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Calculation of Ternary Plait Point from Activity Coefficient Equation

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Plait points are meaningful for the shapes of the ternary solubility curves. However, no report is found for calculation of the ternary plait point from activity coefficient equation. The ternary plait point was able to be calculated from the NRTL equation for three ternary systems.

Ternary solubility curves and liquid-liquid equilibria are required for the practical use such as for the design and operation of extraction equipment. For the prediction and correlation of phase equilibria, several activity coefficient equations have been proposed and their precisions have been improved.1-5) For the ternary liquid-liquid equilibria, excellent prediction results have recently been reported by Katayama et al.2,4) and Kojima et al.3) The plait point is the meaningful point defining the shape of the solubility curve for ternary systems. Three component systems are univariant in the immiscible area with two liquid phases at constant pressure and temperature. At the critical or plait point, provided that the two liquid phases are identical, the system is invariant. Consequently, the plait point seems to be fixed thermodynamically, when the activity coefficient equation and its parameters are given. However, no calculation result of the plait point from activity coefficient equation is shown in the literature. In the present investigation, the calculation of the plait point is tried from the activity ceefficient equation for ternary systems.

Gibbs6) had derived the classical thermodynamic equations required for the critical points of multicomponent mixtures. Scott7) discussed the thermodynamics of critical phenomena for fluid mixtures. The literature states that critical phenomena in fluid mixtures are substantially analogous to those in one-component fluids when appropriate allowance is made for the increase in the number of independent thermodynamic variables. By use of the analogies, the plait point for a three component fluid is written as follows:

$$\begin{vmatrix} \left(\frac{\partial^2 \tilde{G}}{\partial X_2^2}\right)_{T,P,X3} & \left(\frac{\partial^2 \tilde{G}}{\partial X_2 \partial X_3}\right)_{T,P} \\ \left(\frac{\partial^2 \tilde{G}}{\partial X_2 \partial X_3}\right)_{T,P} & \left(\frac{\partial^2 \tilde{G}}{\partial X_3^2}\right)_{T,P,X2} \end{vmatrix} \equiv Z = 0 \qquad (1)$$

$$\begin{vmatrix} \left(\frac{\partial Z}{\partial X_2}\right)_{T,P,X3} & \left(\frac{\partial Z}{\partial X_3}\right)_{T,P,X2} \\ \left(\frac{\partial^2 \tilde{G}}{\partial X_2 \partial X_3}\right)_{T,P} & \left(\frac{\partial^2 \tilde{G}}{\partial X_3^2}\right)_{T,P,X2} \end{vmatrix} = 0 \qquad (2)$$

where, G, x, T, P, respectively, represent molar Gibbs free energy, liquid mole fraction, absolute temprature, and pressure. Subscripts, 1, 2, and 3, denote components. From Eqs.(1) and (2), the following thermodynamic equations can be easily derived.

$$\begin{vmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{vmatrix} \equiv F = 0 \qquad (3)$$

$$\begin{vmatrix} B_{11} & B_{12} \\ B_{21} & B_{22} \end{vmatrix} = 0 \qquad (4)$$

where

$$A_{11} = \left(\frac{1}{X_1} + \frac{1}{X_2}\right) + \left(\frac{\partial^2 Q}{\partial X_2^2}\right)_{T,P,X3} \qquad (5)$$

$$A_{12} = A_{21} = B_{12} = \left(\frac{1}{X_1}\right) + \left(\frac{\partial^2 Q}{\partial X_2 \partial X_3}\right)_{T,P} \qquad (6)$$

$$A_{22} = B_{22} = \left(\frac{1}{X_1} + \frac{1}{X_3}\right) + \left(\frac{\partial^2 Q}{\partial X_3^2}\right)_{T,P,X2} \qquad (7)$$

$$B_{11} = \left(\frac{\partial F}{\partial X_2}\right)_{T,P,X3} \qquad (8)$$

$$B_{21} = \left(\frac{\partial F}{\partial X_3}\right)_{T,P,X2} \qquad (9)$$

The thermodynamic equations shown above are required for the plait point of ternary systems.

Based on Eqs.(3) to (9), the ternary plait point compositions can be thermodynamically solved when the activity coefficient equation and its parameters are given. The following NRTL equation,[1] the most widely-known activity coefficient equation capable for partially immiscible mixtures, was used in the present work.

$$Q = \sum_{i=1}^{3} x_i \frac{\sum_{j=1}^{3} \tau_{ji} G_{ji} x_j}{\sum_{k=1}^{3} G_{ki} x_k} \tag{10}$$

$$G_{ji} = \exp(-\alpha_{ji} \tau_{ji}), \quad \alpha_{ji} = \alpha_{ij} \tag{11}$$

where α and τ are the NRTL parameters.

Table 1 shows the calculation examples of the ternary plait point compositions, using Eqs.(3) to (11). The NRTL parameters listed in Table 1 were obtained from the work of Katayama et al.[2,4] As shown in Table 1, the calculation results of the plait points seem satisfactory.

Table 1. Calculation examples of plait points

System	NRTL parameters[2,4]									Calculated Plait Point		
	α_{12}	τ_{12}	τ_{21}	α_{23}	τ_{23}	τ_{32}	α_{31}	τ_{31}	τ_{13}	x_1	x_2	x_3
1	0.47	2.6714	1.5258	0.30	0.8799	0.5499	0.20	1.7803	1.5525	0.4264	0.3454	0.2282
2	0.30	1.8559	0.6750	0.30	0.2391	0.1791	0.20	0.1464	4.3581	0.6349	0.3582	0.0069
3	0.47	1.261	2.405	0.30	-0.473	0.721	0.42	2.333	2.188	0.2259	0.6798	0.0943

System **1** : *n*-Hexane(1) - Ethanol(2) - Acetonitrile(3) at 313.15 K.
2 : Water(1) - Acetonitrile(2) - Ethyl acetate(3) at 333.15 K.
3 : Methanol(1) - Carbon tetrachloride(2) - Cyclohexane(3) at 298.15 K.

Consequently, the thermodynamic equations given by Eqs.(3) to (9) are considered effective in the evaluation of the ternary plait points from activity coefficient equations. As the plait point is meaningful for the shape of the ternary solubility curve, the authors are planning the determination of the parameters of activity coefficient equations satisfying the experimental plait point and the binary solubility data, by use of Eqs.(3) and (4) on the experimental plait point.

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