Improved algorithm for calculation of binary liquid-liquid equilibrium compositions with NRTL model based on equal area rule

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Abstract−Typical methods for calculation of binary liquid-liquid equilibrium compositions such as surfactant systems need proper initial guesses and/or checking the sign of the second derivative of molar Gibbs energy change of mixing, ΔG. Eubank and Hall [1] have shown the equal area rule (EAR) applies to the composition derivative of the Gibbs energy of a binary system at fixed pressure and temperature. Methods based on EAR do not need to check the sign of the second derivative of ΔG because EAR is a necessary and sufficient condition for phase equilibrium. However, the algorithm proposed by Eubank and Hall needs a reasonable initial guess. Furthermore, it is not easy to apply the algorithm to activity coefficient models such as Non-Random Two Liquid (NRTL) because the first and second derivatives of ΔG as a function of composition have various shapes for some sets of NRTL parameters. In this work, we have developed an improved algorithm for calculation of binary liquid-liquid equilibrium compositions based on EAR considering the various shapes of NRTL model. This algorithm needs neither any initial guess nor checking the sign of the second derivative of ΔG.

Key words: Binary Mixture, Liquid-liquid Equilibria (LLE), Equal Area Rule (EAR), NRTL, Algorithm

INTRODUCTION

1. Importance of Liquid-Liquid Equilibria

Extraction is one of the typical processes for separation of liquid mixtures. Selectivity and equilibrium constant are the most important properties in the selection of proper solvent and the estimation of extraction performance. Preparation of liquid-liquid equilibrium data and techniques to predict liquid-liquid equilibria are essential to estimate these properties.

2. Expression of Liquid-Liquid Equilibria

Prausnitz et al. [2] explained the phase equilibrium problem as the task of finding temperature (or pressure) and compositions of one phase with given pressure (or temperature) and compositions of the other phase. The liquid-liquid equilibrium can be expressed in one of two different ways as follows:

with an equation of state: $x_i^I \hat{\phi}_i^I = x_i^{II} \hat{\phi}_i^{II}$ (1)

with an activity coefficient equation: $x_i^I \gamma_i^I = x_i^{II} \gamma_i^{II}$ (2)

The expression using an activity coefficient equation can be different from the phase equilibrium problem that Prausnitz et al. explained, because the activity coefficient, γ_i, calculated from the activity coefficient equation usually depends only on temperature and compositions. Most liquid-liquid equilibria are expressed by using activity coefficient equations because the liquid phase is nearly insensitive to pressure.

3. Typical Methods for Calculation of Binary Liquid-Liquid Equilibrium Compositions

Typical methods for calculation of binary liquid-liquid equilibrium compositions are (a) solving simultaneous iso-activity equations and (b) finding global minimum of the molar Gibbs energy change of mixing, ΔG. A short description of each method follows:

3-1. Solving Simultaneous Iso-activity Equations

This method solves iso-activity equations applied for each component as the following simultaneously:

$$x_1^I \gamma_1^I = x_1^{II} \gamma_1^{II} \quad (3)$$

$$x_2^I \gamma_2^I = x_2^{II} \gamma_2^{II} \quad (4)$$

This method is a necessary, but not sufficient condition for liquid-liquid equilibrium because this condition came from the fact that the derivative of ΔG is zero. Therefore, the resultant compositions must be confirmed by checking the sign of the second derivative of ΔG. Initial guesses of equilibrium compositions are also important to make sure that the simultaneous equations are safely solved.

3-2. Finding Global Minimum of ΔG of the System

This method finds the global minimum of ΔG of the system as the following:

$$(n^I + n^{II})\Delta G = n^I \Delta G^I + n^{II} \Delta G^{II} \quad (5)$$

where

$$\Delta G^I = RT(x_1^I \ln x_1^I + x_2^I \ln x_2^I) + RT(x_1^I \ln \gamma_1^I + x_2^I \ln \gamma_2^I) \quad (6)$$

and

$$\Delta G^{II} = RT(x_1^{II} \ln x_1^{II} + x_2^{II} \ln x_2^{II}) + RT(x_1^{II} \ln \gamma_1^{II} + x_2^{II} \ln \gamma_2^{II}) \quad (7)$$

This method is a necessary and sufficient condition for liquid-liquid equilibrium, but it has the risk of mistaking the local minimum for the global minimum depending on the initial guesses.

4. Common Tangent and Equal Area Rule at Equilibrium Compositions

Eubank and Hall [1] have shown the equal area rule (EAR) applies to the composition derivative of the Gibbs energy of a binary

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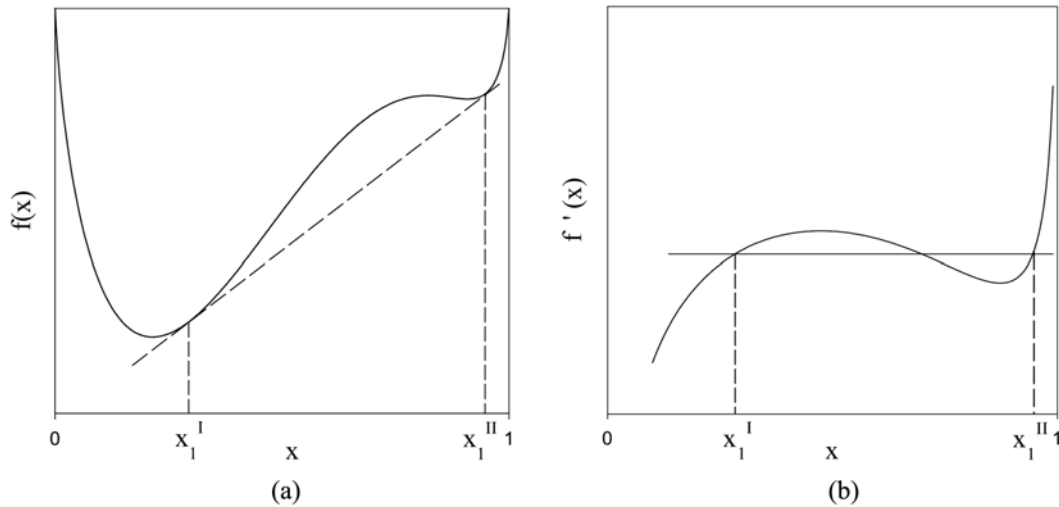†To whom correspondence should be addressed.
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Fig. 1. Common tangent and equal area phenomena at equilibrium compositions. (a): y=f(x), (b): y=f'(x).
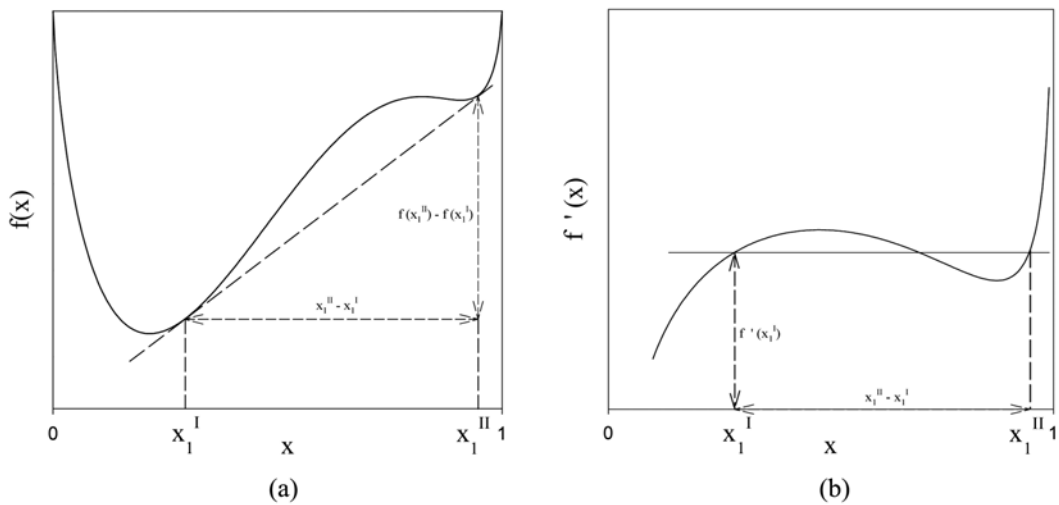

Fig. 2. Relation between common tangent and equal area phenomena. (a): y=f(x), (b): y=f'(x).

system at fixed pressure and temperature.

For binary liquid-liquid equilibrium, the molar Gibbs energy change of mixing, ΔG can be expressed as follows:

$$\Delta G = \Delta G^{id} + G^{E} \tag{8}$$

where

$$\Delta G^{id} = RT(x_1 \ln x_1 + x_2 \ln x_2) \tag{9}$$

and G^{E} depends on which activity coefficient equation is used. Since temperature is constant when the system is in equilibrium and $x_2 = 1-x_1$, ΔG can be expressed as a dimensionless function of x_1 as follows:

$$f(x_1) = \frac{\Delta G}{RT} \tag{10}$$

If y=f(x) and y=f'(x) is plotted, y=f(x) shows a common tangent and y=f'(x) shows EAR at the equilibrium compositions as shown in Fig. 1(a) and Fig. 1(b), respectively.

So y=f(x), which shows the common tangent phenomenon, and

that y=f'(x), which shows equal area phenomenon, are exactly the same. This can be proved as follows:

Since y=f(x) has common tangent at x_1^{I} and x_1^{II} as shown in Fig. 2(a),

$$f'(x_1^{I}) = f'(x_1^{II}) \tag{11}$$

and

$$\frac{f(x_1^{II}) - f(x_1^{I})}{x_1^{II} - x_1^{I}} = f'(x_1^{I}) \tag{12}$$

If shows equal area at x_1^{I} and x_1^{II} as shown in Fig. 2(b),

$$f'(x_1^{I}) = f'(x_1^{II}) \tag{13}$$

and

$$\int_{x_1^{I}}^{x_1^{II}} f'(x)dx = f(x_1^{II}) - f(x_1^{I}) = f'(x_1^{I})(x_1^{II} - x_1^{I}) \tag{14}$$

Eq. (11) is identical with Eq. (13), and Eq. (12) is identical with Eq. (14). Therefore, y=f(x), which shows common tangent phe-

nomenon, and which y=f'(x) shows equal area phenomenon, are exactly the same.

Methods based on EAR do not need to check the sign of the second derivative of ΔG because EAR is a necessary and sufficient condition for phase equilibrium.

5. Proposed Algorithm by Eubank and Hall for Determining Phase Compositions

The algorithm proposed by Eubank and Hall is summarized by Shyu et al. [3] as follows:

(a) Check for the existence of van der Waals loops by determining cusp or inflection points along the Gibbs energy path. If no cusp, or less than two inflection points, exist, the system exhibits no phase splitting; if a cusp or inflections exist, proceed to steps (b) to (e).

(b) Choose an initial value of f'(x) by calculating the average value of the two extremes in Fig. 1(b).

(c) Find the corresponding compositions x_1^I and x_1^{II} at f'(x).

(d) Calculate a new f'(x) using Eq. (12).

(e) Check convergence by comparing the difference between the new f'(x) and the old one. If the difference is less than an acceptable tolerance, then the corresponding compositions are the equilibrium compositions. Otherwise, use the new f'(x) and return to step (c) and repeat until convergence.

This algorithm needs an initial guess. An additional algorithm is needed to find two extremes in step (b) for removing the initial guess. In addition, a detailed algorithm for step (c) must be developed.

6. Non-Random Two Liquid (NRTL) Equation

An NRTL equation was developed by Renon and Prausnitz [4] based on the local composition concept, and the expression for binary liquid-liquid equilibrium is as follows:

$$\frac{G^E}{RT} = x_1 x_2 \left(\frac{\tau_{21} G_{21}}{x_1 + x_2 G_{21}} + \frac{\tau_{12} G_{12}}{x_2 + x_1 G_{12}} \right) \tag{15}$$

where

$$\tau_{12} = \frac{g_{12} - g_{22}}{RT} \tag{16}$$

$$\tau_{21} = \frac{g_{21} - g_{11}}{RT} \tag{17}$$

$$G_{12} = \exp(-\alpha \tau_{12}) \tag{18}$$

$$G_{21} = \exp(-\alpha \tau_{21}) \tag{19}$$

$$g_{12} = g_{21} \tag{20}$$

Although the NRTL equation has three parameters (τ_{12}, τ_{21}, and α), only τ_{12} and τ_{21} are regarded as adjustable parameters with α as a constant in most cases. In those cases, α is usually set as 0.2 or 0.3.

The NRTL is known as a widely used equation handling the liquid phase in vapor-liquid and/or liquid-liquid equilibria in chemical process industries since it can handle even highly non-ideal liquid mixtures.

In this work, we have developed an improved algorithm for calculation of binary liquid-liquid equilibrium compositions based on EAR for applying to the NRTL. This method needs neither any initial guess nor checking the sign of the second derivative of ΔG.

THEORY

1. Various Shapes of y=f''(x) and y=f'(x) for NRTL and Difficulties in Application of the Original Algorithm to NRTL

Understanding various shapes of y=f''(x) and y=f'(x) for NRTL is important in building the algorithm for calculation of binary liquid-liquid equilibrium compositions. The NRTL shows various shapes of y=f''(x) and y=f'(x), as shown in Fig. 3 to Fig. 7, depending on τ_{12} and τ_{21} with α as a constant (0.2 in this example). Newton's method is not proper when the slope can be near zero as shown on the left-hand side of Fig. 6(a) and Fig. 7(a), or the right-hand side of Fig. 4(a) and Fig. 5(a). The bisection method, whcih can be considered instead of Newton's method, needs two starting points of different signs. Since f'(x)>0 at both x=0.00001 and x=0.99999, a point where f''(x)<0 must be found prior to using bi-section method. Scanning for the point is also possible, but the interval can be a problem. For example, scanning with an interval of 0.001 cannot find the point where f''(x)<0, if the equilibrium compositions are x_1^I=0.2001 and x_1^{II}=0.2002. In this case, the interval must be changed to narrower than 0.0001, but the number of investigations might be

Fig. 3. Shapes of y=f''(x) and y=f'(x) using NRTL for τ_{12}=2 and τ_{21}=3. (a): y=f''(x), (b): y=f'(x).

Fig. 4. Shapes of y=f″(x) and y=f′(x) using NRTL for $\tau_{12}=-2$ and $\tau_{21}=7$. (a): y=f″(x), (b): y=f″(x).

Fig. 5. Shapes of y=f″(x) and y=f′(x) using NRTL for $\tau_{12}=-3$ and $\tau_{21}=9$. (a): y=f″(x), (b): y=f′(x).

Fig. 6. Shapes of y=f″(x) and y=f′(x) using NRTL for $\tau_{12}=7$ and $\tau_{21}=-2$. (a): y=f″(x), (b): y=f′(x).

more than 10000, which is not realistic.

2. The Improved Algorithm for Applying EAR to NRTL
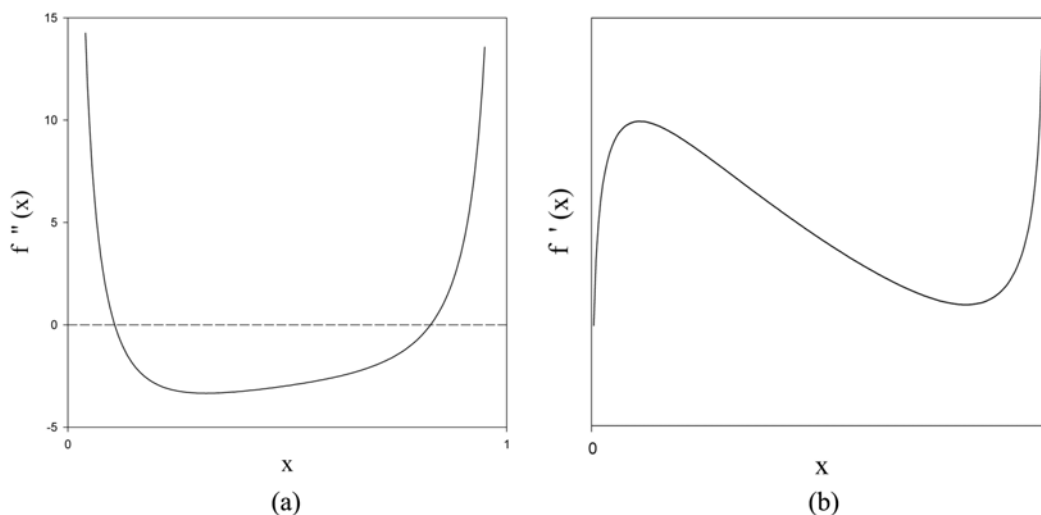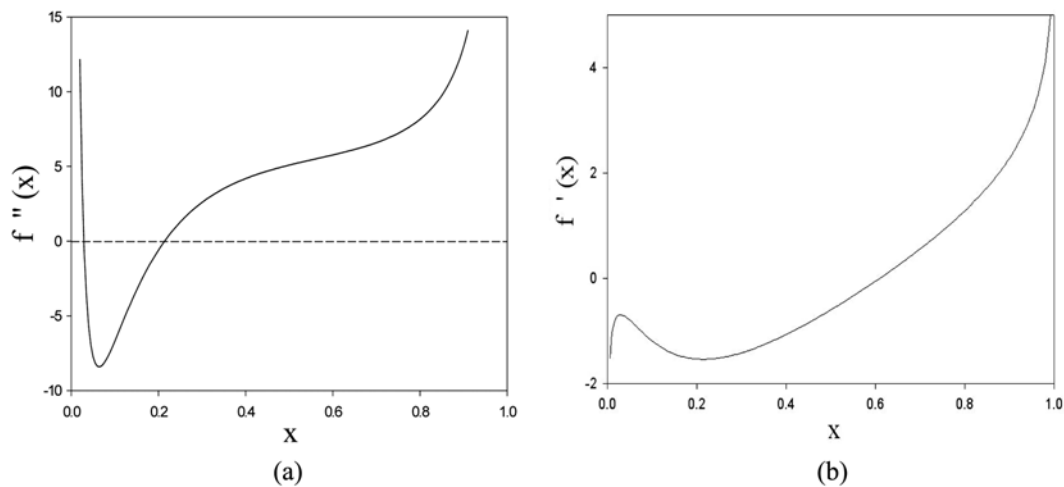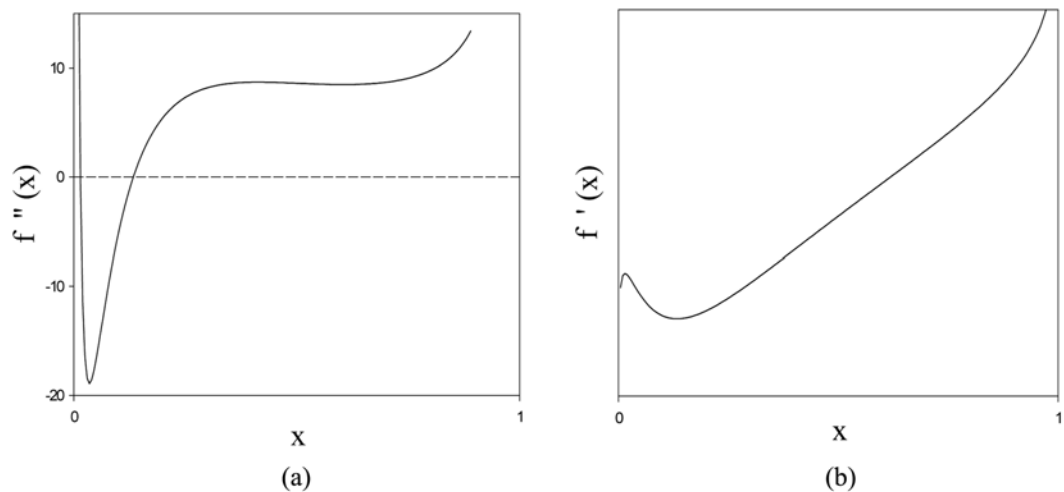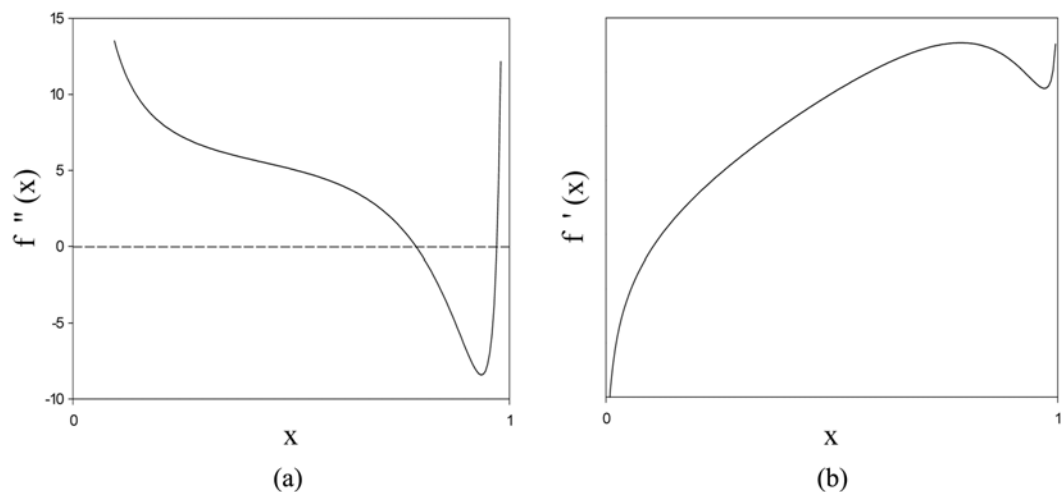
Two ideas have been developed to improve the original algorithm:
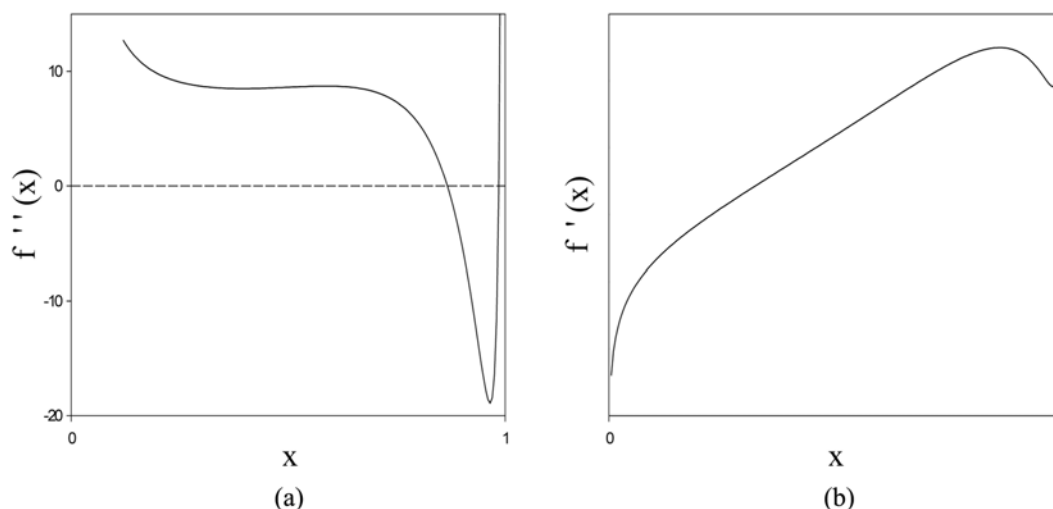
Fig. 7. Shapes of y=f''(x) and y=f'(x) using NRTL for τ_{12}=9 and τ_{21}=−3. (a): y=f''(x), (b): y=f'(x).
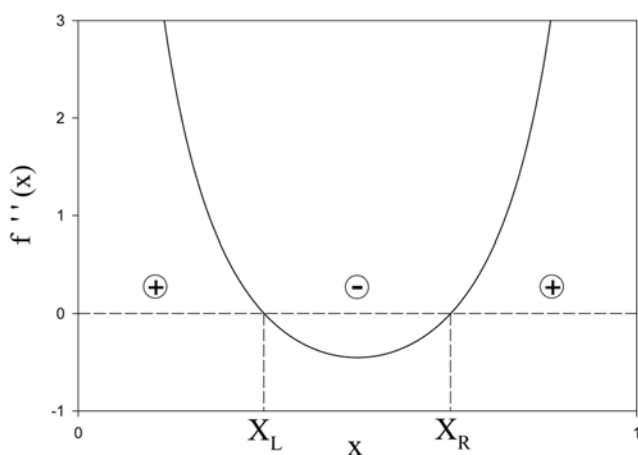
Fig. 8. Relation between signs of y=f''(x) and two solutions.

Fig. 9. The improved algorithm for calculation of binary liquid-liquid equilibrium compositions based on EAR for applying to NRTL.

2-1. Idea 1

Since the slope of y=f''(x) can be zero only on either side, not both sides, it means that Newton's method must be valid on at least one side. For example, Newton's method cannot be used with 0.00001 as initial guess, but can be used with 0.99999 as initial guess for the cases as shown in Fig. 6(a) and Fig. 7(a). In the same way, New-ton's method cannot be used with 0.99999 of initial guess, but can be used with 0.00001 of initial guess for the cases as shown in Fig. 4(a) and Fig. 5(a). If no solution can be found both 0.00001 and 0.99999 of initial guesses, it means that the system has a single liquid phase.

Now, name the solution found above as x_{tmp}. If another solution is found by bisection method with 0.00001 and x_{tmp}, then x_{tmp} corresponds to x_R in Fig. 8 and the new solution corresponds to x_L in Fig. 8. If no solution is found by bisection method with 0.00001 and x_{tmp}, x_{tmp} corresponds to x_L in Fig. 8, and another solution will be found by bisection method with 0.99999 and x_{tmp}. The new sol-ution corresponds to x_R in Fig. 8. If x_L is equal to x_R, it means that the system is at the critical point; otherwise, the system has two liquid phases.

Starting Row=> 6   Ending Row=> 1013   Calc Start!

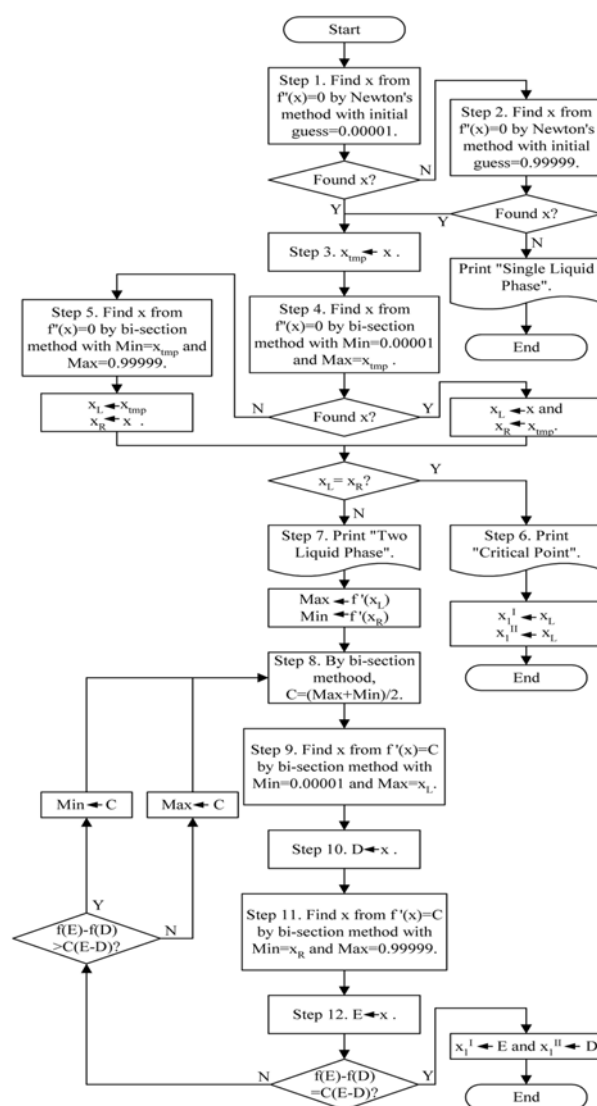| | from LLE Data Collection (DECHEMA) | | | | | Conversion from DECHEMA Data Collection | | | | Calculation Results from t12 and t21 | | No. of Phase |
| Temp (oC) | Solubilites (Mol%) | | NRTL Parameter | | | | | | | | | |
	(1) in (2)	(2) in (1)	A12	A21	alpha	t12	t21	x1(1)	x1(2)	x1(1)	x1(2)	
25	2.037	10.28	285.5	981.65	0.2	0.957572	3.29247	0.8972	0.0204	0.8972	0.0204	Two
5	29.5	5.22	892.41	27.379	0.2	3.208377	0.098433	0.9478	0.2950	0.9478	0.2950	Two
10	33.6	6.38	891.31	3.7499	0.2	3.147837	0.013244	0.9362	0.3360	0.9362	0.3360	Two
15	38.4	7.97	887.83	−19.445	0.2	3.081138	−0.06748	0.9203	0.3840	0.9203	0.3840	Two
20	44.9	10.1	894.93	−52.069	0.2	3.052806	−0.17762	0.8990	0.4490	0.8990	0.4490	Two
25	56.9	15.6	892.72	−93.662	0.2	2.994198	−0.31414	0.8440	0.5690	0.8440	0.5690	Two
25	31.3	3.1	1141.1	−46.328	0.2	3.827268	−0.15538	0.9690	0.3130	0.9690	0.3130	Two
30	34.5	3.75	1137.2	−68.594	0.2	3.751278	−0.22627	0.9625	0.3450	0.9625	0.3450	Two
40	41.4	5.52	1126.7	−108.54	0.2	3.597956	−0.34661	0.9448	0.4140	0.9448	0.4140	Two
50	51.1	8.15	1142.6	−166.5	0.2	3.535819	−0.51524	0.9185	0.5110	0.9185	0.5110	Two
30	43.7	5.148	1140.6	−139.72	0.2	3.762494	−0.46089	0.9485	0.4370	0.9485	0.4370	Two
25	48	0.23	2110.4	−366.79	0.2	7.078316	−1.23022	0.9977	0.4800	0.9977	0.4800	Two
30	50	0.329	2072.9	−395.47	0.2	6.837869	−1.30454	0.9967	0.5000	0.9967	0.5000	Two
40	55.1	0.575	2050.8	−465.17	0.2	6.548938	−1.48545	0.9943	0.5510	0.9943	0.5510	Two
50	61.9	0.917	2081.6	−559.79	0.2	6.441591	−1.73229	0.9908	0.6190	0.9908	0.6190	Two
60	70.6	1.64	2117.9	−676.81	0.2	6.357196	−2.03155	0.9836	0.7060	0.9836	0.7060	Two
70	82.2	3.94	2146.3	−811.21	0.2	6.254699	−2.36401	0.9606	0.8220	0.9606	0.8220	Two
60	25.6	7.44	891.21	141.55	0.2	2.675101	0.424884	0.9256	0.2560	0.9256	0.2560	Two
65	29.3	8.97	883.71	119.31	0.2	2.613367	0.352832	0.9103	0.2930	0.9103	0.2930	Two
70	34.7	11	887	84.315	0.2	2.584875	0.245709	0.8900	0.3470	0.8900	0.3470	Two
75	42.2	14	896.86	41.041	0.2	2.576074	0.117883	0.8600	0.4220	0.8600	0.4220	Two
80	57.1	22	907.08	−16.999	0.2	2.56854	−0.04814	0.7800	0.5710	0.7800	0.5710	Two
25	4.405	11.86	312.86	774.35	0.2	1.049338	2.597183	0.8814	0.0441	0.8814	0.0440	Two
25	29.7	3.66	1070.8	−10.935	0.2	3.591481	−0.03668	0.9634	0.2970	0.9634	0.2970	Two
35	38.1	6.42	1019.6	−48.66	0.2	3.308778	−0.15791	0.9358	0.3810	0.9358	0.3810	Two
40	44	8.06	1025.9	−83.521	0.2	3.276066	−0.26671	0.9194	0.4400	0.9194	0.4400	Two
45	52.8	10.1	1067.1	−145.08	0.2	3.354078	−0.45601	0.8990	0.5280	0.8990	0.5280	Two
50	36.3	3.13	1296	−114.73	0.2	4.010521	−0.35504	0.9687	0.3630	0.9687	0.3630	Two
60	44	4.24	1327.7	−182.58	0.2	3.985292	−0.54804	0.9576	0.4400	0.9576	0.4400	Two
70	54.5	7.14	1313.1	−242.8	0.2	3.826606	−0.70756	0.9286	0.5450	0.9286	0.5450	Two
20	67.9	0.711	2075.2	−617.11	0.2	7.07897	−2.1051	0.9929	0.6790	0.9929	0.6790	Two
25	71.3	0.9	2108	−671.06	0.2	7.070267	−2.25075	0.9910	0.7130	0.9910	0.7130	Two
30	74.9	1.21	2129.8	−725.23	0.2	7.025565	−2.39231	0.9879	0.7490	0.9879	0.7490	Two
35	79.1	1.72	2153.8	−786.69	0.2	6.989453	−2.55294	0.9828	0.7910	0.9828	0.7910	Two
40	84.2	2.74	2176.4	−854.77	0.2	6.950024	−2.72959	0.9726	0.8420	0.9726	0.8420	Two
0	0.16	0.219	1184.3	1271.2	0.2	4.335713	4.653853	0.9978	0.0016	0.9978	0.0016	Two
10	0.136	0.367	1085.3	1374.1	0.2	3.832951	4.852905	0.9963	0.0014	0.9963	0.0014	Two
20	0.123	0.517	1027.1	1463.6	0.2	3.503667	4.992666	0.9948	0.0012	0.9948	0.0012	Two
25	0.119	0.586	1009	1503.6	0.2	3.384203	5.043099	0.9941	0.0012	0.9941	0.0012	Two
30	0.117	0.664	989.93	1539.9	0.2	3.265479	5.079664	0.9934	0.0012	0.9934	0.0012	Two
40	0.114	0.819	960.53	1610.5	0.2	3.067316	5.142903	0.9918	0.0011	0.9918	0.0011	Two
50	0.113	0.964	941.72	1675.3	0.2	2.914188	5.18428	0.9904	0.0011	0.9904	0.0011	Two
60	0.114	1.12	925.19	1735.1	0.2	2.777097	5.208164	0.9888	0.0011	0.9888	0.0011	Two
20	77.4	0.754	2279.6	−794.55	0.2	7.776224	−2.71039	0.9925	0.7740	0.9925	0.7740	Two
25	80.9	0.983	2336	−866.49	0.2	7.834982	−2.90622	0.9902	0.8090	0.9902	0.8090	Two
30	84.6	1.28	2415.4	−951.77	0.2	7.967673	−3.1396	0.9872	0.8460	0.9872	0.8460	Two
35	88.6	1.8	2507.1	−1049.5	0.2	8.135973	−3.40581	0.9820	0.8860	0.9820	0.8860	Two
0	0.499	0.4	1048.1	982.36	0.2	3.837086	3.596412	0.9960	0.0050	0.9960	0.0050	Two
10	0.448	0.525	1008	1057.3	0.2	3.559951	3.734063	0.9948	0.0045	0.9948	0.0045	Two
20	0.423	0.682	967.6	1122.7	0.2	3.300693	3.82978	0.9932	0.0042	0.9932	0.0042	Two
25	0.417	0.784	943.65	1153.4	0.2	3.165018	3.868523	0.9922	0.0042	0.9922	0.0042	Two
30	0.416	0.917	913.8	1182.8	0.2	3.014349	3.901699	0.9908	0.0042	0.9908	0.0042	Two
25	2.073	2.74	674.69	783.89	0.2	2.262921	2.62918	0.9726	0.0207	0.9726	0.0207	Two
10	14	8.12	585.71	324.92	0.2	2.06855	1.147519	0.9188	0.1400	0.9188	0.1400	Two
15	15.6	9.05	585.37	313.35	0.2	2.031477	1.087454	0.9095	0.1560	0.9095	0.1560	Two
20	18	10.1	593.31	290.21	0.2	2.023913	0.989971	0.8990	0.1800	0.8990	0.1800	Two
25	21.9	11.5	610.67	251.08	0.2	2.048197	0.842126	0.8850	0.2190	0.8850	0.2190	Two
30	28.7	13.7	641.4	189.81	0.2	2.115784	0.626126	0.8630	0.2870	0.8630	0.2870	Two
35	39.7	18.3	668.6	122.36	0.2	2.169723	0.397079	0.8170	0.3970	0.8170	0.3970	Two
20	15.5	7.89	637.38	299.66	0.2	2.174245	1.022207	0.9211	0.1550	0.9211	0.1550	Two
25	16.1	8.53	631.88	304.42	0.2	2.119336	1.02103	0.9147	0.1610	0.9147	0.1610	Two
30	17.1	9.4	624.85	305.24	0.2	2.061191	1.006894	0.9060	0.1710	0.9060	0.1710	Two
40	20.1	11.4	620.84	293.1	0.2	1.982564	0.935973	0.8860	0.2010	0.8860	0.2010	Two
50	25.6	13.6	648.53	246.26	0.2	2.006901	0.762061	0.8640	0.2560	0.8640	0.2560	Two
60	32.6	17	668.86	203.9	0.2	2.007684	0.612037	0.8300	0.3260	0.8300	0.3260	Two
70	43.6	24.4	668.9	170.56	0.2	1.949293	0.497042	0.7560	0.4360	0.7560	0.4360	Two
25	18.15	4.339	874.37	176.74	0.2	2.932651	0.592789	0.9566	0.1815	0.9566	0.1815	Two
25	16.78	3.064	962.67	168.06	0.2	3.228811	0.563676	0.9694	0.1678	0.9694	0.1678	Two
60	13	11.4	550	473.81	0.2	1.650908	1.422212	0.8860	0.1300	0.8860	0.1300	Two
70	14.8	12.1	575.23	452.05	0.2	1.676322	1.317354	0.8790	0.1480	0.8790	0.1480	Two
80	17.7	13.2	605.7	414.43	0.2	1.715135	1.173524	0.8680	0.1770	0.8680	0.1770	Two
90	23.1	15.8	631.23	358.79	0.2	1.738207	0.987994	0.8420	0.2310	0.8420	0.2310	Two
100	31.9	20.8	650.12	297.37	0.2	1.742248	0.796918	0.7920	0.3190	0.7920	0.3190	Two
25	5.78	12.7	324.64	703.71	0.2	1.088848	2.360255	0.8730	0.0578	0.8730	0.0578	Two

Fig. 10. Screenshot of a Microsoft Excel worksheet.

2-2. Idea 2

In finding the value of f′(x) that shows equal area, Newton's method with 0.00001 and 0.99999 of initial guesses may diverge depending on the shape of y=f′(x). Instead, the solution can be found safely if the bisection method is used with 0.00001 and x_L. In the same way, the solution can be found safely if the bisection method is used with 0.99999 and x_R.

The improved algorithm for calculation of binary liquid-liquid equilibrium compositions based on equal area rule for applying to NRTL is shown as Fig. 9.

The source code in visual basic for application (VBA) for Microsoft Excel is shown as Appendix A. A part of a Microsoft Excel

Table 1. Comparison between the results of DECHEMA liquid-liquid equilibrium data collection and the results by the universal method with the same NRTL parameters

Given data from DECHEMA				Results of DECHEMA		Results by the universal method	
Temp (°C)	A12 (K)	A21 (K)	α	x_1^I	x_1^{II}	x_1^I	x_1^{II}
30	2415.4	−951.77	0.2	0.9872	0.8460	0.9872	0.8460
35	2507.1	−1049.5	0.2	0.9820	0.8860	0.9820	0.8860
25	285.5	981.65	0.2	0.8972	0.0204	0.8972	0.0204
5	892.41	27.379	0.2	0.9478	0.2950	0.9478	0.2950
10	891.31	3.7499	0.2	0.9362	0.3360	0.9362	0.3360
15	887.83	−19.445	0.2	0.9203	0.3840	0.9203	0.3840
20	894.93	−52.069	0.2	0.8990	0.4490	0.8990	0.4490
25	892.72	−93.662	0.2	0.8440	0.5690	0.8440	0.5690
25	1141.1	−46.328	0.2	0.9690	0.3130	0.9690	0.3130
30	1137.2	−68.594	0.2	0.9625	0.3450	0.9625	0.3450
40	1126.7	−108.54	0.2	0.9448	0.4140	0.9448	0.4140
50	1142.6	−166.5	0.2	0.9185	0.5110	0.9185	0.5110
30	1140.6	−139.72	0.2	0.9485	0.4370	0.9485	0.4370
25	2110.4	−366.79	0.2	0.9977	0.4800	0.9977	0.4800
30	2072.9	−395.47	0.2	0.9967	0.5000	0.9967	0.5000
40	2050.8	−465.17	0.2	0.9943	0.5510	0.9943	0.5510
50	2081.6	−559.79	0.2	0.9908	0.6190	0.9908	0.6190
60	2117.9	−676.81	0.2	0.9836	0.7060	0.9836	0.7060
70	2146.3	−811.21	0.2	0.9606	0.8220	0.9606	0.8220
60	891.21	141.55	0.2	0.9256	0.2560	0.9256	0.2560
65	883.71	119.31	0.2	0.9103	0.2930	0.9103	0.2930
70	887	84.315	0.2	0.8900	0.3470	0.8900	0.3470
75	896.86	41.041	0.2	0.8600	0.4220	0.8600	0.4220
80	907.08	−16.999	0.2	0.7800	0.5710	0.7800	0.5710
25	1070.8	−10.935	0.2	0.9634	0.2970	0.9634	0.2970
35	1019.6	−48.66	0.2	0.9358	0.3810	0.9358	0.3810
40	1025.9	−83.521	0.2	0.9194	0.4400	0.9194	0.4400
45	1067.1	−145.08	0.2	0.8990	0.5280	0.8990	0.5280
50	1296	−114.73	0.2	0.9687	0.3630	0.9687	0.3630
60	1327.7	−182.58	0.2	0.9576	0.4400	0.9576	0.4400

worksheet is shown as Fig. 10.

3. Verification of the Improved Algorithm

The improved algorithm has been verified with data from DECHEMA liquid-liquid equilibrium data collection [5].

VERIFICATION RESULTS

The results of verification of the improved algorithm with data from DECHEMA liquid-liquid equilibrium data collection are shown as Table 1. Calculation results are exactly the same with those from the DECHEMA data collection.

CONCLUSIONS

Methods for calculation of binary liquid-liquid equilibrium compositions based on EAR do not need to check the sign of the second derivative of ΔG because EAR is a necessary and sufficient condition for phase equilibrium. However, the algorithm proposed by Eubank and Hall needs a reasonable initial guess. Furthermore, it is not easy to apply the algorithm to activity coefficient models such as NRTL because the first and second derivatives of ΔG as a function of composition have various shapes for some sets of NRTL parameters. In this work, we have developed an improved algorithm for calculation of binary liquid-liquid equilibrium compositions based on EAR for applying to NRTL considering the various shapes. This algorithm needs neither any initial guess nor checking the sign of the second derivative of ΔG.

APPENDIX A. THE SOURCE CODE IN VBA FOR MICROSOFT EXCEL

Private Sub CommandButton1_Click()

'Preset of handling unit of composition (usually 0.0001)
unit = 0.0001

'Preset of initial guess and convergence radius (do not change!!)
init_min = unit / 10

```
init_max = 1 - init_min
isconverge = unit / 4
delta_in_newton = unit / 100
delta_in_bisection = unit / 100


'Reading of starting and ending row from Microsoft Excel Work-
sheet
Start_Row = TextBox1.Value
End_Row = TextBox2.Value

For r = Start_Row To End_Row

'Reading of NRTL parameters from Microsoft Excel Worksheet
t12 = Cells(r, 7)
t21 = Cells(r, 8)
a = 0.2


'Finding X_tmp for f''(x)=0
f2z = init_min
trial = 1
loop1:
f2zold = f2z
f2z = f2zold - f2(f2zold, t12, t21, a) / f3(f2zold, t12, t21, a)
If (f2z < 0 Or f2z > 1) And trial = 1 Then trial = 2: f2z = init_max:
GoTo loop1
If (f2z < 0 Or f2z > 1) And trial = 2 Then Cells(r, 15) = "Single":
Cells(r, 11) = "---": Cells(r, 12) = "---": GoTo Ending
If Abs((f2z - f2zold) / f2z) < delta_in_newton Then GoTo
loop1end
GoTo loop1
loop1end:


'Finding X_L and X_R for f''(x)=0 (Trial 1)
f2xmin = init_min
f2xmax = f2z
loop2:
f2xmean = (f2xmax + f2xmin) / 2
If Abs((f2xmax - f2xmin) / f2xmean) < delta_in_bisection Then
GoTo loop2end
If f2(f2xmean, t12, t21, a) > 0 Then f2xmin = f2xmean Else
f2xmax = f2xmean
GoTo loop2
loop2end:
If Abs(f2z - f2xmean) > isconverge Then f2x1 = f2xmean: f2x2 =
f2z: GoTo loop4start:
'Finding X_L and X_R for f''(x)=0 (Trial 2)

f2xmin = f2z
f2xmax = init_max
loop3:
f2xmean = (f2xmax + f2xmin) / 2
If Abs((f2xmax - f2xmin) / f2xmean) < delta_in_bisection Then
GoTo loop3end
If f2(f2xmean, t12, t21, a) < 0 Then f2xmin = f2xmean Else
f2xmax = f2xmean
GoTo loop3
loop3end:
```

```
If Round(f2z / unit) <> Round(f2xmean / unit) Then f2x1 = f2z:
f2x2 = f2xmean: GoTo loop4start:
Cells(r, 15) = "Critical": Cells(r, 11) = f2z: Cells(r, 12) = f2z: GoTo
Ending


'Finding Equal Area

loop4start:
Cells(r, 15) = "Two"
f1max = f1(f2x1, t12, t21, a)
f1min = f1(f2x2, t12, t21, a)
loop4:
f1mean = (f1max + f1min) / 2
f1x1max = f2x1
f1x1min = 0.0001
loop4_1:
f1x1mean = (f1x1max + f1x1min) / 2
If Abs((f1x1max - f1x1min) / f1x1mean) < 0.00001 Then f1x1 =
f1x1mean: GoTo loop4_1end
If f1(f1x1mean, t12, t21, a) > f1mean Then f1x1max = f1x1mean
Else f1x1min = f1x1mean
GoTo loop4_1
loop4_1end:
f1x2max = 0.9999
f1x2min = f2x2
loop4_2:
f1x2mean = (f1x2max + f1x2min) / 2
If Abs((f1x2max - f1x2min) / f1x2mean) < 0.00001 Then f1x2 =
f1x2mean: GoTo loop4_2end
If f1(f1x2mean, t12, t21, a) > f1mean Then f1x2max = f1x2mean
Else f1x2min = f1x2mean
GoTo loop4_2
loop4_2end:
area1 = f(f1x2, t12, t21, a) - f(f1x1, t12, t21, a)
area2 = f1mean * (f1x2 - f1x1)
If area2 < 0.00001 Then
 If Abs(area1 - area2) < 0.00001 Then Cells(r, 11) = f1x2: Cells(r,
12) = f1x1: GoTo Ending
Else
 If Abs((area1 - area2) / area2) < 0.00001 Then Cells(r, 11) = f1x2:
Cells(r, 12) = f1x1: GoTo Ending
End If
If area1 > area2 Then f1min = f1mean Else f1max = f1mean
GoTo loop4
Ending:
Next r
End Sub


Function f(x1, t12, t21, a)
f = (1 - x1) * x1 * (t12 / (-Exp(a * t12) * (-1 + x1) + x1) + t21 / (1
+ (-1 + Exp(a * t21)) * x1)) - (-1 + x1) * Log(1 - x1) + x1 *
Log(x1)
End Function


Function f1(x1, t12, t21, a)
f1 = t21 * ((-1 + x1) ^ 2 - Exp(a * t21) * x1 ^ 2) / (1 + (-1 + Exp(a
* t21)) * x1) ^ 2 + (Exp(a * t12) * t12 * (-1 + x1) ^ 2 - t12 * x1 ^
```

2) / (-Exp(a * t12) * (-1 + x1) + x1) ^ 2 - Log(1 - x1) + Log(x1)
End Function

Function f2(x1, t12, t21, a)
f2 = 2 * Exp(a * t12) * t12 / (Exp(a * t12) * (-1 + x1) - x1) ^ 3 - 2 * Exp(a * t21) * t21 / (1 + (-1 + Exp(a * t21)) * x1) ^ 3 + 1 / (x1 - x1 ^ 2)
End Function

Function f3(x1, t12, t21, a)
f3 = -6 * Exp(a * t12) * (-1 + Exp(a * t12)) * t12 / (-Exp(a * t12) * (-1 + x1) + x1) ^ 4 + ((-1 + 2 * x1) / (-1 + x1) ^ 2 - 6 * t21 * (-1 + x1) / (1 + (-1 + Exp(a * t21)) * x1) ^ 4 + 6 * t21 * (-2 + x1) / (1 + (-1 + Exp(a * t21)) * x1) ^ 3 + 6 * t21 / (1 + (-1 + Exp(a * t21)) *

x1) ^ 2) / x1 ^ 2

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