drop coalescence, respectively. Comparing, individual mass transfer rates in Eqs. (20), (21) and (22) with the total diffusive mass transfer in Eq. (1), the net resistance ($\mathfrak{R}^p$) can be written as:

$$\mathfrak{R}^p_{kt} = \mathfrak{R}^p_{kf} + \mathfrak{R}^p_{kr} + \mathfrak{R}^p_{kc} \qquad (23)$$

Substituting the appropriate expression for the resistance terms,

$$\frac{1}{a_{kr}(k^p_{ij})_{nt}} = \frac{1}{a_{kf}(k^p_{ij})_{kf}} + \frac{1}{a_{kr}(k^p_{ij})_{kr}} + \frac{1}{a_{kc}(k^p_{ij})_{kc}} \qquad (24)$$

The net mass transfer coefficient can be calculated as

$$a_{kr}(k^p_{ij})_{kt} = \frac{a_{kr}a_{kf}a_{kc}(k^p_{ij})_{kf}(k^p_{ij})_{kr}(k^p_{ij})_{kc}}{a_{kr}a_{kc}(k^p_{ij})_{kr}(k^p_{ij})_{kc} + a_{kf}a_{kc}(k^p_{ij})_{kf}(k^p_{ij})_{kc} + a_{kr}a_{kf}(k^p_{ij})_{kf}(k^p_{ij})_{kr}} \qquad (25a)$$

The above equation can be written in terms of area ratios:

$$(k^p_{ij})_{kt} = \frac{c_{kf}c_r c_{kc}(k^p_{ij})_{kf}(k^p_{ij})_{kr}(k^p_{ij})_{kc}}{c_r c_{kc}(k^p_{ij})_{kr}(k^p_{ij})_{kc} + c_{kf}c_{kc}(k^p_{ij})_{kf}(k^p_{ij})_{kc} + c_{kf}c_r(k^p_{ij})_{kf}(k^p_{ij})_{kr}} \qquad (25b)$$

where c_{kf}, c_r, c_{kc} are same as shown in the Eq. (8).

The diffusive mass transfer rate equations for the multi-component system for the series resistance model in the dispersed and the continuous phase will be same as Eqs. (9) through (19). The difference will be in the binary mass transfer coefficients expression.

3. Combinations of the Resistance Models

In the LLXSIM model, the mass transfer resistances appear in both the continuous (c) and dispersed (d) phases. The four possible resistance combinations are given below:

Parallel (c) - Parallel (d) : Eqs. (5) & (7) and Eqs. (5) & (7)
Series (c) - Series (d) : Eqs. (23) & (25) and Eqs. (23) & (25)
Parallel (c) - Series (d) : Eqs. (5) & (7) and Eqs. (23) & (25)
Series (c) - Parallel (d) : Eqs. (23) & (25) and Eqs. (5) & (7)

AVAILABLE CORRELATIONS

The published correlations for the binary (between component "i" and "j") mass transfer coefficients for the circulating drops and the diffusivities for concentrated and the infinite diluted binary mixtures for the pth phase on the kth stage are shown below. Also some of the expressions of the binary diffusion coefficient are applicable only for the binary systems; these expressions can be made suitable for the multi-component systems. To use these expressions for the multi-component systems, one can propose modified expressions as shown in Eqs. (42) through (46).

1. Binary Mass Transfer Coefficients

1-1. Skelland and Conger, 1973

drop formation

$$d\text{-phase} : (k_{ij}^d)_k = 0.0423 \left(\frac{d_{pk}\rho_k^d}{t_{fk}M_{av\,k}^d} \right) \left(\frac{u_{Nk}^2}{d_{pk}g} \right)^{0.089} \left(\frac{d_{pk}^2}{t_{fk}(D_{ij})_k} \right)^{-0.334}$$
$$[\mu_k^d / \sqrt{(\rho_k^d d_{pk}\gamma_k)}]^{-0.6} \tag{26}$$

$$c\text{-phase} : (k_{ij}^c)_k = 0.386(\rho_k^c / M_{av\,k}^c)[(D_{ij})_k / t_{fk}]^{0.5}$$
$$(\rho_k^c \gamma_k / \Delta \rho_k g t_{fk} \mu_k^c)^{0.407} (g t_{fk}/d_{pk})^{0.148} \tag{27}$$

drop coalescence

$$d\text{-phase} : (k_{ij}^d)_k = 0.173 \left(\frac{d_{pk}\rho_k^d}{t_{ck}M_{av\,k}^d} \right) [\mu_k^d / \rho_k^d (D_{ij}^d)_k]^{-1.115}$$
$$(\Delta \rho_k g d_{pk}^2 / \gamma_k)^{1.302} [u_{Sk}^2 t_{ck}/(D_{ij}^d)_k]^{0.146} \tag{28}$$

$$c\text{-phase} : (k_{ij}^c)_k = 0.5959 \left(\frac{\rho_k^c}{M_{av\,k}^c} \right) [(D_{ij}^c)_k / t_{ck}]^{0.5}$$
$$(\rho_k^c u_{Sk}^3 / g \mu_k^c)^{0.332} (d_{pk}^2 \rho_k^d \rho_k^c u_{Sk}^3 / \mu_k^c \gamma_k)^{0.525} \tag{29}$$

Circulating drop fall/rise

$$d\text{-phase} : (k_{ij}^d)_k = 31.4 \left(\frac{(D_{ij}^d)_k \rho_k^d}{d_{pk} M_{av\,k}^d} \right) \left(\frac{4(D_{ij}^d)_k t_{rk}}{d_{pk}^2} \right)^{-0.34}$$
$$\left(\frac{\mu_k^d}{\rho_k^d (D_{ij}^d)_k} \right)^{-0.125} \left(\frac{d_{pk} u_{Sk}^2 \rho_k^d}{\gamma_k} \right)^{0.37} \tag{30}$$

$$c\text{-phase} : (k_{ij}^c)_k = 0.725 \left(\frac{\rho_k^c}{M_{av\,k}^c} \right) \left(\frac{d_{pk} u_{Sk} \rho_k^c}{\mu_k^c} \right)^{-0.43}$$
$$\left(\frac{\mu_k^c}{\rho_k^c (D_{ij}^c)_k} \right)^{-0.58} u_{Sk}(1-\phi_k) \tag{31}$$

1-2. Handlos and Baron, 1957

$$d\text{-phase} : (k_{ij}^d)_k = 0.00375 u_{Sk} / (1 + \mu_k^d / \mu_k^c) \tag{32}$$

$$c\text{-phase} : (k_{ij}^c)_k = 0.725(Re^c)_k^{-0.43} (1-\phi_k) u_{Sk} (Sc_{ij}^c)_k^{-0.58} \tag{33}$$

1-3. Rocha and Fair-modified by Lao et al., 1989

drop formation

$$d\text{-phase} : (k_{ij}^d)_k = [-6.0 + 0.07 We_k + 6.5(\gamma_{ref\,k}/\gamma_k)]$$
$$\sqrt{(D_{ij}^d)_k u_{Nk}/d_{pk}} \tag{34}$$

$$c\text{-phase} : (k_{ij}^c)_k = [-6.0 + 0.07 We_k + 6.5(\gamma_{ref\,k}/\gamma_k)]$$
$$\sqrt{(D_{ij}^c)_k u_{Nk}/d_{pk}} \tag{35}$$

drop fall/rise

$$d\text{-phase} : (k_{ij}^d)_k = (0.70 + 0.03 We_k)[0.00375 u_{Sk}/(1+\mu_k^d/\mu_k^c)] \tag{36}$$

$$c\text{-phase} : (k_{ij}^c)_k = (0.70 + 0.20 We_k) 0.725(d_{pk} u_{Sk} \rho_k^c / \mu_k^c)^{-0.43}$$
$$(\mu_k^c / [\rho_k^c (D_{ij}^c)_k])^{-0.58}(1-\phi_k) u_{Sk} \tag{37}$$

1-4. Seibert and Fair, 1993

drop formation

$$d\text{-phase} : (k_{ij}^d)_k = 1.3 \left[\frac{(D_{ij}^d)_k}{\pi t_{fk}} \right]^{1/2} \tag{38}$$

$$c\text{-phase} : (k_{ij}^c)_k = 1.3 \left[\frac{(D_{ij}^c)_k}{\pi t_{fk}} \right]^{1/2} \tag{39}$$

drop fall/rise

$$d\text{-phase} : \text{if} \frac{(Sc_{ij}^c)_k^{0.5}}{(1+\mu_k^d/\mu_k^c)} > 6, \quad (k_{ij}^d)_k = 0.023 u_{Sk}[1+(Sc_{ij}^d)_k]^{0.5} \tag{40a}$$

$$\text{if} \frac{(Sc_{ij}^c)_k^{0.5}}{(1+\mu_k^d/\mu_k^c)} < 6, \quad (k_{ij}^d)_k = 0.00375 u_{Sk}/(1+\mu_k^d/\mu_k^c) \tag{40b}$$

$$c\text{-phase} : (k_{ij}^c)_k = 0.698 \left[\frac{(D_{ij}^c)_k}{d_{pk}} \right] Re_{ck}^{0.5} (Sc_{ij}^c)_k^{0.4}(1-\phi_k) \tag{41}$$

2. Binary Diffusion Coefficients for Concentrated Mixtures

Dullien and Asfour, 1985 :
$$(D_{ij}^p)_k / \mu_k^p = [(D_{ij}^0)_k^p / \mu_{jk}]^{\bar{z}_j} [(D_{ji}^0)_k^p / \mu_{ik}]^{\bar{z}_i} \tag{42}$$

Vignes, 1966 :
$$(D_{ij}^p)_k = (D_{ij}^0)_k^{p\bar{z}_j} (D_{ji}^0)_k^{p\bar{z}_i} \tag{43}$$

Wesselingh and Krishna, 1990 :
$$(D_{ij}^p)_k = (D_{ij}^0)_k^{p(1+\bar{z}_j-\bar{z}_i)/2} (D_{ji}^0)_k^{p(1+\bar{z}_i-\bar{z}_j)/2} \tag{44}$$

Caldwell and Babb, 1956 :
$$(D_{ij}^p)_k = \bar{z}_j (D_{ij}^0)_k^p + \bar{z}_i (D_{ji}^0)_k^p \tag{45}$$

Leffler and Cullinan, 1970 :
$$(D_{ij}^p)_k \mu_k^p = [(D_{ij}^0)_k^p \mu_{jk}]^{\bar{z}_j} [(D_{ji}^0)_k^p \mu_{ik}]^{\bar{z}_i} \tag{46}$$

where

$$\bar{z}_i = \frac{z_{ik}^p}{z_{ik}^p + z_{jk}^p}, \quad \bar{z}_j = \frac{z_j^p}{z_{ik}^p + z_{jk}^p} \tag{47}$$

3. Infinite Dilution Maxwell-Stefan Binary Diffusion Coefficients

Wilke and Chang, 1955 : $(D_{ij}^0)_k^p = 7.4 * 10^{-8} (\phi_j M_j)^{0.5} T_k^p / \mu_{jk} V_{ik}^{0.6}$ (48)

Siddiqi and Lucas, 1986 :
$$(D_{ij}^0)_k^p = 9.89 * 10^{-8} \mu_{jk}^{-0.907} V_{ik}^{-0.45} V_{jk}^{-0.265} T_k^p \tag{49}$$

Hayduk and Minhas, 1982 :
$$(D_{ij}^0)_k^p = 1.55 * 10^{-8} V_{jk}^{-0.23} \mu_{jk}^{-0.92} P_j^{0.5} P_i^{-0.42} T_k^{p1.29} \tag{50}$$

Tyn and Calus, 1975 :

$$(D_{ij}^0)_k^p = 8.93*10^{-8} V_{ik}^{1/6} V_{jk}^{-1/3} \mu_{jk}^{-1} (P_j/P_i)^{0.6} T_k^p \tag{51}$$

4. Mass Transfer Areas

The expressions of the areas for three different mass transfer phenomena are presented.

Drop formation area : $a_{fk} = n_{0k} \pi d_{pk}^2$ (52)

Drop fall/rise area : $a_{rk} = \dfrac{6(A_0 - A_D)(h_0 - h_{ck})\phi_k}{d_{pk}}$ (53)

Drop coalescence area : $a_c = A_0 - A_D$ (54)

The question arises, as so many expressions are available for the mass transfer, diffusion and infinite dilution coefficients, which will be suitable for simulation of a specific liquid-liquid extraction column. In these circumstances, it is better to mention that all expressions will not be valid because some are valid for polar, some for non-polar and some are valid for aqueous systems. A set of the equations (coefficients) is suitable if the results of the simulator match with the actual operation within acceptable tolerance.

LOCAL MASS TRANSFER MODEL

As mentioned and shown earlier, the expressions for the binary diffusitivites and mass transfer coefficients are complicated functions of basic physical properties and time consuming to use in the rigorous simulator. For simulation with the large number of components in an industrial liquid-liquid extraction column, the number of "calls" the diffusitivity and mass transfer coefficient functions are more than several million times in a single iteration. Completion of a full rigorous simulation of an industrial column takes more than two hours using a Pentium-III, 1 Ghz workstation. To make the calculation faster, a novel technique of local mass transfer model has been proposed here. Local model approach has been used for the calculation of non-ideal multicomponent LLE phase equilibria [Chimowitz et al., 1983, 1984] and thermodynamic property [Hillestad et al., 1989]. In this work for the local model of mass transfer coefficient a simple expression has been proposed. This expression has been used in the inner iterations of simulation when the basic physical properties (such as the phasic density, phasic viscosity, phasic molecular weight and the interfacial tension) do not change more than 0.1% of the previous iteration value. If the change in any of the basic properties is more than 0.1% then the simulator uses the actual detailed mass transfer coefficient expression. The expression used for the local mass transfer coefficient, a function of the Sherwood number, is given below:

$$[(k_{ij}^p)_k^{local}]^{n+1} = [(Sh_{ij}^p)_k]^n \left[\left(\frac{c^p D_{ij}^p}{d_p} \right)_k \right]^{n+1} \tag{55}$$

where

n+1, n=the present and previous iterations, respectively.

After introducing the local model for the mass transfer coefficient calculation, the simulation runs are approximately 20 to 25 times faster than earlier.
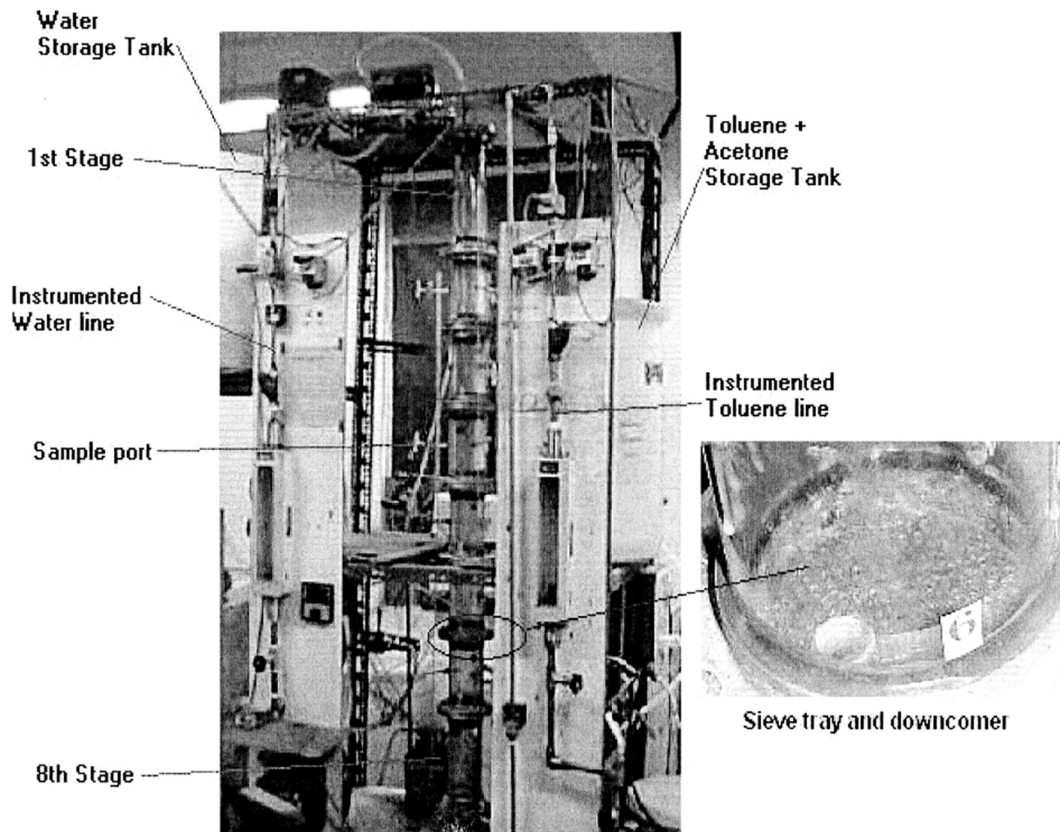

Fig. 1. Experimental liquid-liquid extraction column

Table 1. Column and feed specification

Column specification:	
Column diameter	0.102 m
No. of stages	8
Sieve tray spacing	0.2 m
No. of holes (sieve)	120
Sieve hole diameter	0.00318 m
Feed specification:	
Toluene-Acetone (Feed)	@ 8 stage (bottom)
Water (Solvent)	@ 1 stage (top)
Acetone % in Toluene	15
Column operating temperature	32 degree C (Isothermal)
Solvent to feed molar ratio	3 (Run-I); 4 (Run-II)

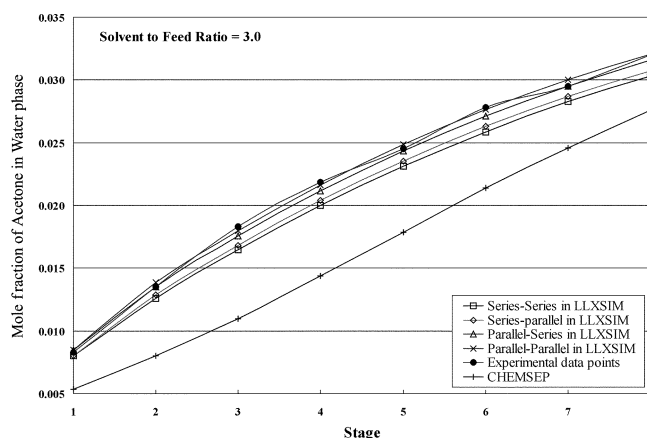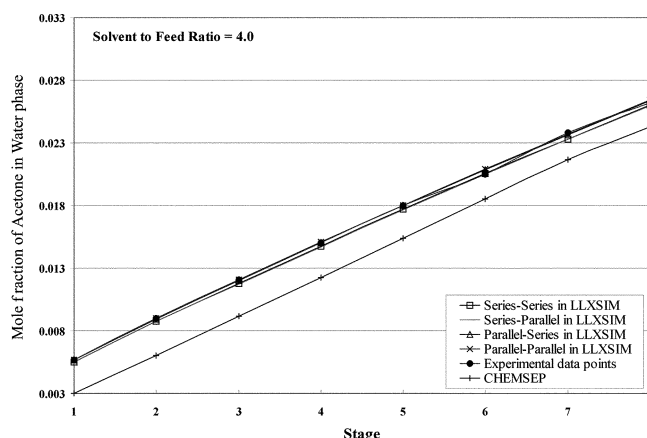## BENCH SCALE EXPERIMENTAL PROCEDURE

Liquid-liquid extraction was studied in a 10.2 cm diameter sieve tray column; total length of the column is 1.78 meter with 8 stages. A cylindrical down-comer (length 13 cm and diameter 17 mm) made of glass was fixed in each tray. To avoid corrosion stainless steel and teflon pipelines were used. To draw the samples for both phases separate sample ports have been provided at each stage in the glass column. The complete experimental setup is shown in Fig. 1. Brief column and feed specifications are shown in Table 1. In this study, heavy continuous phase water is fed from top and the light dispersed phase toluene-acetone mixture is fed from bottom of the column. A spiral-shaped distributor was used to disperse the light toluene phase at the bottom of the column. At start of the run, the column was filled with water (the heavy continuous phase) approximately up to the continuous phase inlet. Then light dispersed phase line was opened. When the toluene phase reaches the topmost stage, the water line is also opened. The column was operated isothermally at 32 °C. For both the runs steady state was attained after 20 minutes. Steady-state condition is indicated by constant height of coalesced layer in each tray. After steady state of the column was attained, samples from all the eight stages were collected and kept in the airtight glass bottles. The column was operated for 45 minutes for each run. All the samples were analyzed on a Gas Chromatograph (GC) with the Porapac-Q packed column (SS column, 1/8" OD, 1.5 meter length with). The GC was operated in isothermal mode at 200 °C oven temperature and 210 °C detector (TCD) temperature. Calibration of GC was done with different known concentrations of Toluene-Acetone along with known amount of Water (0 to 5% in interval of 1%); and Acetone-Water along with known amount of Toluene (0 to 5% in interval of 1%) mixtures. The mole fraction vs area curves for these known samples were prepared.

RESULTS AND DISCUSSION

For the comparison of experimental and simulation results, we have taken two LLX runs (solvent to feed molar ratio [S/F] 3 and 4) of one bench-scale extraction column. As mentioned earlier, considering the parallel-parallel, the parallel-series, the series-series and the series-parallel resistance combinations and using all the binary mass transfer coefficients and diffusion coefficients (concentrated

mixtures, infinite dilution) as shown earlier, we have run our rate-based simulator - LLXSIM. In the CHEMSEP [Kooijman et al., 1988] simulator, there is provision of Handlos-Baron, 1957 mass transfer coefficient only. The stage-wise composition profiles of the acetone in both the toluene and water phase of the bench-scale extraction column have been compared with CHEMSEP (possible runs) and LLXSIM results.

From the simulation results, it has been observed that the best possible (matching closely with the experimental results) mass transfer and the diffusivities combination is *Skelland-Conger*, *Wesselingh-Krishna* and *Siddiqi-Lucas*. All the four possible combinations of the resistance models have been tried. Acetone composition profiles in both the water and toluene phases for the two runs (Run-I and II) have been shown in Figs. 2 through 5. The bench-scale extraction column results closely match with the **LLXSIM parallel-parallel** mass transfer resistance model. The comparisons of the composition profiles are not sufficient for the validation of a model. Thus the LLXSIM simulated (with best combination of mass transfer and diffusion coefficients and resistance model) and experimental profiles for the number of drops and static holdup on stages are given in Figs. 6 and 7 (CHEMSEP does not provide any such kind of profiles). Error analysis for one set of all the mass transfer coefficients, all the diffusivities in the concentrated mixture with

Fig. 2. Acetone composition profiles in water phase for S/F=3.0.

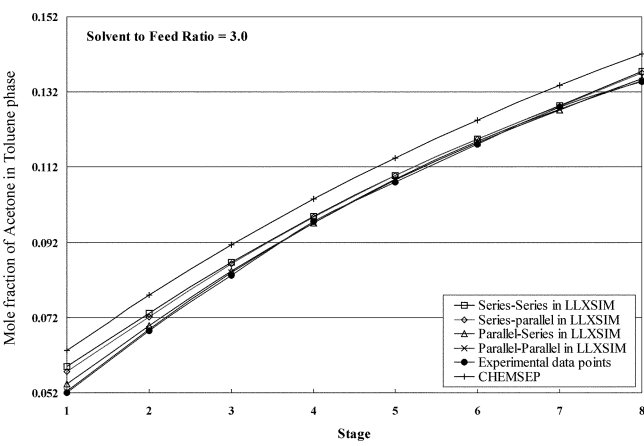**Fig. 3. Acetone composition profiles in water phase for S/F=4.0.**

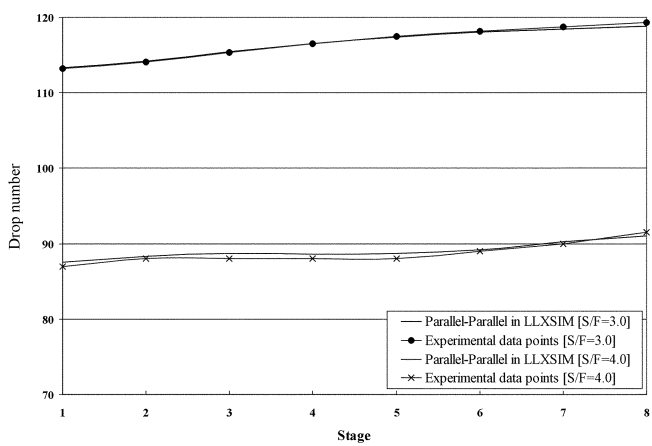**Fig. 4. Acetone composition profiles in toluene phase for S/F=3.0.**

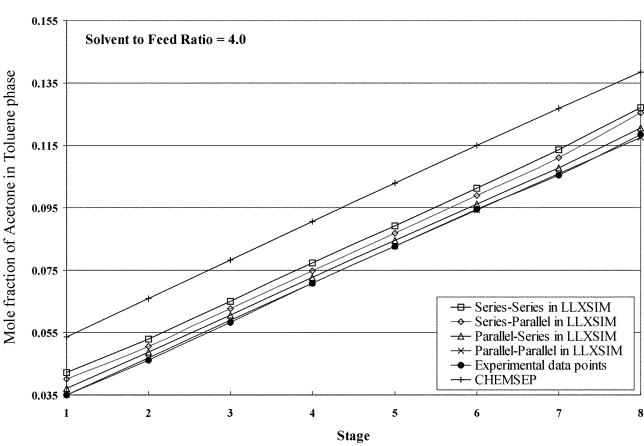**Fig. 6. Drop number in stages for S/F=3 and 4.**

Fig. 5. Acetone composition profiles in toluene phase for S/F=4.0.
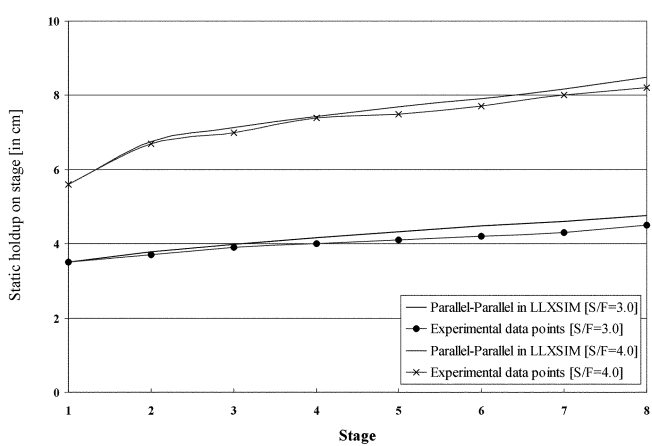

Fig. 7. Static holdup in stages for S/F=3 and 4.

Siddiqi-Lucas infinite dilution diffusion coefficient are shown in Table 2. A through C.

The sum of the error squares between the experimental and prediction from the simulators (LLXSIM and CHEMSEP) can be calculated as follows:

$$RESQ = \sum_{k=1}^{NS} \left[\frac{(z_i^p - z_i^{pexp})}{z_i^p} \right]_k^2 \tag{56}$$

where

RESQ=the relative error square of the predicted and the experimental mole fractions in the continuous phase.

Table 2a shows that the diffusion coefficient for concentrated mixture, Wesselingh-Krishna is 3 to 5 times better in comparison with

other correlations for fixed D_{ij}^0. For the CHEMSEP runs, even Wesselingh-Krishna is way far off. Siddiqi-Lucas is the better option in the LLXSIM in comparison with Wilke-Change for fixed D_{ij} using Wesselingh-Krishna with parallel(c)-parallel(d) combination with S/F=3.0 as shown in Table 2b. Table 2c illustrates the Parallel(c)-Parallel(d) resistance is the best combination for all the mass transfer coefficients for fixed D_{ij} using Wesselingh-Krishna and fixed D_{ij}^0 using Siddiqi-Lucas with S/F=3.0. Same pattern for the relative error square (RESQ) has been repeated for S/F=4.0.

CONCLUSIONS

Experimental and the simulated bench-column profiles have been

Table 2a. Relative Error Square [RESQ×10³] for concentrated diffusivity correlations

k_{ij} \ D_{ij}	LLXSIM					CHEMSEP
	Dullien-Asfour	Vignes	Wesselingh-Krishna	Caldwell-Babb	Leffler-Cullinan	Wesselingh-Krishna
Skelland-Conger	15.65	10.34	2.27	8.21	13.58	Not available
Handlos-Baron	16.03	10.97	2.87	9.89	13.98	813.52
Rocha-Fair	16.25	12.05	2.95	10.34	14.75	Not available
Seibert-Fair	16.57	13.32	3.13	12.00	15.31	Not available

Note: LLXSIM has been run for fixed D_{ij}^0 using Siddiqi-Lucas with parallel (c)-parallel (d) combination with S/F=3.0

Table 2b. Relative Error Square [RESQ×10³] for infinite dilution diffusivity correlations

D^0_{ij}	LLXSIM		CHEMSEP	
k_{ij}	Wilke-Chang	Siddiqi-Lucas	Wilke-Chang	Siddiqi-Lucas
Skelland-Conger	3.71	2.27	Not available	Not available
Handlos-Baron	4.52	2.87	795.98	813.52
Rocha-Fair	4.95	2.95	Not available	Not available
Seibert-Fair	5.29	3.13	Not available	Not available

Note: LLXSIM has been run for fixed D_{ij} using Wesselingh-Krishna with parallel (c)-parallel (d) combination with S/F=3.0

Table 2c. Relative Error Square [RESQ×10³] for the resistance combinations

Resistance combinations k_{ij}	Parallel(c)-Parallel(d)	Parallel(c)-Series(d)	Series(c)-Series(d)	Series(c)-Parallel(d)
Skelland-Conger	2.27	4.75	44.63	25.39
Handlos-Baron	2.87	5.61	47.12	26.92
Rocha-Fair	2.95	6.32	50.04	28.09
Seibert-Fair	3.13	6.87	52.73	30.00

Note: LLXSIM has been run for fixed D_{ij} using Wesselingh-Krishna and fixed D^0_{ij} using Siddiqi-Lucas with S/F=3.0

compared. Rate-based (LLXSIM) simulation results match well with experimental results. Out of the four possible schemes for mass transfer resistance models, the parallel-parallel resistance model matches closely with both of the experimental runs. Not only the concentration profiles of acetone in water phase, the hydrodynamic features such as the number of drops and static holdup in the stages also match with the experimental runs. A local model for the mass transfer coefficient calculation minimizes the simulation time substantially. The mass transfer, diffusion coefficients and the resistance models for both the phases have been chosen based on the error analysis.

ACKNOWLEDGMENT

NOMENCLATURE

A_0 : cross sectional area of entire column [m²]
A_D : cross sectional area of downcomer/upcomer [m²]
a : interfacial area [m²]
c : molar density [mol/m³]
D^0 : diffusivity in infinite solution [m²/s]
D : binary diffusivity in concentrated multicomponent mixture [m²/s]
d_p : drop diameter [m]
F : feed [mol/s]
g : acceleration due to gravity [m²/s]
h : height [m]
J : diffusive mass transfer rate [mol/s]
k : binary masstransfer coefficient [mol/m²s]
$\check{\kappa}$: mass transfer coefficient's matrix
M : average molecular weight

N : total mass transfer rate [mol/s]
n_0 : number of perforations per plate
NS : number of stages
P : parachor
P : pressure [N/m²]
Re : Reynolds number
$\Re$: resistance to mass transfer [s/mol]
$\check{R}$: mass transfer coefficient's matrix
Sc : Schmidt number
S : solvent [mol/s]
Sh : Sherwood number
T : temperature [K]
t : time [s]
u : velocity [m/s]
V : molar volume [m³/mol]
We : Weber number
x : mole fraction in dispersed phase
$\bar{x}$: normalized mole-fraction with respect to participating pair ij
y : mole fraction in continuous phase
z : generalized mole fraction

Greek Letters
δ_{ij} : kronecker delta
μ : viscosity [kg/m s]
γ : interfacial tension [N/m]
ρ : density [kg/m³]
$\Delta\rho$: positive difference in density [kg/m³]
ϕ : dispersed phase holdup
$\check{\phi}$: association parameter
Γ, ν : activity coefficient

Superscripts
b : bulk phase i.e., either continuous or dispersed
c : continuous phase
d : dispersed phase

I   : interface
p   : pth phase

Subscripts
av   : average
c   : coalescence, coalesced
f   : formation
i   : component
j   : component
k   : stage
n   : no. of iteration
N   : nozzle
NC   : the number of components in the liquid mixture
ph   : phenomena-formation, rise and coalescence
r   : rise
s   : slip velocity
t   : total

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