

A METHOD OF CALCULATING MULTISTAGE LIQUID-LIQUID EXTRACTION FOR TERNARY SYSTEMS

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Liquid-liquid extraction is a well-known unit operation based on limited liquid miscibility and the different distribution of solutes between two liquid phases, and it is widely used in industry. In spite of its importance, there have been few studies reported on the simulation of extraction processes. There may be two major reasons for this: (1) suitable thermodynamic equations or parameters were not available for the calculation of liquid-liquid equilibria (LLE); (2) the simulation of extraction processes is simple compared with that of distillations. The temperature need not be taken as an independent variable in extraction calculations since the dependence of LLE on temperature can be ignored. However, because the effect of composition change on equilibrium ratio in LLE are much greater than in vapor-liquid equilibria, convergent results for the simulation of extractions are sometimes not easy to obtain.

This work has aimed at developing a simple and stable method for the calculation of solvent extraction processes with sufficient accuracy for practical application.

1. Model and Algorithm

1.1 Correlation of LLE data

LLE has usually been calculated using thermodynamic models, such as NRTL, UNIQUAC, or UNIFAC. However, these models were mainly developed for vapor-liquid equilibria and are not fully successful for LLE, as pointed by Sorensen *et al.*²⁾ Three ternary systems have been investigated by NRTL and UNIQUAC equations with specific parameters³⁾ and it is found that although the binodal curve can be represented well except in the area close to the plait point, the deviation of the solute equilibrium distribution between experimental data and calculated data is significant as shown in **Fig. 1**. Furthermore, when these thermodynamic models are used, the trivial solutions $x_i = y_i$ are sometimes encountered. On the other hand, the parameters of these models for LLE are more difficult to obtain than for vapor-liquid equilibria.

To obtain sufficient accuracy for practical design calculations the following empirical equations are proposed for ternary systems to correlate LLE or the equilibria of liquid and supercritical fluid.

The solubility curve relationships for two phases:

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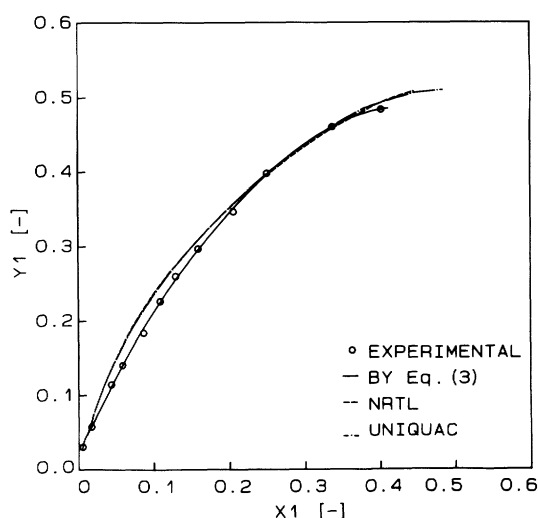


Fig. 1. Equilibrium distribution of solute in two phases for acetic acid(1)/benzene(2)/water(3) system

$$x_{j2} = \phi(x_{j1}) \quad (1)$$

$$y_{j2} = \psi(y_{j1}) \quad (2)$$

The solute distribution relationship:

$$y_{j1} = \pi(x_{j1}) \quad (3)$$

Regressed empirical equations for four ternary systems, including types I and II of LLE³⁾ and supercritical extraction system,⁴⁾ are tabulated in **Appendix**.

1.2 Model equation

A generalized multistage extraction model is presented in **Fig. 2**. F_j ($j=1-N-1$) may be a feed or a fresh solvent. F_0 is a feed and F_N a fresh solvent. Flow rates and compositions for the raffinate phase are represented by R_j and x_{ji} , respectively; and E_j and y_{ji} (or E'_j and y'_{ji}) for the extract phase. The equilibrium stage model is used and isothermal operation is assumed. When $E'_j=0$ ($j=1, 2, \dots, N$), the process shown in **Fig. 2** becomes a countercurrent extraction with multiple feeds. When $E_j=0$ ($j=1, 2, \dots, N$), it becomes a crosscurrent extraction process. For a ternary system, component (1) is to be a solute and component (3) a solvent.

The total and component material balances for the j th stage:

$$R_{j-1} + E_{j+1} + F_j = M_j = R_j + E_j + E'_j \quad (4)$$

$$\begin{aligned} R_{j-1}x_{j-1,i} + E_{j+1}y_{j+1,i} + F_jz_{ji} &= M_jx_{ji}^M \\ &= R_jx_{ji} + E_jy_{ji} + E'_jy'_{ji} \end{aligned} \quad (5)$$

For the j th stage, the summation point M_j is determined from F_j , z_{ji} , R_{j-1} , $x_{j-1,i}$, E_{j+1} , and $y_{j+1,i}$. According to the "lever-arm rule," the following equations are obtained:

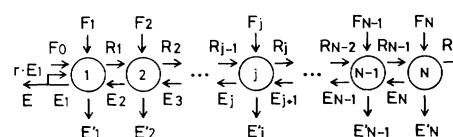


Fig. 2. A generalized model

$$\begin{aligned} f(x_{j1}) &= (x_{j1} - x_{j1}^M)/(x_{j2} - x_{j2}^M) - (x_{j1}^M - y_{j1})/(x_{j2}^M - y_{j2}) \\ &= 0 \end{aligned} \quad (6)$$

$$R_j = (y_{j1} - x_{j1}^M)M_j/(y_{j1} - x_{j1}) \quad (7)$$

$$E_j = (x_{j1}^M - x_{j1})M_j/(y_{j1} - x_{j1}) \quad (8)$$

Equation (6) is a function of x_{j1} alone, because x_{j2} , y_{j1} , and y_{j2} can be eliminated by substituting Eqs. (1)–(3) into it. The calculation for each stage becomes the solving of the nonlinear equation, Eq. (6), for x_{j1} .

1.3 Calculation for multistage extractions

For the j th stage, the computation can be performed by the following procedures:

1) Calculate the summation point M_j by Eqs. (9) and (10).

$$x_{ji}^M = (F_jx_{ji}^F + R_{j-1}x_{j-1,i} + E_{j+1}y_{j+1,i})/M_j \quad (9)$$

$$M_j = F_j + R_{j-1} + E_{j+1} \quad (10)$$

2) Solve Eq. (6) after substituting Eqs. (1)–(3) and x_{ji}^M into it for x_{j1} .

3) Calculate other compositions according to Eqs. (1)–(3).

4) Calculate R_j and E_j (or E'_j) by Eqs. (7)–(8).

For crosscurrent extractions, the calculation can be easily carried out stage by stage, using the method described above.

For countercurrent extractions, firstly, assuming that the whole extraction process is one extraction stage, the solutions to the assumed stage, $E^{(0)}$, $y_i^{(0)}$ and $R^{(0)}$, $x_i^{(0)}$, can be obtained.

$$\text{where } M = \sum_{j=0}^N F_j \quad (11)$$

$$x_j^M = \sum_{j=0}^N F_j z_{ji} / M \quad (12)$$

A set of initial values for the compositions and flow rates of two phases are obtained by setting $x_{ji}^{(0)} = x_i^{(0)}$; $R_j^{(0)} = R^{(0)}$; $y_{ji}^{(0)} = y_i^{(0)}$; $E_j^{(0)} = E^{(0)}$ ($j=1, 2, \dots, N$; $i=1, 2, \dots, m$). Then the calculation is performed stage-to-stage, firstly from $j=1$ to $j=N$ and then from $j=N$ to $j=1$, till the following criteria are reached. Direct substitution is used in the convergence of the whole process.

$$\sum_{i=1}^3 |E_2^{(k)}y_{2i}^{(k)} - E_2^{(k+1)}y_{2i}^{(k+1)}| < \varepsilon_1 \quad (13)$$

$$\sum_{i=1}^3 |1 - (E_1y_{1i} + R_Nx_{Ni}) / \left(\sum_{j=0}^N F_jx_{ji}^F \right)| < \varepsilon_2 \quad (14)$$

2. Results and Discussion

The specifications of six examples involving four ternary systems are given in **Table 1**. These examples include: (1) ordinary countercurrent extraction processes (Examples I-1, III-1, IV-1); (2) complex countercurrent extractions with multiple feeds (Example I-2); (3) optimal solvent distribution problem of crosscurrent extractions (Example I-3); (4) supercritical fluid extractions (Examples II-1). The calculated results given in **Table 2** show that the method presented is very stable and effective.

The method is also compared with others, such as the Newton-Raphson method, the relaxation method¹⁾ and the SR method. The partial derivatives in the Jacobian for the Newton-Raphson method is calculated by numerical differentiation. A series of computations has proved that the method presented here not only offers the fastest speed of convergence, as shown in **Table 3**, but also can avoid trivial solutions, which are often encountered with the other methods when the solute composition is small.

Nomenclature

E	= flow rate of extract phase	[mol/s]
F	= flow rate of feed	[mol/s]
M	= total flow rate	[mol/s]
N	= number of theoretical stages	[—]
R	= flow rate of raffinate phase	[mol/s]
r	= reflux ratio	[—]
re	= relative deviation	[—]
x	= mole fraction of raffinate phase	[—]
y	= mole fraction of extract phase	[—]
ε	= convergence criteria	[—]

<Subscript>

F	= feed
i	= component
j	= stage
av	= average value
max	= maximum value

<Superscript>

k	= iteration number
M	= total
0	= initial value

Literature Cited

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Table 1. Specifications of examples

Example No.	No. stages	Feed condition				Other conditions
		F	x_{f1}^F	x_{f2}^F	x_{f3}^F	
I-1	5	$F_0 = 1.36$.245	.755	.000	$r = 0$
		$F_5 = .556$.000	.000	1.000	$E'_1 - E'_5 = 0$
I-2	6	$F_0 = .600$.350	.650	.000	$r = 0$
		$F_3 = 1.60$.170	.830	.000	$E'_1 - E'_5 = 0$
		$F_6 = 1.10$.000	.000	1.000	
I-3	4	$F_0 = 2.76$.314	.686	.000	$r = 0$
		$\sum_{i=1}^4 F_i = 2.0$.000	.000	1.000	$E_1 - E_5 = 0$
II-1	6	$F_0 = 30.$.220	.780	.000	$r = 0$
		$F_6 = 60.0$.000	.000	1.000	$E'_1 - E'_6 = 0$
III-1	12	$F_0 = 12$.200	.800	.000	$r = 0$
		$F_{12} = 100$.000	.000	1.000	$E'_1 - E'_{12} = 0$
IV-1	9	$F_0 = 16$.220	.780	.000	$r = 0$
		$F_9 = 50$.000	.000	1.000	$E'_1 - E'_9 = 0$

* I—acetic acid(1)/benzene(2)/water(3) system
 * II—ethanol(1)/water(2)/carbon dioxide(3) system
 * III—cyclohexane(1)/2,2,4-trimethyl pentane(2)/furfural(3) system
 * IV—toluene(1)/heptane(2)/sulfolane(3) system

Table 2. Calculated results of examples

Examples	x_{N1}	x_{N2}	R_N	Y_{11}	y_{12}	E_1	$I.N.*$
I-1	.0251	.9663	1.0406	.3516	.0230	.8741	11
I-2	.0065	.9886	1.7179	.2978	.0124	1.5823	12
I-3**	.0646	.9238	2.0132	.3670	.0274	.8477	37
II-1	.1505	.8026	28.2795	.0380	.0108	61.6609	8
III-1	.0624	.8809	6.0522	.0191	.0403	105.9478	13
IV-1	.0017	.9979	12.1068	.0649	.0074	53.8932	12

* $I.N.$ —Iterative Number
 ** $F_{opt} = (F_1, \dots, F_4) = (.5943, .4706, .4719, .4632)$

Table 3. Comparison of four methods for the computations of <Example I-1>*

Method	$I.N.$	$ER1$	$ER2$	T
This work	11	$.67 \times 10^{-5}$	$.81 \times 10^{-5}$	5
Newton-Raphson method	5	$.39 \times 10^{-5}$		11
Relaxation method	35	$.49 \times 10^{-5}$	$.92 \times 10^{-5}$	9
SR method	27	$.61 \times 10^{-5}$	$.53 \times 10^{-5}$	8

* Note: T —Computation Time [s]; Computation executed on PC-9801RX.

System I Acetic acid(1)/Benzene(2)/Water(3) ³⁾		
$x_{j2} = 1.90326 - .899609 \exp(x_{j1}) - .049380 x_{j1}^{1/3} - .210065 x_{j1}^3 - .951032 x_{j1}^4$	$(re_{av} = .00154 \ re_{max} = .00343)$	(I-1)
$y_{j3} = 1.97138 + .674740 \times 10^{-6} / y_{j1}^2 + 2.49446 y_{j1}^3 - 4.64183 y_{j1}^4 - .973313 \exp(y_{j1})$	$(re_{av} = .00137 \ re_{max} = .00763)$	(I-2)
$y_{j1} = -.220344 + 1.15759 x_{j1}^{-5} + .019725 / x_{j1}^5 - 2.68311 x_{j1}^4 + .10540 \times 10^{-3} \ln(x_{j1}) / x_{j1} - .023949 x_{j1} \ln(x_{j1})$	$(re_{av} = .00539 \ re_{max} = .01314)$	(I-3)
System II Ethanol(1)/Water(2)/Carbon dioxide(3) ⁴⁾		
$x_{j2} = -18.31116 - 41.9810 x_{j1}^{-5} + 56.5590 x_{j1}^{1/3} + .475385 \times 10^{-3} / x_{j1}^2 - .188095 / x_{j1} + 2.53874 / x_{j1}^5$	$(re_{av} = 2. \times 10^{-5} \ re_{max} = 3. \times 10^{-5}) \quad x_{j1} \leq .2845$	(II-1)
$= 647.8281 - .186478 \times 10^4 x_{j1} \exp(x_{j1}) + .143805 \times 10^4 \exp(x_{j1}) + .311181 \times 10^4 x_{j1} \ln(x_{j1}) + .589136 \times 10^3 \ln(x_{j1})$	$(re_{av} = .0019 \ re_{max} = .0025) \quad x_{j1} > .2845$	(II-2)
$y_{j3} = .994409 - 1.07163 y_{j1} \exp(y_{j1}) - .123460 \times 10^{-5} / y_{j1}^2 - 13.2488 y_{j1}^4$	$(re_{av} = .0008 \ re_{max} = .0011)$	(II-2)
$y_{j1} = 0.1(8.07602 + 11.0889 x_{j1}^2 - .979671 \times 10^{-3} / x_{j1}^2 + .266798 / x_{j1} - 8.94292 x_{j1}^{-5} - 2.44370 / x_{j1}^5)$	$(re_{av} = .0079 \ re_{max} = 0.0115)$	(II-3)
System III Cyclohexane(1)/2,2,4-Trimethyl pentane(2)/Furfural(3) (Type II) ³⁾		
$x_{j2} = .945584 - 1.00311 x_{j1} + .574229 \times 10^{-3} x_{j1}^4$	$(re_{av} = .0002 \ re_{max} = .0005)$	(III-1)
$y_{j3} = .957849 - .763946 x_{j1} - 26.0851 x_{j1}^4 - .283076 \times 10^{-6} / x_{j1}^2 + 7.19843 x_{j1}^3$	$(re_{av} = .0001 \ re_{max} = .0001)$	(III-2)
$y_{j1} = -.075512 - .0815775 \exp(x_{j1}) - .111328 \times 10^{-3} / x_{j1}^2 + .0011715 x_{j1}^4$	$(re_{av} = .0013 \ re_{max} = .0061)$	(III-3)
System IV Toluene(1)/Heptane(2)/Sulfolane(3) ³⁾		
$x_{j2} = 17.4815 - 16.5831 \exp(x_{j1}) + .863165 \times 10^{-3} / x_{j1} - 13.0634 x_{j1}^4 + 20.7998 x_{j1}^3 + 17.1155 x_{j1}$	$(re_{av} = .0046 \ re_{max} = .0091)$	(IV-1)
$y_{j3} = -60.5276 + 61.5194 \exp(x_{j1}) - .223776 x_{j1} \ln(x_{j1}) + 4.71285 x_{j1}^4 - 34.8529 x_{j1} - 28.4085 x_{j1} \exp(x_{j1})$	$(re_{av} = .0008 \ re_{max} = .0012)$	(IV-2)
$y_{j1} = .088382 + 8.72094 x_{j1}^2 - .680602 \times 10^{-5} / x_{j1}^2 + 15.5359 x_{j1}^4 - 19.4900 x_{j1}^3 - 1.11758 x_{j1}$	$(re_{av} = .0073 \ re_{max} = .0110)$	(IV-3)