

# LIQUID-LIQUID EQUILIBRIA INCLUDING CRITICAL REGION FROM NRTL MODEL WITH MULTIPLE-STATE INTERACTION

MING YU AND HIDEO NISHIUMI

*Chemical Engineering Laboratory, Hosei University, Tokyo 184*

**Key Words:** Liquid-Liquid Equilibria, Critical Region, Multiple-State Interaction, NRTL model

This work presents a phenomenological approach to describing the complex phase diagrams of binary liquid mixtures. The NRTL free energy expression is modified by the generalization of local pairwise energies to the corresponding free energies which, for systems with specific interactions such as hydrogen bonds, are described in terms of multiple-level partition functions. The model gives a good representation of binodal curves over wide temperature ranges, including both upper and lower critical conditions.

## Introduction

Many binary liquid mixtures that form a single, homogeneous phase at higher temperature possess an upper critical solution temperature (UCST) below which phase separation occurs<sup>1,4)</sup>. In simple systems of structureless particles, such as rare gas binary mixtures, the existence and specific value of a UCST are the consequences of the energetic of interparticle interactions balanced against the entropy of mixing. Lower critical solution temperatures (LCST) are not

confined to mixtures of small molecules, but in fact have been observed in some complex mixtures, such as aqueous solutions of surfactants and of water-soluble polymers<sup>11,14,17)</sup>. Phase separation occurs above the LCST. While UCST is readily understood in terms of intermolecular forces, interpretation of a LCST is much more difficult<sup>13)</sup>. One of the possible explanations is that phase equilibria in the systems possessing an LCST are influenced by strong, directional interaction forces such as hydrogen bonds.

Knowledge of the coexistence curves with an UCST or an LCST is of great importance for understanding some important properties of some mixtures of

Received August 20, 1991. Correspondence concerning this article should be addressed to H. Nishiumi.

interest. For example, the mean temperature of the three-phase interval  $\Delta T$  of microemulsion systems composed of oil, water, and a surfactant is essentially determined by the critical solution temperatures of the binary water-surfactant and oil-surfactant mixtures<sup>8)</sup>. To describe binary systems possessing critical solution points, several thermodynamic models have been proposed. The decorated lattice model proposed by Wheeler *et al.*<sup>1,18)</sup> and a modification of the model<sup>9)</sup> were used in several cases and very encouraging results have been obtained. However, the mathematical complexity of these models makes extension to more complex systems difficult. de Pablo *et al.*<sup>2,3)</sup> extended Fox's method of transforming the coordinates of the classical equation of state to nonclassical coordinates and applied their extension to some binary and ternary liquid mixtures. Their method gives good representation of LLE, including the critical region. However, the required calculations are complex and take longer time. Recently, Ochi *et al.*<sup>10)</sup> correlated the mutual solubilities of four binary mixtures with an NRTL model, for which the temperature dependency of its parameters was assumed. There are six parameters for each binary pair. It seems that there is still some room for their method to be refined, especially at the critical point and its surroundings. In one of their mixtures, the mixture of EMK and water, for example, the second and third derivatives of  $(\Delta g/RT)$  with respect to  $x_1$  at the critical point were respectively  $-0.4242$  and  $2.1610$  rather than  $0.0$ , which is desirable theoretically for the method and the parameters given in their paper.

Goldstein and Walker<sup>5)</sup> used a lattice model with multiple interaction sites which was reformulated in the form of the Migdal-Kadanoff approximation to evaluate the effective molecular interactions. UCSTs and LCSTs were calculated in terms of multiple intermolecular forces, but their model could predict only symmetrically shaped phase diagrams. Goldstein's phenomenological approaches partially resolved this situation with multiple-level partition functions and the Flory-Huggins free energy expression. These approaches were applied to polymer solutions<sup>6)</sup> and micellar solutions of non-ionic surfactant<sup>7)</sup>. Qualitative results were obtained.

In this work, we combine the concept of multiple-state interactions of Goldstein<sup>6)</sup> with the NRTL equation<sup>12)</sup>. The object of the work was to correlate LLE quantitatively along the coexistence curve close to or remote from both upper and lower critical conditions in binary liquid mixtures.

## 1. NRTL Model with Multiple Interaction

### 1.1 NRTL equation

The NRTL model for  $g^E$ , the molar excess Gibbs energy of a liquid mixture, is given by

$$\frac{g^E}{RT} = \sum_i x_i \frac{\sum_j x_j G_{ji} \tau_{ji}}{\sum_j x_j G_{ji}} \quad (1)$$

where the NRTL parameter for  $ij$  pair  $\tau_{ij}$  is defined as

$$\tau_{ij} = (u_{ij} - u_{jj}) / (RT) \quad (2)$$

and

$$G_{ji} = \exp(-a_{ji} \tau_{ji}) \quad (3)$$

In this work, nonrandom parameter  $a_{ji} = a_{ij} = 0.2$ .

The NRTL equation has been used to describe LLE for binary and ternary liquid mixtures<sup>15,16)</sup>. Although the model is flexible enough to fit the coexistence curve at a given temperature and has a moderate built-in temperature dependence, this built-in temperature dependence is insufficient for adequate representation of LLE over a wide range of temperature, especially in a critical region. If we use the standard NRTL model and the model parameters obtained from the experimental data remote from the critical condition, the calculated critical temperature  $T_c$  is too large. Similarly, when the model is used with parameters determined from the experimental critical point, the miscibility gap is too narrow<sup>2,3)</sup>. Generally speaking, classical models for the excess Gibbs energy give a coexistence curve which, near  $T_c$ , is quadratic in composition, in conflict with experimental data and the modern theory of critical phenomena. Near the consolute temperature, the coexistence curve is much flatter than that predicted by the classical model. Further, the standard NRTL model cannot account for the existence of lower critical solution temperatures. One of the possible reasons is that no orientation-dependent interactions are taken into account in the model in spite of their large contribution to the total energy of systems.

### 1.2 Decorated NRTL model

Previous theoretical work shows that the most important microscopic property is the existence of a multiple-state structure to the local interactions<sup>6)</sup>. There may exist several distinct modes of interaction, such as van der Waals forces and low-entropy but energy-favored hydrogen bonds and some others. It is assumed phenomenologically that the totality of relative orientational states may be grouped into levels, each with a characteristic energy and "degeneracy". In the simpler cases, the interactions can be grouped into two classes, *e.g.*, van der Waals-like and hydrogen bonds, and the local Helmholtz energy can be described by the two-level partition function  $Q_{ij}$ , with

$$f_{ij} = -RT \ln(Q_{ij}) \quad (4)^*$$

\*  $u_{ij}$  is treated as molar (or local molar) Helmholtz energy; that is,  $u_{ij}$  is assumed to be equal to  $f_{ij}$ .

and

$$Q_{ij} = \omega_{ij}^0 \exp(-e_{ij}^0/RT) + \omega_{ij}^* \exp(-e_{ij}^*/RT) \quad (5)$$

where  $\omega_{ij}^0$  and  $\omega_{ij}^*$  are orientational phase factors associated, respectively, with the nonbonding and bonding states, with energies  $e_{ij}^0$  and  $e_{ij}^*$ .

If the interaction energy between molecules  $i$  and  $j$ ,  $u_{ij}$  in Eq. (2), is treated as molar Helmholtz energy, the corresponding formulae to Eq. (4) give the interrelations with the NRTL parameters  $\tau_{ij}$  directly.

$$\tau_{12} = -\ln \left\{ \frac{\omega_{12}^0 + \omega_{12}^* \exp((e_{12}^0 - e_{12}^*)/(RT))}{\left( \frac{\omega_{22}^0 \exp((e_{12}^0 - e_{22}^0)/(RT))}{+ \omega_{22}^* \exp((e_{12}^0 - e_{22}^*)/(RT))} \right)} \right\} \quad (6)$$

and

$$\tau_{21} = -\ln \left\{ \frac{\omega_{21}^0 + \omega_{21}^* \exp((e_{21}^0 - e_{21}^*)/(RT))}{\left( \frac{\omega_{11}^0 \exp((e_{21}^0 - e_{11}^0)/(RT))}{+ \omega_{11}^* \exp((e_{21}^0 - e_{11}^*)/(RT))} \right)} \right\} \quad (7)$$

where  $e_{ij}^0 = e_{ji}^0$  and  $e_{ij}^* = e_{ji}^*$ . In this decorated NRTL model, for each binary mixture, there are twelve adjustable parameters, but arbitrarily we set  $\omega_{ij}^0 = 1.0$  and  $\omega_{ij}^* = \omega^*$ . Though the original NRTL parameters are monotonic increasing or decreasing functions of temperature, the parameters of Eqs. (6) and (7) exhibit a complex temperature dependency. Eq. (1) can be evaluated with the constraints of Eqs. (6) and (7).

In our derivation of the decorated NRTL model, the concept of local composition and the form of the NRTL are maintained. After obtaining effective energy parameters, the calculation procedure follows that of Prausnitz *et al.*<sup>12)</sup>

## 2. Description of Complex Phase Diagrams

To use the decorated NRTL model to correlate the coexistence curves including the critical points, the parameters in Eqs. (6) and (7) should be such that for liquid-liquid equilibria

$$a_i' = a_i'' \quad (i = 1 \text{ and } 2) \quad (8)$$

and at the critical point

$$\frac{\partial^2 \Delta g}{\partial x_1^2} = 0 \quad (9)$$

$$\frac{\partial^3 \Delta g}{\partial x_1^3} = 0 \quad (10)$$

where single- and double-prime superscripts refer respectively to the bottom and top phase,  $a_i$  is the activity of component  $i$ , and  $\Delta g$  is the molar Gibbs energy of mixing. The criteria used in this work are that the absolute value of  $(a_i' - a_i'')/a_i'$  is less than 0.00001 and the absolute values of the second and third derivatives of  $(\Delta g/R)$  with respect to  $x_1$  at the critical point are less than 0.0001.

Two type of examples of complex phase diagrams

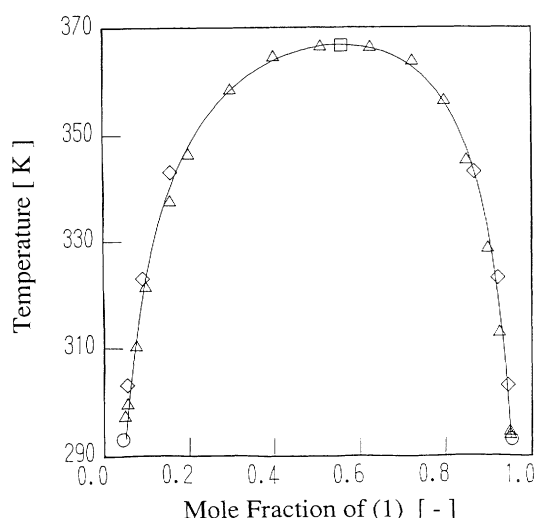


Fig. 1. LLE for the system of furfural (1) and heptane (2) Full line: calculated curve (this work); O, data of Koljutschkina *et al.*; ◇, data of Chueh *et al.*; △, data of Pennington *et al.*; □, consolute point

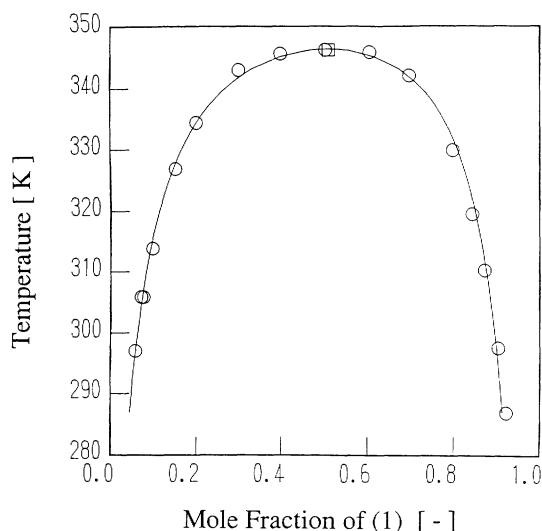


Fig. 2. LLE for the system of furfural (1) and methyl cyclohexane (2)

Full line: calculated curve (this work); O, data of Pennington *et al.*; □, consolute point

are calculated: (1) systems exhibiting UCSTs and (2) systems possessing LCSTs.

### 2.1 Phase diagrams with UCST

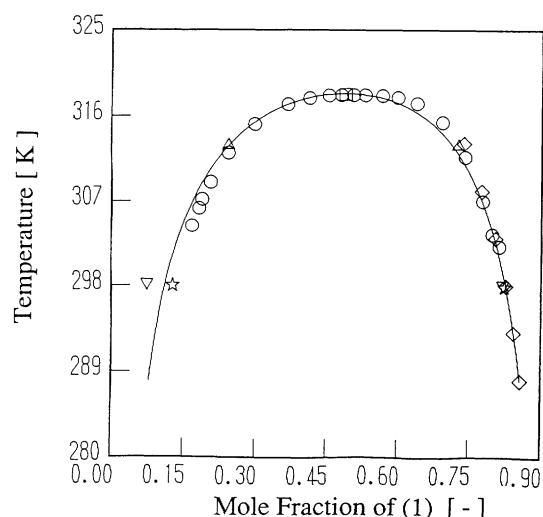
The phase separation at the highest CST is due to the relatively favorable nondirectional interactions between like-molecule pairs. The coexistence curve in the critical region is very flat. Empirical modification can possibly supply the strong temperature dependence desired in the regions.

Typical results of fitting the present model to such systems are shown in Figs. 1–3. Good agreement with experimental LLE data in both the critical regions and the regions remote from critical point are obtained. In our calculation, the experimental LLE data remote

**Table 1.** Model parameters and coordinates of critical points

System	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6
$\Delta e_{22}^0$ [K]	607.2522	380.1708	289.9626	-292.4041	-1342.7349	-316.5328
$\Delta e_{11}^0$ [K]	720.0659	845.0660	822.1107	2168.0836	1195.7432	1577.1241
$\Delta e_{22}^*$ [K]	492.4466	1861.3022	1134.4231	-116.2527	6921.0736	104.5408
$\Delta e_{11}^*$ [K]	53.8382	63.1278	60.8520	4183.6504	1008.9644	-630.3381
$\Delta e_{12}^*$ [K]	1189.3216	1549.3406	1225.0133	-0.3297	124.5553	-155.7450
$\omega^*$	-6.4113	-10.6690	-13.0799	-0.2338	-1.4200	-0.4850
$T_c$ (K)	366.90	346.40	318.398	297.59	268.27	307.15
$x_{1c}$	0.56	0.51	0.49	0.0592	0.0775	0.075

Note: In the table,  $\Delta e_{ii}^0 = -(e_{12}^0 - e_{ii}^0)/R$ ,  $\Delta e_{ij}^* = (e_{12}^0 - e_{ij}^*)/R$ , and system No. 1: Furfural-Heptane; system No. 2: Furfural-Methyl cyclohexane; system No. 3: Methanol-Cyclohexane; system No. 4: 2-Isobutoxy ethanol-Water; system No. 5: Dipropyl amine-Water; system No. 6: 1-Isopropoxy-2,3-pentane-diol-Water.

**Fig. 3.** LLE for the system of methanol (1) and cyclohexane (2)

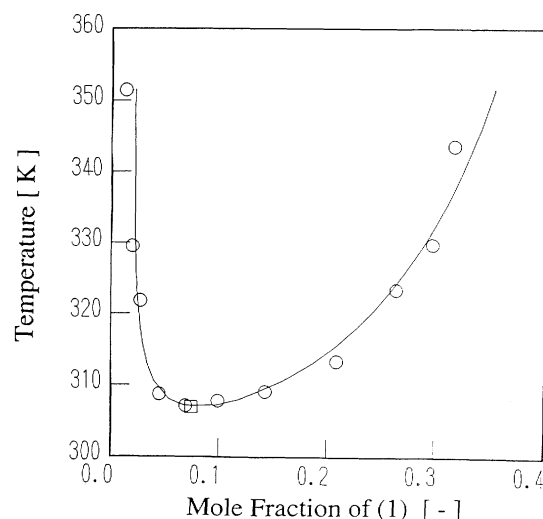
Full line: calculated curve (this work);  $\circ$ , data of Eckfeldt *et al.*;  $\diamond$ , data of Kiser *et al.*;  $\triangle$ , data of Sergeeva *et al.*;  $\nabla$ , data of Sergeeva *et al.*;  $\square$ , data of Takeuchi *et al.*;  $\blacksquare$ , consolute point

from critical conditions and the coordinates of the critical point are used. In each case, six parameters are adjusted to obtain the best fitting. **Table 1** gives these parameters for the examples, and the coordinates of known (or estimated) critical points are also given.

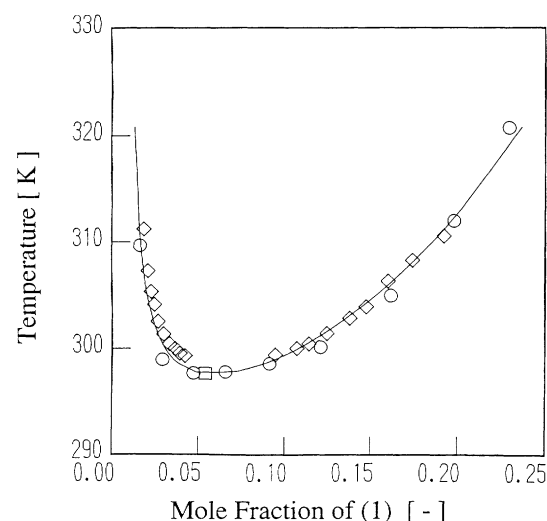
## 2.2 Phase diagrams with LCST

**Figs. 4–6** show the coexistence curves for three binary liquid mixtures possessing LCST from the model and the experimental results. It can be seen that all three coexistence curves lack compositional symmetry. However, in our model no asymmetries of molecular geometry are considered and all asymmetries in the coexistence curves are attributed to the asymmetries of molecular interactions because our model is constructed on the basis of NRTL. The model parameters and critical-point coordinates for these systems are also listed in Table 1.

All the experimental data used in Figs. 1–6 are from DECHEMA Chemical Data Series<sup>15</sup>.

**Fig. 4.** LLE for the system of 1-isopropoxy-2,3-pentane-diol (1) and water (2)

Full line: calculated curve (this work);  $\circ$ , data of Davison *et al.*;  $\blacksquare$ , consolute point

**Fig. 5.** LLE for the system of 2-isobutoxy ethanol (1) and water (2)

Full line: calculated curve (this work);  $\circ$ , data of Cox *et al.*;  $\diamond$ , data of Rudd *et al.*;  $\blacksquare$ , consolute point

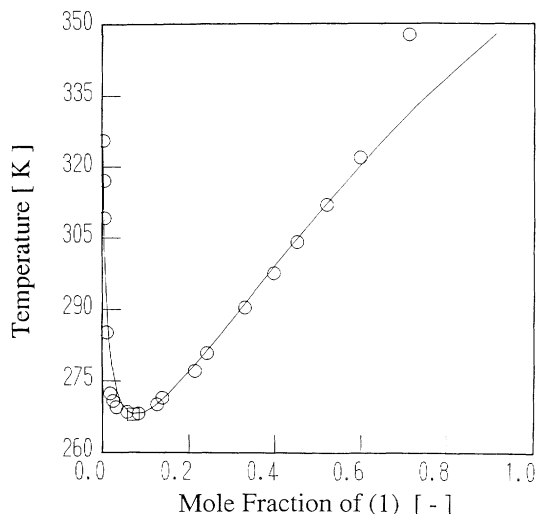


Fig. 6. LLE for the system of dipropyl amine (1) and water (2) Full line: calculated curve (this work);  $\circ$ , data of Hobson *et al.*;  $\square$ , consolute point

## Conclusion

In this work we have proposed a semiempirical modification to the NRTL model. By distinguishing between hydrogen-bond and dispersion-force interaction, the model can correlate LLE of some binary mixtures that may contain hydrogen-bonding solutes. Satisfactory approximation is obtained for phase equilibria along the coexistence curve close to and remote from both upper and lower critical solution conditions.

## Acknowledgement

The authors thank Prof. R. L. Smith of the University of South Carolina for his critical reading of the manuscript, and one of us (M.Y.) is grateful to Hosei University for a fellowship.

## Nomenclature

$a_i$	= activity coefficient of component $i$	[—]
$e_{ij}^0, e_{ij}^*$	= molar Helmholtz energy between $i$ and $j$ in nonbonding and bonding state	[J/mol]
$f_{ij}, u_{ij}$	= molar Helmholtz energy between $i$ and $j$	[J/mol]
$\Delta g$	= molar Gibbs energy of mixing	[J/mol]
$g^E$	= molar excess Gibbs energy	[J/mol]
$R$	= gas constant	[J/mol · K]

$Q$	= two level partition function	[—]
$T$	= temperature	[K]
$T_c$	= temperature at critical point	[K]
$u_{ij}$	= molar Helmholtz energy between $i$ and $j$	[J/mol]
$x_{1c}$	= mole fraction of component 1 at critical point	[—]
$x_i$	= mole fraction of component $i$	[—]
$\tau_{ij}$	= NRTL parameter	[—]
$\omega_{ij}^0, \omega_{ij}^*$	= phase factors associated with nonbonding and bonding state	[—]

## Literature Cited

- Anderson, G. R. and J. C. Wheeler: *J. Chem. Phys.*, **69**, 3403 (1978).
- de Pablo, J. J. and J. M. Prausnitz: *Fluid Phase Equilibria*, **50**, 101 (1988).
- de Pablo, J. J. and J. M. Prausnitz: *Fluid Phase Equilibria*, **59**, 1 (1990).
- Francis, A. W.: "Liquid-Liquid Equilibrium," Wiley, New York (1963).
- Goldstein, R. E. and J. S. Walker: *J. Phys. Chem.*, **78**, 1492 (1983).
- Goldstein, R. E.: *J. Chem. Phys.*, **83**, 1246 (1985).
- Goldstein, R. E.: *J. Chem. Phys.*, **84**, 3367 (1986).
- Kahlweit, M., R. Strey and G. Busse: *J. Phys. Chem.*, **94**, 3881 (1990).
- Kim, Y. C. and J. D. Kim: *Fluid Phase Equilibria*, **41**, 229 (1988).
- Ochi, K., M. Tada and K. Kojima: *Fluid Phase Equilibria*, **56**, 341 (1990).
- Prange, M. M., H. H. Hooper and J. M. Prausnitz: *AIChE J.*, **34**, 1595 (1989).
- Prausnitz, J. M., R. N. Lichtenthaler and E. Gomes de Azevedo: "Molecular Thermodynamics of Fluid-Phase Equilibria," 2nd Edn., Prentice-Hall, Englewood Cliffs, NJ (1986).
- Rowlinson, J. S. and F. L. Swinton: "Liquids and Liquid Mixtures," 3rd Edn., Butterworths, London (1982).
- Schick, M. J.: "Nonionic Surfactants; Surfactant Science Series, Vol. 1," Marcel Dekker, New York (1967).
- Sorensen, J. M. and W. Arlt: "Liquid-Liquid Equilibrium Data Collection, Binary Systems, Chemistry Data Series, Vol. V, Part 1," DECHEMA, Frankfurt/Main, FRG (1979).
- Sorensen, J. M. and W. Arlt: "Liquid-Liquid Equilibrium Data Collection, Ternary Systems, Chemistry Data Series, Vol. V, Part 2," DECHEMA, Frankfurt/Main, FRG (1980).
- Warr, G. G., T. N. Zemb and M. Drifford: *J. Phys. Chem.*, **94**, 3086 (1990).
- Wheeler, J. C.: *J. Phys. Chem.*, **62**, 433 (1975).