A NEW METHOD OF CALCULATION OF MULTICOMPONENT LIQUID–LIQUID EXTRACTION

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Received February 2nd, 1976

The paper deals with the calculation of the separation of multicomponent liquid–liquid mixtures in a general counter-current extraction cascade with backmixing between the stages, refluxes at both ends and several feeds and withdrawals of the phases.

Numerous methods have been proposed in the literature[1–4,8] for the calculation of the extraction separation based on a relatively very simple model of counter-current cascade of equilibrium stages without back flows between individual stages. However, because backmixing affects mass transfer and may thus strongly alter the concentrations in the exiting streams, it has to be accounted for in more precise calculations. The author of this paper together with Rod have devised a general computational method[5], which respects backmixing between individual stages of the extraction cascade, but after numerous applications of this method has found that the calculation can be substantially expedited while simultaneously providing for a reliable convergence. This has been accomplished by removing the explicit numerical influence of the driving force for mass transfer, expressed in terms of the difference between the actual and equilibrium concentrations of components, as the most sensitive and least stable factor from the view point of the numerics.

The question of a proper description of liquid–liquid equilibria in multicomponent systems is not dealt with in this paper; it is assumed that the equilibrium may be described by the distribution coefficients of the components which are functions of phase composition. It has been known that the rate of transfer of a component in a multicomponent mixture is affected also by transfer rates of the remaining components. Hence, the overall mass transfer coefficients depend not only on the partial coefficients in both phases and the phase equilibrium but also on concentration of the transfered solute and mass fluxes of all components. This fact has been respected in the proposed computational method.

THEORETICAL

A Mass Balance about a Counter-Current Extraction Cascade

A model of the counter-current extraction equipment as a stagewise cascade in its most general form is shown in Fig. 1. The cascade consists of N stages numbered

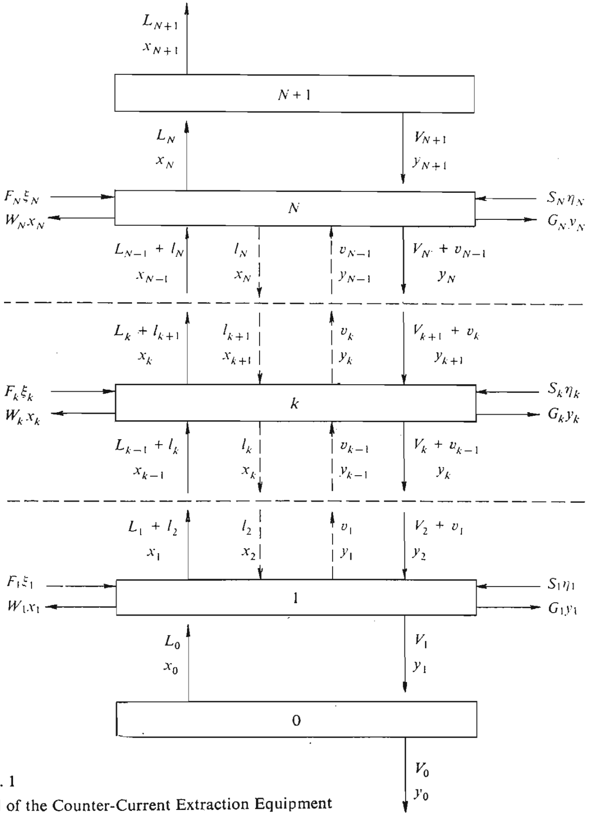

Fig. 1

Model of the Counter-Current Extraction Equipment
Explication see in text.

in the direction of the flow of the raffinate. The stages designated by 0 and $N + 1$ represent technological points where the extract and raffinate refluxes are formed. The feeds of both the extract and the raffinate phase of arbitrary composition may be located in any of the stages of the cascade ($k = 1$ up to N). Also the withdrawal of any of the phases may be situated into any of the stages ($k = 1$ up to N). The existence of the back flows of both phases between neighbouring stages is considered and their intensity may change along the cascade.

The mass transfer in individual stages of the cascade is described by means of the overall mass transfer coefficients relating to the driving force expressed in terms of concentrations of either of the phases. In the following we shall make use of the coefficients relating to concentrations in the raffinate phase.

The transport of mass between the phase in the k-th stage may be expressed for each component by the equation

$$\begin{aligned} &-(L_{k-1} + l_k)\,x_{k-1} + (L_k + l_k + l_{k+1})\,x_k - l_{k+1}x_{k+1} - \lambda_k = \\ &= (V_{k+1} + v_k)\,y_{k+1} - (V_k + v_k + v_{k-1})\,y_k + v_{k-1}y_{k-1} + \omega_k = \\ &= -K_x a_k w_k \overline{(x - x^+)}_k = \chi_k\,, \end{aligned} \tag{1}$$

$$\lambda_k = F_k\xi_k - W_kx_k\,, \quad \omega_k = S_k\eta_k - G_ky_k\,, \quad k = 1, 2, \ldots, N \qquad (2), (3)$$

where $\overline{(x - x^+)}_k$ represents the mean driving force in the k-th stage of the cascade. (The subscript of the component has been omitted for simplicity. Unless stated otherwise, k in the following may take values $1, 2, \ldots, N$).

The boundary conditions for the cascade read

$$l_1,\, l_{N+1},\, v_0,\, v_N = 0\,. \tag{4}$$

The mass balance about the reflux stages is described by the equations

$$V_1y_1 = L_0x_0 + V_0y_0\,, \quad L_Nx_N = L_{N+1}x_{N+1} + V_{N+1}y_{N+1}\,. \qquad (5,)\,(6)$$

The reflux ratios of the transferred solute are defined as

$$R_0 = (L_0x_0)/(V_0y_0)\,, \quad R_{N+1} = (V_{N+1}y_{N+1})/(L_{N+1}x_{N+1})\,. \qquad (7), (8)$$

To express the driving force for mass transfer within the real stage by means of the driving force in an ideally mixed stage, a factor ϕ, defined as

$$\phi_k = \overline{(x - x^+)}/(x_k - x_k^+)\,. \tag{9}$$

is introduced. This factor generally depends on the flow rates of the phases, back flows, composition of the phases and the design of the stage; for an ideal mixer we may put $\phi_k = 1$. Otherwise the model assumes that the composition of the back flows of the phase is identical with that of the bulk flows leaving the stage. The equilibrium between the phases is expressed by means of the distribution coefficients, m_i, which are functions of the composition of the phases at the interface (i is the index of the component). Thus

$$x_k^+ = y_k/m_k\,. \tag{10}$$

On expressing the back flows of the phases l_k, v_k in terms of the coefficients of backmixing $\overline{LL}$, $\overline{VV}$ and the flows of the phase L_k, V_k as

$$l_k = L_{k-1}\overline{LL}\,, \quad v_k = V_{k+1}\overline{VV} \qquad (11), (12)$$

on rearranging Eq. (*1*) formally into the form

$$\begin{aligned} &-L_{k-1}(x_{k-1} + \overline{LL}(x_{k-1} - x_k)) + L_k(x_k + \overline{LL}(x_k - x_{k+1})) - \lambda_k = \\ &= V_{k+1}(y_{k+1} + \overline{VV}(y_{k+1} - y_k)) - V_k(y_k + \overline{VV}(y_k - y_{k-1})) + \omega_k = \\ &= -K_x a_k w_k \overline{(x - x^+)_k} = \chi_k \end{aligned}$$

and on defining the so-called modified concentration variables X, Y as

$$X_k = x_k + \overline{LL}(x_k - x_{k+1})\,, \tag{13}$$

$$Y_k = y_k + \overline{VV}(y_k - y_{k-1})\,, \tag{14}$$

$$X_0 = x_0\,, \quad Y_0 = y_0\,, \quad X_{N+1} = x_{N+1}\,, \quad Y_{N+1} = y_{N+1}\,, \qquad (15)-(18)$$

the set of the balance equations (*1*), (*5*)–(*8*) may be written in the form

$$U_k - U_{k-1} - \lambda_k = -Z_k + Z_{k+1} + \omega_k = E_k(x_k - y_k/m_k) = \chi_k\,, \tag{19}$$

$$Z_1 = U_0 + Z_0\,, \quad U_N = U_{N+1} + Z_{N+1}\,, \quad R_0 = U_0/Z_0\,, \quad R_{N+1} = Z_{N+1}/U_{N+1} \qquad (20)-(23)$$

where

$$E_k = -\phi_k K_x a_k w_k\,, \quad U_k = L_k X_k\,, \quad Z_k = V_k Y_k\,, \qquad (24)-(26)$$

$$k = 0, 1, 2, \ldots, N, N + 1\,.$$

In terms of the modified variables X, Y the balance set simplifies to the form convenient for an iterative method of calculation as the modified set formally corresponds to a counter-current cascade without backmixing between the stages. Clearly, for a real cascade without backmixing $X_k = x_k$ and $Y_k = y_k$ for all k.

THE MASS TRANSFER RATE

In the balance equations (*1*) and (*19*) the mass flux of the solute i across the interface in the k-th stage is expressed by the relation (the subscript of the stage $k = 1, 2, \ldots, N$ has been omitted for simplicity)

$$\chi_i = E_i(x_i - y_i/m_i) \, . \qquad (27)$$

The theory of mass transfer based on the concept of the diffusion of individual species near the interface indicates that the rate of transfer of a species is affected by the concentration profile of all components on both sides of the interface. The quantity K_{xi} thus is not a constant but depends on all partial transfer coefficients of the components and composition of both phases. From the theory of diffusion[6] it follows for the flux of a species away from the interface into the bulk of the phase x that

$$H_{xi} = \bar{k}_{xi}(x_i^+ - x_i) + x_i^+ \sum_j H_{xj} \, ; \quad i, j = 1, 2, \ldots, P \, , \qquad (28)$$

where the coefficient $\bar{k}_{xi}$ depends on the mass transfer. This dependence can be expressed by means of a correction factor φ_x as

$$\bar{k}_{xi} = \varphi_x k_{xi} \, , \qquad (29)$$

where k_{xi} is the coefficient of mass transfer independent of the mass transfer rate. For this factor[6] the following relation has been derived from the film theory of mass transfer

$$\varphi_x = \left(\sum_j H_{xj}/k_{xj}\right) / \left(\exp\left(\sum_j H_{xj}/k_{xj}\right) - 1\right) . \qquad (30)$$

Similarly we may write for the flux of the component away from the interface into the bulk of the phase y.

$$H_{yi} = \bar{k}_{yi}(y_i^+ - y_i) + y_i^+ \sum_j H_{yj} \, , \qquad (31)$$

$$\bar{k}_{yi} = \varphi_y k_{yi} \, , \qquad (32)$$

$$\varphi_y = \left(\sum_j H_{yj}/k_{yj}\right) / \left(\exp\left(\sum_j H_{yj}/k_{yj}\right) - 1\right) . \qquad (33)$$

Taking the mass flux across the interface, H_i, in the direction from phase x into y as positive we may write

$$H_{yi} = -H_{xi} = H_i = -\chi_i/(\phi_i a w)\,. \tag{34}$$

The assumption of equilibrium conditions at the interface is expressed by

$$y_i^+ = m_i x_i^+\,, \tag{35}$$

where the distribution coefficient m_i is a function of $(P\text{-}2)$ concentrations of the components at the interface.

From Eqs (*28*), (*31*) and (*34*) it follows for the interfacial concentrations that

$$x_i^+ = (\bar{k}_{xi}x_i - H_i)/(\bar{k}_{xi} - \sum_j H_j)\,, \quad y_i^+ = (\bar{k}_{yi}y_i + H_i)/(\bar{k}_{yi} + \sum_j H_j) \qquad (36), (37)$$

Combining Eqs (*35*)–(*37*) we obtain

$$H_i = \frac{x_i - y_i/m_i + (x_i/\bar{k}_{yi} + y_i/(m_i\bar{k}_{xi}))\sum_j H_j}{1/\bar{k}_{xi} + 1/(m_i\bar{k}_{yi}) + (1/(m_i\bar{k}_{xi}\bar{k}_{yi}))\,(m_i - 1)\sum_j H_j}\,. \tag{38}$$

A comparison of Eqs (*24*), (*27*), (*34*) and (*38*) leads to an expression for the overall coefficient of mass transfer

$$K_{xi} = \frac{1 + [(x_i/\bar{k}_{yi} + y_i/(m_i\bar{k}_{xi}))/(x_i - y_i/m_i)]\sum_j H_j}{1/\bar{k}_{xi} + 1/(m_i\bar{k}_{yi}) + (1/(m_i\bar{k}_{xj}k_{yi}))\,(m_i - 1)\sum_j H_j}\,. \tag{39}$$

In a particular case, when the convective flow across the interface is zero, *i.e.* $\sum_j H_j = 0$, Eq. (*39*) simplifies to

$$K_{xi} = (1/\bar{k}_{xi} + 1/(m_i\bar{k}_{yi}))^{-1}\,. \tag{40}$$

If, in addition, the mass fluxes of individual components are negligible $(H_i \to 0)$ then φ_x, $\varphi_y \to 1$ and

$$K_{xi} \approx (1/k_{xi} + 1/(m_i k_{yi}))^{-1}\,. \tag{41}$$

THE CASCADE OF REAL STAGES

By means of Eqs (*13*)–(*18*), (*25*), (*26*) the concentrations of the components x, y may be expressed as

$$x_{N+1} = U_{N+1}/L_{N+1}\,, \quad x_N = U_N/L_N\,, \tag{42}$$

$$x_k = (U_k/L_k + \overline{L}\overline{L}x_{k+1})/(1 + \overline{L}\overline{L})\,; \quad k = N-1, N-2, \ldots, 1\,, \tag{43}$$

$$x_0 = U_0/L_0\,, \quad y_0 = Z_0/V_0\,, \quad y_1 = Z_1/V_1\,, \tag*{(44)–(46)}$$

$$y_k = (Z_k/V_k + \overline{V}\overline{V}y_{k-1})/(1 + \overline{V}\overline{V})\,; \quad k = 2, 3, \ldots, N\,, \tag{47}$$

$$y_{N+1} = Z_{N+1}/V_{N+1}\,. \tag{48}$$

Substituting Eqs (*42*)–(*48*) into Eq. (*27*) we obtain

$$\chi_k = E_k\Big(\sum_{j=k}^{N} \alpha_{k,j}U_j/L_j - (1/m_k)\sum_{j=1}^{k} \beta_{k,j}Z_j/V_j\Big)\,; \quad k = 1, \ldots, N\,, \tag{49}$$

where

$$\alpha_{k,j} = \begin{cases} 1/(1 + \overline{L}\overline{L})\,, & \text{for} \quad j = k \\ \overline{L}\overline{L}\alpha_{k,j-1}/(1 + \overline{L}\overline{L})\,, & \text{for} \quad k + 1 \leqq j \leqq N - 1\,; \quad k = 1, \ldots, N - 1 \\ \overline{L}\overline{L}\alpha_{k,N-1}\,, & \text{for} \quad j = N \end{cases} \tag{50}$$

$$\alpha_{N,N} = 1\,, \quad \beta_{1,1} = 1 \tag*{(51), (52)}$$

$$\beta_{k,j} = \begin{cases} 1/(1 + \overline{V}\overline{V})\,, & \text{for} \quad j = k \\ \overline{V}\overline{V}\beta_{k,j+1}/(1 + \overline{V}\overline{V})\,, & \text{for} \quad k - 1 \geqq j \geqq 2\,; \quad k = 2, \ldots, N\,. \\ \overline{V}\overline{V}\beta_{k,2}\,, & \text{for} \quad j = 1\,. \end{cases} \tag{53}$$

For the feeds and withdrawals we still introduce partial sums

$$A_k = \sum_{j=k}^{N}(\lambda_j + \omega_j)\,; \quad k = 1, \ldots, N\,, A_{N+1} = 0\,. \tag*{(54), (55)}$$

The modified balance set (*19*)–(*23*), (*49*) can be solved analytically with respect to U, Z after elimination of Z or U. From the analytical point of view both approaches are identical; the preference for only one of these approaches, however, is essential as shall be explained below.

Elimination of Z by means of U

From Eqs (*19*)–(*23*), (*54*) it follows for the variable Z that

$$Z_{N+1} = R_{N+1}U_{N+1}\,, \tag{56}$$

$$Z_k = U_{k-1} - U_{N+1} + A_k\,; \quad k = 1, \ldots, N\,, \tag{57}$$

$$Z_0 = Z_1/(1 + R_0)\,, \tag{58}$$

$$U_{N+1} = U_N/(1 + R_{N+1}), \quad U_0 = R_0(A_1 - U_{N+1}). \qquad (59), (60)$$

Substituting Eqs (*56*)–(*60*) into Eq. (*49*) we obtain

$$\chi_k = \sum_{j=k}^{N} \gamma_{k,j} U_j - \sum_{j=1}^{k-1} \vartheta_{k,j+1} U_j - \sum_{j=1}^{k} \vartheta_{k,j} A_j ; \quad k = 1, \ldots, N \qquad (61)$$

where

$$\vartheta_{k,1} = (1 + R_0)\, \beta_{k,1} E_k/(m_k V_1), \qquad (62)$$

$$\vartheta_{k,j} = \beta_{k,j} E_k/(m_k V_j); \quad j = 2, \ldots, k \qquad (63)$$

$$\gamma_{k,j} = \alpha_{k,j} E_k/L_j; \quad j = k, \ldots N - 1 \qquad (64)$$

$$\gamma_{k,N} = \alpha_{k,N} E_k/L_N + \left(\sum_{j=1}^{k} \vartheta_{k,j}\right)/(1 + R_{N+1}), \quad k = 1, \ldots, N \qquad (65)$$

while it is true that

$$U_k - U_{k-1} - \lambda_k = \chi_k; \quad k = 1, \ldots, N. \qquad (66)$$

Combining Eqs (*61*) and (*66*) and uniting the coefficients γ, ϑ according to the following formulas

$$c_{1,j} = \begin{cases} 1 - \gamma_{1,1}, & \text{for} \quad j = 1 \\ -\gamma_{1,j}, & \text{for} \quad 2 \leqq j \leqq N - 1 \\ -\gamma_{1,N} + R_0/(1 + R_{N+1}), & \text{for} \quad j = N \end{cases} \qquad (67)$$

$$c_{k,j} = \begin{cases} \vartheta_{k,j+1}, & \text{for} \quad 1 \leqq j \leqq k - 2 \\ \vartheta_{k,k} - 1, & \text{for} \quad j = k - 1; \quad k = 2, \ldots, N \\ 1 - \gamma_{k,k}, & \text{for} \quad j = k \\ -\gamma_{k,j}, & \text{for} \quad k + 1 \leqq j \leqq N \end{cases} \qquad (68)$$

a set of equations is obtained, linear with respect to U

$$\sum_{j=1}^{N} c_{k,j} U_j - B_k = 0; \quad k = 1, \ldots, N, \qquad (69)$$

where

$$B_1 = \lambda_1 - (\vartheta_{1,1} - R_0)\, A_1, \; B_k = \lambda_k - \sum_{j=1}^{k} \vartheta_{k,j} A_j; \quad k = 2, \ldots, N. \qquad (70), (71)$$

A solution of the set (*69*) is then given by

$$U_k = D_k/\varepsilon(k, k)\,; \quad k = 1, \ldots, N\,, \tag{72}$$

where

$$D_N = C_N\,, \quad D_k = C_k - \sum_{j=k+1}^{N} \frac{\varepsilon(k, j)}{\varepsilon(j, j)} D_j\,; \quad k = N - 1, \ldots, 1 \tag{73}$$

$$C_1 = B_1\,, \quad C_k = B_k - \sum_{r=1}^{k-1} \frac{C_r}{\varepsilon(r, r)} b_{k,r}\,; \quad k = 2, \ldots, N \qquad (74), (75)$$

$$\varepsilon(1, j) = c_{1,j}\,; \quad j = 1, \ldots, N \tag{76}$$

$$\varepsilon(k, j) = c_{k,j} - \sum_{r=1}^{k-1} \frac{\varepsilon(r, j)}{\varepsilon(r, r)} b_{k,r}\,; \quad k = 2, \ldots, N; \; j = k, \ldots, N \tag{77}$$

$$b_{k,1} = c_{k,1}\,; \quad k = 1, \ldots, N \tag{78}$$

$$b_{k,r} = c_{k,r} - \sum_{p=1}^{r-1} \frac{\varepsilon(p, r)}{\varepsilon(p, p)} b_{k,p}\,; \quad k = 1, \ldots, N; \; r = 2, \ldots, k\,. \tag{79}$$

Elimination of U by means of Z

From Eqs (*19*)–(*23*), (*54*) it follows for the variable U that

$$U_0 = R_0 Z_0\,, \tag{80}$$

$$U_k = Z_{k+1} - Z_0 + A_1 - A_{k+1}\,; \quad k = 1, \ldots, N\,, \tag{81}$$

$$U_{N+1} = U_N/(1 + R_{N+1})\,, \tag{82}$$

and further that

$$Z_0 = Z_1/(1 + R_0)\,, \quad Z_{N+1} = R_{N+1}(A_1 - Z_0)\,. \qquad (83), (84)$$

Substituting Eqs (*80*)–(*84*) into Eq. (*49*) we obtain

$$\chi_k = -\sum_{j=1}^{k} \vartheta_{k,j} Z_j + \sum_{j=k+1}^{N} \gamma_{k,j-1} Z_j + \sum_{j=k}^{N} \gamma_{k,j}(A_1 - A_{j+1})\,; \quad k = 1, \ldots, N\,, \tag{85}$$

where the quantities $\gamma_{k,j}$ ($j = k, \ldots, N - 1$), $\vartheta_{k,j}$ ($j = 2, \ldots, k$) ($k = 1, \ldots, N$) are given by Eqs (*63*) and (*64*) and

$$\gamma_{k,N} = \left(1 + R_{N+1}\right) \alpha_{k,N} E_k / L_N \tag{86}$$

$$\vartheta_{k,1} = \beta_{k,1} E_k / (m_k V_1) + \left(\sum_{j=k}^{N} \gamma_{k,j}\right) / \left(1 + R_0\right), \quad k = 1, \ldots, N \tag{87}$$

while it is also true that

$$Z_{k+1} - Z_k + \omega_k = \chi_k ; \quad k = 1, \ldots, N . \tag{88}$$

Combining Eqs (*85*) and (*88*) and uniting the coefficients γ, ϑ according to the formula

$$c_{k,j} = \begin{cases} \vartheta_{k,j} , & \text{for} \quad 1 \leqq j \leqq k - 1 ; \\ \vartheta_{k,k} - 1 , & \text{for} \quad j = k ; \\ 1 - \gamma_{k,k} , & \text{for} \quad j = k + 1 \\ -\gamma_{k,j-1} , & \text{for} \quad k + 2 \leqq j \leqq N \end{cases} \qquad k = 1, \ldots, N - 1 \tag{89}$$

$$c_{N,j} = \begin{cases} \vartheta_{N,1} - R_{N+1} / \left(1 + R_0\right) , & \text{for} \quad j = 1 \\ \vartheta_{N,j} , & \text{for} \quad 2 \leqq j \leqq N - 1 \\ \vartheta_{N,N} - 1 , & \text{for} \quad j = N \end{cases} \tag{90}$$

the following set of equations is obtained, linear in Z

$$\sum_{j=1}^{N} c_{k,j} Z_j - B_k = 0 ; \quad k = 1, \ldots, N , \tag{91}$$

where

$$B_k = -\omega_k + \sum_{j=k}^{N} \gamma_{k,j} \left(A_1 - A_{j+1}\right) ; \quad k = 1, \ldots, N - 1 , \tag{92}$$

$$B_N = -\omega_N + \left(\gamma_{N,N} - R_{N+1}\right) A_1 . \tag{93}$$

The set (*91*) is analogous to (*69*) and its solution is therefore given by the relation

$$Z_k = D_k / \varepsilon(k, k) ; \quad k = 1, \ldots, N \tag{94}$$

and (*73*)–(*79*) where the quantities c, B are determined by Eqs (*89*), (*90*), (*92*), (*93*).

The Cascade of Equilibrium Stages

If equilibrium exists between both phases in the stage then

$$y_k = m_k x_k \tag{95}$$

and $E_k \rightarrow -\infty$. Accordingly, the modified balance system is then given, aside from the equations (*20*)–(*23*), by Eqs (*66*) and (*88*). Similarly as in the case of the cascade of real stages we distinguish solutions with respect to U and Z while in the sense of Eqs (*42*)–(*48*) we determine the relation between the variables and the concentrations x and y as

$$x_k = \sum_{j=k}^{N} \alpha_{k,j} U_j / L_j \,, \quad y_k = \sum_{j=1}^{k} \beta_{k,j} Z_j / V_j \,, \quad k = 1, \ldots, N \,. \tag{96), (97}$$

Elimination of Z by means of U

Combination of Eqs (*95*), (*96*) and Eqs (*45*)–(*48*) helps express Z by means of U as

$$Z_1 = m_1 V_1 \sum_{j=1}^{N} \alpha_{1,j} U_j / L_j \,, \tag{98}$$

$$Z_k = \sum_{j=k}^{N} \left(\left(1 + \overline{V}\overline{V}\right) m_k V_k \alpha_{k,j} - \overline{V}\overline{V} m_{k-1} V_k \alpha_{k-1,j} \right) U_j / L_j - \\ - \overline{V}\overline{V} m_{k-1} V_k \alpha_{k-1,k-1} U_{k-1} / L_{k-1} \,; \quad k = 2, \ldots, N \,. \tag{99}$$

The variables Z_{N+1} and U_0 are determined by Eqs (*56*), (*59*), (*60*). Combining Eqs (*66*) and (*88*) and substituting Eqs (*98*), (*99*) for Z the following set of equations is obtained

$$\sum_{j=1}^{N} c_{1,j} U_j - B_1 = 0 \,, \quad \sum_{j=k-1}^{N} c_{k,j} U_j - B_k = 0 \,; \quad k = 2, \ldots, N \tag{100), (101}$$

where

$$B_1 = \lambda_1 + \omega_1 + R_0 A_1 \,, \quad B_k = \lambda_k + \omega_k \,; \quad k = 2, \ldots, N \tag{102), (103}$$

$$c_{1\,j} = \begin{cases} 1 + (\gamma_{1,1} + \vartheta_{1,1})/L_1 \,, & \text{for} \quad j = 1 \\ (\gamma_{1,j} - \gamma_{2,j} + \vartheta_{1,j})/L_j \,, & \text{for} \quad 2 \leqq j \leqq N \end{cases} \tag{104}$$

$$c_{k,j} = \begin{cases} -1 - (\vartheta_{k-1,k-1})/L_{k-1} \,, & \text{for} \quad j = k - 1 \\ 1 + (\gamma_{k,k} + \vartheta_{k,k} - \vartheta_{k-1,k})/L_k \,, & \text{for} \quad j = k \,; \quad k = 2, \ldots, N \\ (\gamma_{k,j} - \gamma_{k+1,j} + \vartheta_{k,j} - \vartheta_{k-1,j})/L_j \,, & \text{for} \quad k + 1 \leqq j \leqq N \end{cases} \tag{105}$$

$$\gamma_{1,j} = \begin{cases} m_1 \alpha_{1,j} V_1 \,, & \text{for} \quad j = 1, \ldots, N - 1 \\ m_1 \alpha_{1,N} V_1 + R_0 L_N / (1 + R_{N+1}) \,, & \text{for} \quad j = N \end{cases} \tag{106}$$

$$\gamma_{k,j} = m_k \alpha_{k,j} \left(1 + \overline{V}\overline{V}\right) V_k \,, \qquad \text{for} \quad k = 2, \ldots, N \,; \quad j = k, \ldots, N \tag{107}$$

$$\vartheta_{k,j} = m_k \alpha_{k,j} \overline{V}\overline{V} V_{k+1} \,, \qquad \text{for} \quad k = 1, \ldots, N - 1 \,; \quad j = k, \ldots, N \tag{108}$$

$$\vartheta_{N,N} = -R_{N+1}L_N/(1 + R_{N+1}) \,. \tag{109}$$

A solution of the set (*100*), (*101*) is given by Eqs (*72*), (*73*), where the quantities B, c, γ, ϑ are determined by Eqs (*102*)–(*109*) and the quantities ε, C by

$$\varepsilon(1, j) = c_{1,j} \,; \quad j = 1, \ldots, N \tag{110}$$

$$\varepsilon(k, j) = c_{k,j} - \varepsilon(k-1, j)\, c_{k,k-1}/\varepsilon(k-1, k-1) \,; \quad k = 2, \ldots, N \,; \quad j = k, \ldots, N \tag{111}$$

$$C_1 = B_1 \,, \quad C_k = B_k - C_{k-1}c_{k,k-1}/\varepsilon(k-1, k-1) \,; \quad k = 2, \ldots, N \,. \qquad (112), (113)$$

Elimination of U by means of Z

A combination of Eqs (*95*), (*97*) and Eqs (*42*), (*44*) enables one to express U in terms of Z as

$$U_k = \sum_{j=1}^{k}((1 + \overline{LL})\, L_k\beta_{k,j}/m_k - \overline{LL}\beta_{k+1,j}L_k/m_{k+1})\, Z_j/V_j - \\ - \overline{LL}\beta_{k+1,k+1}L_kZ_{k+1}/(m_{k+1}V_{k+1}) \,; \quad k = 1, \ldots, N-1 \tag{114}$$

$$U_N = (1/m_N)\, L_N \sum_{j=1}^{N} \beta_{N,j}Z_j/V_j \,. \tag{115}$$

The variables U_{N+1} and Z_{N+1} are determined by Eqs (*82*), (*83*), (*84*). Combining Eqs (*66*) and (*88*) and substituting Eqs (*114*), (*115*) for the variable U the following set of equations is obtained

$$\sum_{j=1}^{k+1} c_{k,j}Z_j - B_k = 0 \,; \quad k = 1, \ldots, N-1 \,, \tag{116}$$

$$\sum_{j=1}^{N} c_{N,j}Z_j - B_N = 0 \,, \tag{117}$$

where

$$B_k = \lambda_k + \omega_k \,; \quad k = 1, \ldots, N-1 \tag{118}$$

$$B_N = \lambda_N + \omega_N + R_{N+1}A_1 \,. \tag{119}$$

$$c_{k,j} = \begin{cases} (\gamma_{k,j} - \gamma_{k-1,j} + \vartheta_{k,j} - \vartheta_{k+1,j})/V_j \,, & \text{for} \quad 1 \leqq j \leqq k-1 \\ 1 + (\gamma_{k,k} + \vartheta_{k,k} - \vartheta_{k+1,k})/V_k \,, & \text{for} \quad j = k \,; \quad k = 1, \ldots, N-1 \\ -1 - (\vartheta_{k+1,k+1})/V_{k+1} \,, & \text{for} \quad j = k+1 \end{cases} \tag{120}$$

$$c_{N,j} = \begin{cases} (\gamma_{N,j} - \gamma_{N-1,j} + \vartheta_{N,j})/V_j \,, & \text{for} \quad 1 \leqq j \leqq N-1 \\ 1 + (\gamma_{N,N} + \vartheta_{N,N})/V_N \,, & \text{for} \quad j = N \end{cases} \tag{121}$$

$$\gamma_{k,j} = \beta_{k,j}(1 + \overline{LL})\, L_k/m_k\,, \quad \text{for} \quad k = 1, \ldots, N - 1\,; \quad j = 1, \ldots, k \qquad (122)$$

$$\gamma_{N,j} = \begin{cases} \beta_{N,1}L_N/m_N + R_{N+1}V_1/(1 + R_0)\,, & \text{for} \quad j = 1 \\ \beta_{N,j}L_N/m_N\,, & \text{for} \quad j = 2, \ldots, N \end{cases} \qquad (123)$$

$$\vartheta_{1,1} = -R_0V_1/(1 + R_0) \qquad (124)$$

$$\vartheta_{k,j} = \beta_{k,j}\overline{LL}L_{k-1}/m_k\,, \quad \text{for} \quad k = 2, \ldots, N\,; \quad j = 1, \ldots, k \qquad (125)$$

A solution of the set (*116*), (*117*) is given by Eq. (*94*) where

$$D_1 = C_1\,, \quad D_k = C_k - \sum_{j=1}^{k-1} \frac{\varepsilon(k, j)}{\varepsilon(j, j)} D_j\,; \quad k = 2, \ldots, N\,, \qquad (126), (127)$$

$$C_N = B_N\,, \quad C_k = B_k - C_{k+1}c_{k,k+1}/\varepsilon(k + 1, k + 1)\,; \quad k = N - 1, \ldots, 1 \qquad (128), (129)$$

$$\varepsilon(N, j) = c_{N,j}\,; \quad j = 1, \ldots, N \qquad (130)$$

$$\varepsilon(k, j) = c_{k,j} - \varepsilon(k + 1, j),\ c_{k,k+1}/\varepsilon(k + 1, k + 1)\,;$$
$$k = N - 1, \ldots, 1\,, \quad j = 1, \ldots, k\,. \qquad (131)$$

Summing U, or Z, over all components for individual stages of the cascade we obtain the values of the flow rates of the phases

$$L_k = \sum_{i=1}^{P} U_{i,k}\,, \quad V_k = \sum_{i=1}^{P} Z_{i,k}\,, \quad k = 0, 1, \ldots, N, N + 1\,. \qquad (132), (133)$$

This also ensures that the sum of concentrations of all components in each phase and stage of the cascade equals unity.

For known values $\overline{LL}$, $\overline{VV}$, m, k_x, k_y, a, w the equations (*1*)–(*133*) form a complete mathematical model of multicomponent liquid–liquid extraction for given feeds, withdrawals and refluxes as well as for the composition of the feeds.

Algorithm of the computation. The presented mathematical model for direct calculation of mass flow rates of the phases and concentrations of the components in both phases and iterative calculation of mass transfer rate and phase equilibrium serves to formulate a computational algorithm. The proposed algorithm consists of two iteration loops, the first of which, the so-called inner loop, seeks the mass flow rates of the phases and concentrations of the components for a given phase equilibrium and the transfer rate. The determination of the latter quantities is sought by the calculations in the second, outer iteration loop. A criterion for terminating the two iterations is a certain bound of the relative change of the absolute value of mass flow rate of the raffinate in each stage of the cascade ($k = 1, \ldots, N$) in two consecutive iterations. This conditions is fully sufficient because the chief bearer of the balance deviations in the model is the mass flow rate of one of the phases and a maximum deviation less than 0·01% practically does not reflect in the concentration profiles within the phases, nor phase equilibria, nor the rate of mass transfer.

The calculation starts from the following input data: the number of components, P, present in the liquid mixture passing through the cascade; number of stages of the cascade, N; reflux ratio in the extract phase, $R_{0,i}$; reflux ratio in the raffinate phase, $R_{N+1,i}$; feed of the component on the side of raffinate $F_k\xi_{i,k}$; feed of the component on the side of extract $S_k\eta_{i,k}$; rate of withdrawal of the raffinate phase from the stage, W_k; rate of withdrawal of the extract phase from the stage, G_k; coefficient of backmixing in the raffinate phase, $\overline{LL}$; coefficient of backmixing in the extract phase, $\overline{VV}$; partial mass transfer coefficients of the component, k_{xi}, k_{yi}; input data and relations for the calculation of the distribution coefficient, $m_{i,k}$, in dependence on composition of the phases; values of the factor ϕ_k or relationships for its calculation; magnitude of interfacial are in the stage, $a_k w_k$.

In order that the calculation may start for a given set of input data, an initial estimate of the flow rates of the phases and of the concentration profiles of individual components is needed. A series of estimates of the flow rates and concentrations was tested, all based on the feed rate of the phases and eventual refluxes of the components. For simplicity and good convergence we took the approach based on the assumptions that there is no mass transfer between the phases in the cascade; no backmixing occurs; no side withdrawals of the phases exist.

The initial estimate is thus calculated from the following equations

$$U_0 = [R_0/(1 + R_0 + R_{N+1})] \left(R_{N+1} \sum_{j=1}^{N} F_j\xi_j + (1 + R_{N+1}) \sum_{j=1}^{N} S_j\eta_j\right), \quad (134)$$

$$Z_{N+1} = [R_{N+1}/(1 + R_0 + R_{N+1})] \left((1 + R_0) \sum_{1=j}^{N} F_j\xi_j + R_0 \sum_{j=1}^{N} S_j\eta_j\right), \quad (135)$$

$$U_k = U_0 + \sum_{j=1}^{k} F_j\xi_j, \quad Z_k = Z_{N+1} + \sum_{j=k}^{N} S_j\eta_j, \quad k = 1, \ldots, N \quad (136), (137)$$

$$U_{N+1} = U_N - Z_{N+1}, \quad Z_0 = Z_1 - U_0. \quad (138), (139)$$

The flow rates of the phases are then estimated from Eqs (*132*), (*133*); the concentrations are obtained from Eqs (*42*)–(*48*) assuming zero coefficients of backmixing in both phases.

The initial estimate of the quantities E is obtained from Eqs (*41*) and (*24*).

An important role for the convergence of the calculation routine is that of the ratio of the quantities γ and ϑ (for the cascade with real stages) or the quantity γ (for the cascade of equilibrium stages). These quantities determine the values of the recurrence formulas ε and C and depend primarily on the distribution coefficients m. If for some of the components $m \ll 1$ then particularly for a cascade with a large number of stages ε and C may become large, this being accompanied with a considerable loss of precision due to a limited number of digits carried in the computer memory. In order to ensure convergence of the routine this phenomenon has to be

obviated by proper choice of the path of the calculation either by elimination of the quantities Z or U. A logical analysis of the model and its applications furnished the following criteria for the choice.
For the cascade of real stages

$$(\gamma_{\mathrm{ks,ks}} - 1)/(\vartheta_{\mathrm{ks,ks}} - 1) \tag{140}$$

for the cascade of equilibrium stages

$$\gamma_{\mathrm{ks,ks}}/L_{\mathrm{ks}}\,; \tag{141}$$

(the quantities γ, ϑ relate to the path of elimination of the quantities Z, *i.e.* they are calculated from Eqs (*64*), (*63*) and (*107*)), where the subscript ks represents the integral part of the fraction $(N + 1)/2$. If the value of this criterion is greater than unity we proceed to eliminate the quantities Z; if the criterion is less than 1 we eliminate the quantities U.

The algorithm consists of the following steps (the figures in the parentheses indicate the number of the pertaining equation):

A. Calculation of α (*50*), (*51*), β (*52*), (*53*). Estimation of the rates of the phases L, V (*134*) to (*139*), (*132*), (*133*). Estimation concentrations of the components x, y (*42*)—(*48*) ($\overline{LL}$, $\overline{VV} = 0$). Estimation of λ, ω (*2*), (*3*).

B. Calculation of the distribution coefficients m (auxiliary subroutine) ($m = m(x, y)$). Calculation of E (*41*), (*24*) (cascade of real stages).

C. Calculation of the criteria (*140*) (for real stages) or (*141*) (for equilibrium stages) for individual components.

D. Individually for each component: Calculation of A (*54*), (*55*). Calculation of γ, ϑ: *via* elimination of Z (*62*)—(*65*) (for the real stages), or (*106*)—(*109*) (for equilibrium stages); *via* elimination of U (*63*), (*64*), (*86*), (*87*) (for the real stages), or (*122*)—(*125*) (for equilibrium stages). Calculation of c: *via* elimination of Z (*67*), (*68*) (for real stages), or (*104*), (*105*) (for equilibrium stages); via elimination of U (*89*), (*90*) (for real stages), or (*120*), (*121*) (for equilibrium stages). Calculation of B: *via* elimination of Z (*70*), (*71*) (for real stages), or (*102*), (*103*) (for equilibrium stages); *via* elimination of U (*92*), (*93*) (for real stages), or (*118*), (*119*) (for equilibrium stages). Calculation of the functions ε, b (only for real stages), C, D (*73*)—(*79*) (for real stages and both ways of eliminating Z or U); (*110*)—(*113*), (*73*) (for equilibrium stages via elimination of Z), or (*126*)—(*131*) (for equilibrium stages *via* elimination of U). Calculation of U (*72*) (for real and equilibrium stages *via* elimination of Z), (*59*), (*60*), Z (*56*)—(*58*). Calculation of Z (*94*) (for real and equilibrium stages *via* elimination of U), (*83*), (*84*), U (*80*)—(*82*).

E. Calculation of the flow rates of the phases L, V (*132*), (*133*). If a satisfactory agreement of the requested value of L in comparison with the previous iterative step is obtained, the calculation proceeds to step *F*; in the opposite case the calculation returns to step *D*.

F. Calculation of concentrations x, y (*42*)—(*48*). In case of the cascade of real stages the calculation continues by step *G*; for the cascade of equilibrium stages by step *J*. Individually for each stage of the cascade ($k = 1, \ldots, N$) (steps *G*., *H*., *I*.):

G. Calculation of mass fluxes *H* (*34*)

H. Calculation of the correction factors φ_x, φ_y (*30*), (*33*). Calculation of individual coefficients of mass transfer corrected on the convective flow across the interface $\bar{k}_x$, $\bar{k}_y$ (*29*), (*32*). Calculation of mass fluxes *H* (*38*). If a satisfactory agreement of the value *H* and that from the previous iterative step is obtained the calculation continues to step *I*; in the opposite case the calculation returns to step *H*.

I. Calculation of the concentrations at the interface x^+, y^+ (*36*), (*37*). Calculation of the distribution coefficients *m* (auxiliary subroutine) ($m = m(x^+, y^+)$). Calculation of the overall mass transfer coefficient K_x (*39*). Calculation of *E* (*24*).

J. If a satisfactory agreement of the flow rate of raffinate *L* (step *E*) is achieved without the necessity to repeat the step *D*, the calculation is terminated; in the opposite case the calculation continues by step *K*.

K. Calculation of λ, ω (*2*), (*3*).

The calculation proceeds either to step *C* for the cascade of real stages or to step *B* for the cascade of equilibrium stages.

The computational algorithm as described in steps *A*—*K* utilizes simple iteration in both loops. However, it was found that for the calculation of the flow rates of the phases it is benefitial to relax the results of the current iteration by the results of the previous step. This is accomplished by means of the relaxation formula of the type

$$r_{\text{new}} = r_{\text{old}} + p(r_{\text{calculated}} - r_{\text{old}}), \qquad (142)$$

where *r* is the calculated quantity and *p* is the relaxation factor. The quantities that were relaxed were the flow rates of raffinate *L* and mass fluxes *H* for which the recommended values of the relaxation factor *p* are 1·5 (over-relaxation) for *L* and 0·5 (under-relaxation) for *H*. Both values of the relaxation factor appear in the routine as input data. The removal of the relaxation is subject to the same conditions as the termination of the whole calculation. This means that the terminated calculation with the relaxed quantities is repeated (mostly in a single iteration) without applying the relaxation technique. This is important not only for expediting the calculation in its final phase when the relative changes in consecutive iterations are relatively small, but also ensures a sound balance of all computed quantities which could be partly upset by the relaxation (it is apparent that the disagreement of the balance diminishes with gradual convergence because the difference in the relaxation expression diminishes).

In order that we may achieve maximum accuracy at minimum number of iterations in both loops it is advantageous to make the requirement on minimum relative change in a single iteration more stringent, namely from 10% initially to 0·01% in the final stage.

RESULTS AND DISCUSSION

It is a common practice to neglect the effect of convective flow across the interface in determining the rate of mass transfer. Thus the overall mass transfer coefficient from Eq. (*24*) is determined from Eq. (*41*) from given values of the partial mass transfer coefficients k_{xi}, k_{yi}. If the rate of mass transfer may be regarded as independent of composition of the phases, the overall mass transfer coefficients K_{xi} may then be fed directly and remains constant throughout the calculation. However, the neglected convective flow across the interface causes that the determination of the efficiency of the extraction is in error. This error is the larger the stronger is the convective flow with respect to the rate of transfer proper. The existence of the convective flow shows through the change of the flow rates of the phases between individual stages of the cascade. The deviation of the approximate value of K_{xi} obtained from Eq. (*39*) depends first of all on the net convective flow $\sum_j H_j$. The correction of individual coefficients by the correction factors φ_x, φ_y is of only secondary importance for the calculation because the effect of these corrections, according to Eqs (*29*) and (*32*), is to a considerable extent compensated in Eq. (*39*). Generally it may be said that the deviation of the flux of a component and the net convective flow will be greater in those cases when the flux of the component is opposite to the net convective flow against the case when the flux of the component and the net convective flow have the same direction. The deviations of the flux across the interface will show through the inaccuracies of the calculation of the separation efficiency of the components in the cascade. An assessment of these possible inaccuracies has been furnished through the computation of the separation of a three-component mixture in a ten-stage cascade where the flow rates of the phase altered by $0-50\%$ as a consequence of the interfacial transport of the components. In these runs the parameters $k_x aw/L$ and $k_y aw/V$ were altered in the range between 0·1 and 100; the distribution coefficients were varied between 0·001 and 1000 and the unextracted residue between 0·01 and 0·50. It was found that the deviation in the determination of the unextracted residue obtained by the approximate approach using Eq. (*41*) amounted to $0-50\%$ for components transported in the direction of the convective flow and to $0-85\%$ for the components transported in the direction opposite to the direction of the convective flow, these deviations being compared with the values found by the proposed method.

The maximum deviations occurred when the relative change in the flow rates of the phases was at maximum. Accordingly, the effect of the convective flow across the interface must be taken into account, particularly in those cases when it is reasonable to expect a significant change in the flow rates of the phases between individual stages of the cascade[7].

In order to test the proposed computational scheme a computer program NMEXTR has been written in FORTRAN and a number of problems of importance from the view point of practical multicomponent liquid–liquid extraction have been solved. A rapid convergence was found in all cases while the parameters were varied in the following regions:

number of components	$3-10$
number of stages	$3-20$
coefficients of backmixing	$0-20$
number of transfer units in a single stage $(-E_{i,k}/L_k)$	$0{\cdot}1-100$ and ∞

The examined cases included those with refluxes at one or both ends of the cascade as well as those with several feeds and withdrawals of both phases. By analysis of the number of iterations required to solve individual problems on the TESLA 200 computer it was found that the time of the calculation in a single iteration cycle is directly proportional to the product of the number of components, P, and the number of stages, N; the total CPU time per single component, stage and iteration in the inner loop equals approximately 0·04 s. The total number of iterations in the inner loop (calculation of the fluxes of the components) at the chosen accuracy of 0·01% was in the range between 15 and 40 (more iterations were necessary in case of the cascade with real stages and a greater number of feeds and withdrawals of the phases); for the cascade with real stages there were on average 2 to 3 iterations in the cycle for the calculation of the mass transfer rate per one iteration in the inner loop. It can be said that the calculation according to the proposed method is approximately $2-3$ times faster than the calculation according to the method described earlier[5].

The above data regarding CPU time have been given only for illustration as they depend on the type of the computer used. They may be compared with the data typical for other methods of calculation only in case of the cascade of equilibrium stages without backmixing of the phases (see *e.g.* the results given in ref.[8]). The so far published methods of the calculation of multicomponent extraction do not reach comparable generality and broadness.

LIST OF SYMBOLS

F	feed rate of raffinate
G	rate of withdrawal of extract
H_x	mass flux from interface into the phase x
H_y, H	mass flux from interface into the phase y
K_x	overall mass transfer coefficient related to raffinate
L	flow rate of raffinate
$\overline{L}\overline{L}$	coefficient of backmixing in raffinate
N	number of stages in the cascade
P	number of components
R	reflux ratio
S	feed rate of extract
U	modified flux of a component in raffinate
V	flow rate of extract
$\overline{V}\overline{V}$	coefficient of backmixing in extract
W	rate of withdrawal of extract
Z	modified flux of a component in extract
a	specific interfacial area
k_x, k_y	partial coefficient of mass transfer
$\bar{k}_x$, $\bar{k}_y$	partial coefficients of mass transfer corrected on the convective flux.
l	back flow of raffinate
m	distribution coefficient
v	back flow of extract

w	volume of a stage of cascade
x^{+}	interfacial concentration of component in raffinate
y	concentration of component in extract
y^{+}	interfacial concentration of component in extract
φ_x, φ_y	correction coefficients on convective flux
ϕ	correction factor on driving force for mass transfer in a stage
ξ	concentration of component in raffinate feed
η	concentration of component in extract feed
i, j	subscript of component
k	subscript of a stage

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Translated by V. Staněk.