CALCULATION OF THREE-PHASE FLASH AND PARTIAL CONDENSATION FOR TERNARY SYSTEMS

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Several methods have been proposed for three-phase flash calculations based on the minimization of total Gibbs free energy[3] and the solution of iso-activity equations.[2] There is still much to be done, however, especially regarding stability, determination of the phase number, and the accuracy of liquid-liquid equilibrium (**LLE**). This work has aimed at developing a simple and stable method with significant accuracy for the flash calculation of a ternary system with limited misibility.

1. Model equations

Total material balance equation:

$$F = V + M = V + L_1 + L_2 \tag{1}$$

Component material balance equations:

$$Fx_{Fi} = Vy_i + Mx_i^M = Vy_i + L_1 x_{1i} + L_2 x_{2i}$$
$$(i = 1, \cdots, m) \tag{2}$$

Enthalpy balance equation:

$$FH_F + Q = VH + L_1 h_1 + L_2 h_2 \tag{3}$$

where it is a flash distillation process when Q is positive and a partial condensation when Q is negative.

Vapor-liquid equilibria:

$$y_i = \gamma_{ki} p_i^s x_{ki}/P\phi_i \qquad (k = 1 \text{ or } 2; i = 1, \cdots, m) \tag{4}$$

Since the thermodynamic models presently available are not fully successful for describing **LLE** as

pointed out by Sorensen *et al.*,[4] empirical formulas are used to correlate **LLE** of ternary systems in the following way.

For solubility curves:

$$x_{k2} = f_k(x_{k1}) \qquad (k = 1, 2) \tag{5}$$

For tielines:

$$x_{21} = g(x_{11}) \tag{6}$$

According to the "lever-arm rule," the following equations are obtained:

$$f(x_{11}) = (x_{11} - x_1^M)/(x_{12} - x_2^M) - (x_1^M - x_{21})/(x_2^M - x_{22})$$
$$= 0 \tag{7}$$

$$L_1/L_2 = (x_{21} - x_1^M)/(x_1^M - x_{11}) \tag{8}$$

When x_i^M values are given, Eq. (7) becomes a function of only x_{11} after substituting Eqs. (5) and (6) into it. The problem for the calculation of **LLE** is reduced to solving Eq. (7) for x_{11}, and then other x_{ki} values and L_1/L_2 can be obtained from Eqs. (5), (6) and (8), and summation equations of mole fractions.

2. Algorithm

The diagram of a ternary system is divided into two regions by a binodal curve:

(1) Heterogeneous liquid region:

$$x_1^M < x_1^* \text{ and } f_1(x_1^M) < x_2^M < f_2(x_1^M)$$

(2) Homogeneous liquid regions:

$$x_1^M \geqq x_1^* \text{ or } x_2^M \leqq f_1(x_1^M) \text{ or } x_2^M \geqq f_2(x_1^M)$$

where x_1^* is the maximum value of x_{k1} on the binodal curve.

If the total liquid composition x_i^M is known, the phase number can easily be determined by the above criteria.

Based on the above model equations and method of determining the phase number, a calculation procedure for isenthalpic flash and partial condensation is presented as follows:

1) Give the value of x_1^* according to the experimental data of the system and a set of initial values for x_i^M.

2) If $x_1^M \geq x_1^*$, then go to step 4); otherwise go to the next step.

3) Calculate $f_1(x_1^M)$ and $f_2(x_1^M)$; if $f_1(x_1^M) < x_2^M < f_2(x_1^M)$ then go to step 5); otherwise go to the next step.

4) Set $L_1 = 0$, $x_{1i} = 0$ and go to step 7).

5) Substitute Eqs. (5) and (6) into Eq. (7), and then solve Eq. (7) for x_{11}.

6) Calculate x_{12}, x_{13}, x_{2i}'s, and L_1/L_2 by Eqs. (5)–(6), (8), and the summation equations of mole fractions.

7) Solve boiling-point equations for the vapor composition y_i and the equilibrium temperature t.

8) Calculate the enthalpy of each phase, then solve Eqs. (1) and (3) for L_2 and V if L_1 is equal to zero; or together with L_1/L_2 for L_1, L_2, and V if L_1 is not equal to zero.

The enthalpies of liquid and vapor phases are calculated by Prausnitz's method.[1]

9) If the criterion given by Eq. (9) is reached, then stop the calculation; otherwise correct x_i^M by Eq. (10) and then return to step 2) and repeat the calculation.

$$\sum | Fx_{Fi} - Vy_i - L_1 x_{1i} - L_2 x_{2i} | < \varepsilon \qquad (9)$$

$$(x_i^M)_{co} = \frac{\theta Fx_{Fi}}{Vy_i + L_1 x_{1i} + L_2 x_{2i}} (x_i^M)_{as} \qquad (10)$$

where

$$\theta = \left[\sum_{i=1}^{3} \frac{Fx_{Fi}(x_i^M)_{as}}{Vy_i + L_1 x_{1i} + L_2 x_{2i}} \right]^{-1} \qquad (11)$$

3. Discussion and conclusions

In this work a ternary system, methanol (1)/ethyl acetate (2)/water (3), has been taken as an example.

The vapor-liquid equilibrium is calculated using the NRTL model for γ_{ki} and a virial equation for ϕ_i. The NRTL parameters are taken from Table 9 in Ref. 5).

The empirical formula for **LLE** regressed from the experimental data[5] and their relative deviations are given in **Table 1**.

The calculated results for the boiling point of the heterogeneous liquid for several feed compositions are given in **Table 2**. Compared with the experimental data published by Zandijeke,[5] it can be seen that the

Table 1. Empirical formula for **LLE** of methanol (1)/ethyl acetate (2)/water (3) system

$x_{12} = f_1(x_{11})$
$\quad = -0.0882463 + 0.580688 x_{11} - 3.70566 x_{11}^3 + 0.104366 \exp(x_{11})$
$\quad (re_{max} = .0058; re_{av} = .0023) \qquad (12)$

$x_{22} = f_2(x_{21})$
$\quad = 1.013798 + 42.4868 x_{21}^2 - 2.15988 \times 10^3 x_{21}^4 + 2.85112 x_{21} \ln(x_{21})$
$\quad - 3.78166 \times 10^{-5} x_{21}^{-2} \qquad (re_{max} = .0103; re_{av} = .0077) \qquad (13)$

$x_{21} = g(x_{11})$
$\quad = -0.001487 + 1.32054 x_{11} - 1.87015 x_{11}^2 - 1.75728$
$\quad \times 10^{-5} \exp(x_{11})/x_{11} \qquad (re_{max} = .0072; re_{av} = .0029) \qquad (14)$

Note: re_{max}—maximum relative deviation
re_{av}—average relative deviation
phase "1"—water-rich phase
phase "2"—ethyl acetate-rich phase

Table 2. Comparison of calculated and experimental equilibrium data[5] at boiling points

Ex.	No.	1	2	3	4
feed	x_{F1}	.0280	.0380	.0640	.0850
	x_{F2}	.3900	.2880	.3760	.2750
Cal. values	x_{11}	.0255	.0353	.0582	.0803
	x_{12}	.0335	.0402	.0554	.0695
	x_{21}	.0302	.0423	.0686	.0922
	x_{22}	.7079	.6804	.6337	.5878
	y_1	.0491	.0659	.1011	.1290
	y_2	.6590	.6460	.6231	.6039
	t (°C)	70.74	70.55	70.19	69.93
Exp. values	x_{11}	.0260	.0350	.0580	.0780
	x_{12}	.0330	.0420	.0550	.0700
	x_{21}	.0310	.0430	.0680	.0930
	x_{22}	.7020	.6800	.6350	.5850
	y_1	.0560	.0620	.1010	.1500
	y_2	.6500	.6280	.5890	.5670
	t (°C)	69.70	69.45	69.00	68.70

Table 3. Specifications of examples*

Run	feed conditions					Q (kJ/s)
	x_{F1}	x_{F2}	t (°C)	P (kPa)	phase	
1	.06	.35	72.00	101.325	L	$.1254 \times 10^4$
2	.06	.35	177.00	1013.250	L	.0000
3	.06	.35	72.00	101.325	L	$.2299 \times 10^4$
4	.04	.35	107.00	101.325	V	$-.3762 \times 10^4$
5	.04	.35	107.00	101.325	V	$-.3135 \times 10^4$
6	.10	.60	107.00	101.325	V	$-.1672 \times 10^4$
7	.09	.62	107.00	101.325	V	$-.2090 \times 10^4$
8	.03	.30	67.00	101.325	L	$.8360 \times 10^3$
9	.08	.50	67.00	101.325	L	$.2090 \times 10^4$
10	.10	.35	72.00	101.325	L	$.4180 \times 10^3$

* Flashing pressure: 101.325 kPa.

difference in the compositions of both liquid phases and vapor phase are small.

For the methanol/ethyl acetate/water system, it has

Table 4. Calculated results of the examples

Run	t (°C)	y_1	y_2	V	x_{11}	x_{12}	L_1	x_{21}	x_{22}	L_2
1	70.04	.0872	.6025	35.31	.0429	.0453	47.00	.0513	.6619	17.53
2	70.04	.0873	.6024	35.02	.0430	.0454	47.20	.0514	.6617	17.78
3	76.01	.0789	.5442	61.89	.0292	.0346	38.11	.0000	.0000	.00
4	70.29	.0690	.6209	9.88	.0339	.0393	50.85	.0406	.6842	39.27
5	70.40	.0613	.6292	27.23	.0302	.0367	49.67	.0360	.6948	23.10
6	70.07	.1131	.6156	63.49	.0668	.0610	3.01	.0781	.6186	33.50
7	70.14	.1063	.6199	51.66	.0618	.0578	0.64	.0727	.6275	47.70
8	70.77	.0466	.6607	22.17	.0242	.0327	58.94	.0286	.7110	18.89
9	70.24	.0956	.6264	57.09	.0544	.0530	22.55	.0645	.6400	20.36
10	69.88	.1369	.5962	12.33	.0888	.0748	44.12	.1009	.5591	43.55

been found that the method of solving the iso-activity equation always converges to the trivial solutions $x_{1i} = x_{2i}$ when the activity coefficients both in **LLE** and **VLE** are calculated by thermodynamic models, such as NRTL or UNIQUAC. But the trivial solution can be avoided by using the method presented here.

Several examples for different feed compositions are given in **Table 3** and the calculation results are given in **Table 4**. These numerical results show the feasibility of the method for a broad range of feed compositions and various specifications. Further calculated results proved that this method is very stable, even in the regions very close to the transient point from the heterogeneous liquid region to the homogeneous liquid region.

From the above results it can be seen that the method presented here is not only simple but very stable. The phase number can conveniently be determined in the computation. It can provide significant accurate results for practical application and also can ensure that no trivial solution is given.

Nomenclature

H	= molar enthalpy of vapor	[kJ/mol]
h_k	= molar enthalpy of liquid phase k	[kJ/mol]
L_k	= molar flowrate of liquid phase k	[mol/s]
P	= operating pressure	[kPa]

p^s	= saturated vapor pressure of pure substance	[kPa]
Q	= heat duty	[kJ/s]
t	= temperature	[°C]
V	= molar flowrate of vapor	[mol/s]
x_{ki}	= mole fraction of liquid phase	[—]
x_i^M	= mole fraction of two-liquid mixture	[—]
y_i	= mole fraction of vapor phase	[—]
γ_i	= activity coefficient of component i	[—]
ϕ_i	= fugacity coefficient of component i	[—]

⟨Subscript⟩

F	= feed	
i	= component	
k	= phase	

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