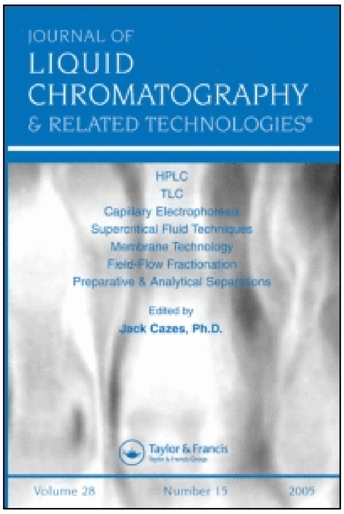

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Accurate Calculation for Liquid–Liquid Equilibria of Typical Solvent Systems Used in CCC

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Abstract: The properties of solvent systems in CCC can be estimated using calculations. In this work, liquid–liquid equilibrium (LLE) data of several typical solvent systems used in CCC are correlated and predicted using a molecular thermodynamic model called the Non-Random Theory of Liquids, NRTL. The parameters in this model are regressed only with the special system considered. The selected solvent systems are widely used in CCC: chloroform–methanol–water; chloroform–ethanol–water; hexane–methanol–water; ethyl acetate–methanol–water; hexane–ethyl acetate–methanol–water; hexane–ethanol–water; ethyl acetate–ethanol–water; butanol–acetic acid–water. Detailed comparison with experimental data shows that LLE of these systems can be predicted with greatly improved accuracy. Together with these results, volume ratio, density, viscosity, dielectric constant, and interfacial tension can be predicted with improved accuracy.

Keywords: Solvent selection, Liquid–liquid equilibrium, Calculation

INTRODUCTION

This work is a continuation of our previous works.[1,2] Since countercurrent chromatography (CCC) was proposed in the late 1960s,[3] it has been widely used in analytical chemistry and product separation in many areas.[4,5] In our previous works,[1,2] we have elaborated on a method for the calculation of the properties of solvent systems in CCC. These properties

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are phase composition, volume ratio, phase polarity, density, viscosity, dielectric constant, and interfacial tension. All the properties are very important for the work in CCC, especially the phase composition and volume ratio obtained from liquid–liquid equilibrium (LLE) calculation.

The LLE calculation can be carried out with two kinds of thermodynamic models: molecular models and group contribution models.[6–9] Compared with experimental LLE data, the results of LLE calculation with group contribution methods are not always very accurate. The reason is that the group interaction parameters were regressed with almost all experimental data for systems with the same group pairs. For example, CH_3Cl–CH_3OH–H_2O is a commonly used solvent system in CCC. But, its calculated LLE results do not coincide satisfactorily with the experimental ones. So, it is necessary to use thermodynamic models with the consideration of molecular interaction parameters.

In this work, LLE data of several typical solvent systems in CCC are correlated and predicted using a molecular thermodynamic model called the NRTL model.[6] The parameters in the models are regressed only with the special system considered. The selected solvent systems are widely used in CCC:[10–14] chloroform–methanol–water;[15] chloroform–ethanol–water;[16] hexane–methanol–water;[17] ethyl acetate–methanol–water;[18] hexane–ethyl acetate–methanol–water;[10] hexane–ethanol–water;[18] ethyl acetate–ethanol–water;[19] butanol–acetic acid–water.[18] Detailed comparison with experimental data shows that LLE of these systems can be predicted with greatly improved accuracy. Together with these results, volume ratio, density, viscosity, dielectric constant, and interfacial tension can be predicted with improved accuracy.

NRTL EQUATION OF STATE

The Non-Random Theory of Liquids (NRTL) model has been widely used to calculate phase equilibria, especially vapor–liquid equilibria and liquid–liquid equilibria.[6] In the equation, the local concentration of compounds are considered according to the molecular interaction, so it is valid for systems including polar and associating compounds, such as water and methanol. Water and methanol are widely used in the solvent systems in CCC, so NRTL is the best thermodynamic equation for calculation and prediction of properties of solvent systems in CCC.

The activity coefficient γ_i of a compound, I, in a mixture can be expressed with NRTL equation as:

$$\ln \gamma_i = \frac{\sum_j \tau_{ji} G_{ji} x_j}{\sum_k G_{ki} x_k} + \sum_j \frac{x_j G_{ij}}{\sum_k G_{kj} x_k} \left(\tau_{ij} - \frac{\sum_k x_k \tau_{kj} G_{kj}}{\sum_k G_{kj} x_k} \right) \tag{1}$$

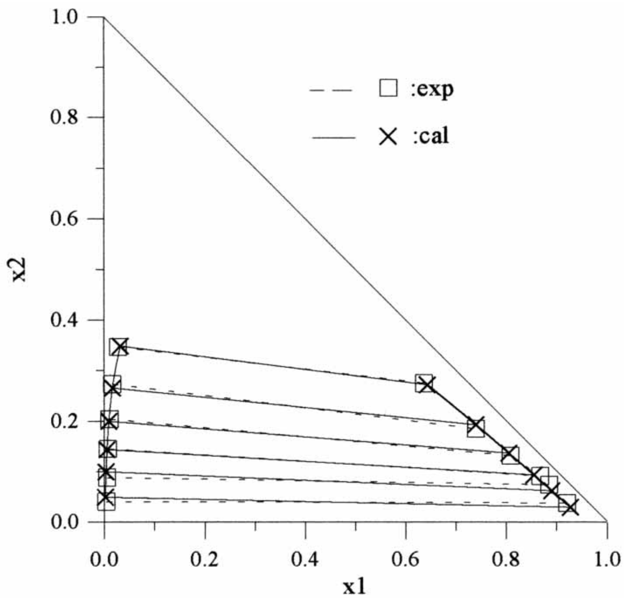

Figure 1. Liquid–liquid equilibrium calculation for the system chloroform (1) methanol (2) water (3) at 298.15 K with the RMSD as 0.006.

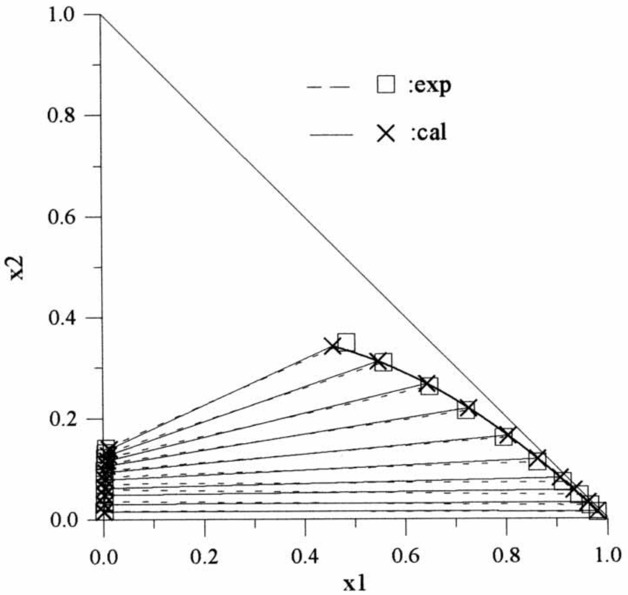

Figure 2. Liquid–liquid equilibrium calculation for the system chloroform (1) ethanol (2) water (3) at 298.15 K with the RMSD as 0.008.

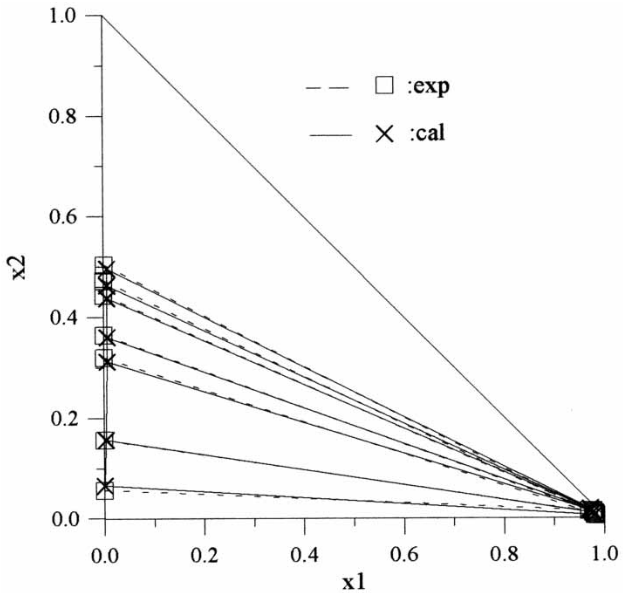

Figure 3. Liquid–liquid equilibrium calculation for the system hexane (1) methanol (2) water (3) at 298.15 K with the RMSD as 0.006.

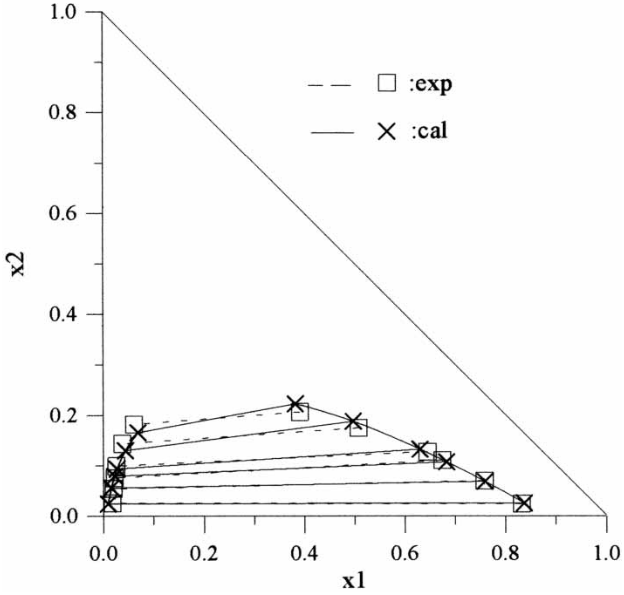

Figure 4. Liquid–liquid equilibrium calculation for the system ethyl acetate (1) methanol (2) water (3) at 293.15 K with the RMSD as 0.008.

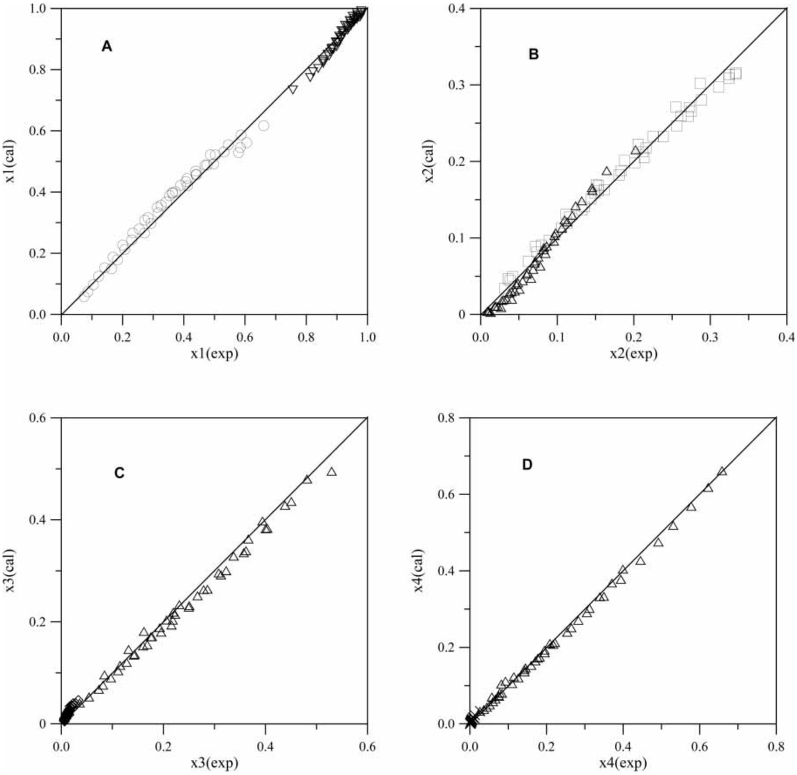

Figure 5. Liquid–liquid equilibrium calculation for the system hexane (1) ethyl acetate (2) ethanol (3) water (4); A: hexane mole fraction; B: ethyl acetate mole fraction; C: ethanol mole fraction; D: water mole fraction, at 298.15 K with the RMSD as 0.015. Triangles: upper phase; Circles or squares: lower phase.

where x_i is the mole fraction of a compound i, and:

$$G_{ij} = \exp(-\alpha_{ij}\,\tau_{ij}); \quad \alpha_{ij} = \alpha_{ji} = 0.2 \tag{2}$$

in which τ_{ij} is the interaction parameter between compounds i and j, and α_{ij} is the third non-randomness parameter which was set to 0.2 for all systems. For the systems in CCC at the temperature around 298 K, the interaction parameters were set to be independent of temperature:

$$\tau_{ij} = a_{ij} + b_{ij}/T \approx a_{ij} \tag{3}$$

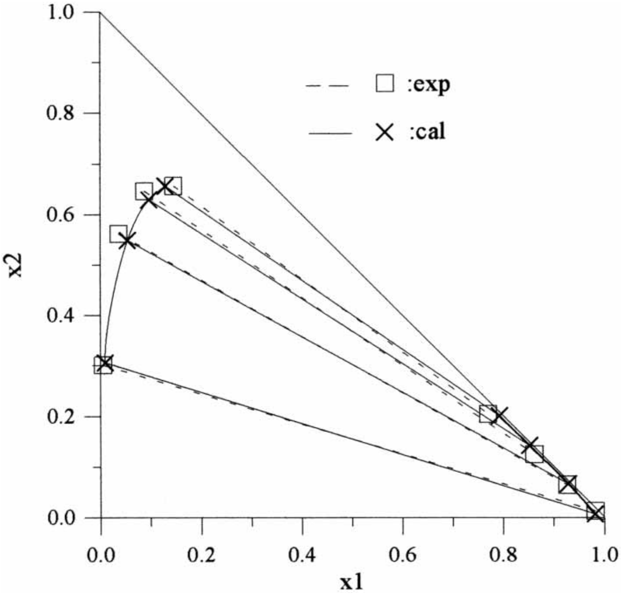

Figure 6. Liquid–liquid equilibrium calculation for the system hexane (1) ethanol (2) water (3) at 298.15 K with the RMSD as 0.011.

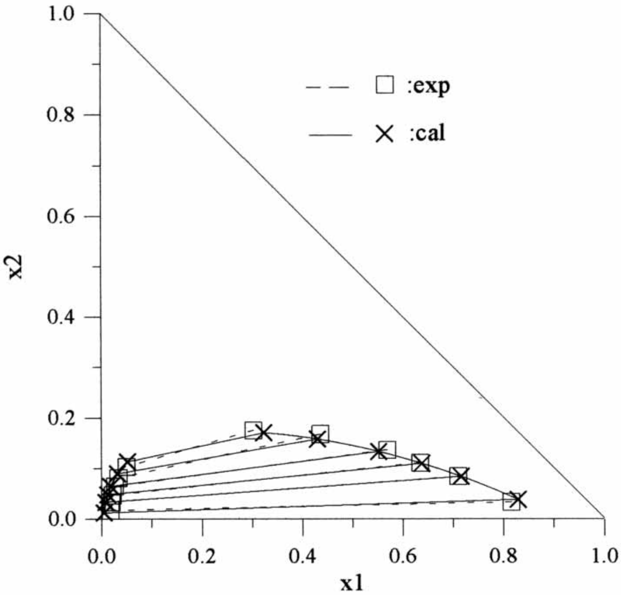

Figure 7. Liquid–liquid equilibrium calculation for the system ethyl acetate (1) ethanol (2) water (3) at 293.15 K with the RMSD as 0.010.

RESULTS

The thermodynamic model NRTL was used to correlate ternary and quaternary liquid–liquid equilibrium data. First, with initial values of parameters in the NRTL equation, the calculation of equilibria was carried out with the minimization of Gibbs energy as the objective function, and the equality of activity for each component in two phases was checked. This procedure confirmed the correct calculation of tie-line concentrations with the given parameters in the NRTL equation. Then, the parameters in NRTL were regressed with the minimization of total root-mean square deviation (RMSD) of mole fractions for all components:

$$\mathrm{RMSD} = \left[\sum_{i=1}^{n} \sum_{j=1}^{2} \sum_{k=1}^{M} \left| (x_{ijk}^{\mathrm{cal}} - x_{ijk}^{\mathrm{exp}})^2 \right| / 2nM \right]^{1/2} \tag{4}$$

x_{ijk}^{cal} is the calculated mole fraction. x_{ijk}^{exp} is the experimental one. i is for the number of components. j is for the number of phases. k is for the number of tie-lines. M is the total number of the tie-lines.

Correlation results are shown in Figures 1–8 for eight systems, respectively: chloroform–methanol–water; chloroform–ethanol–water; hexane–methanol–water; ethyl acetate–methanol–water; hexane–ethyl

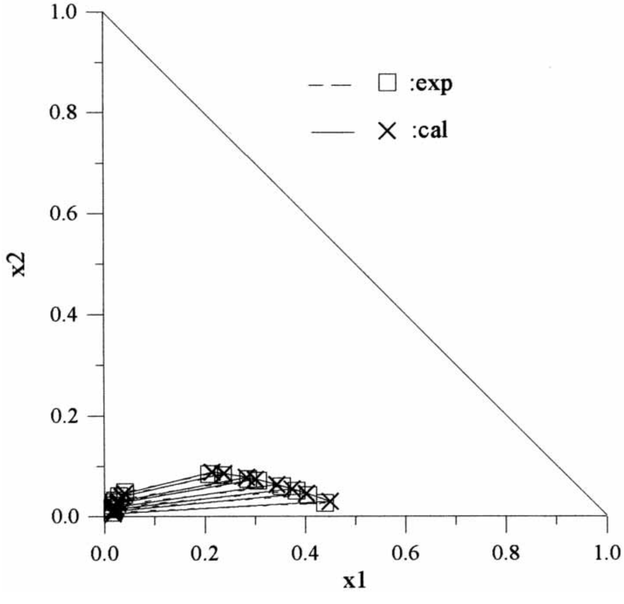

Figure 8. Liquid–liquid equilibrium calculation for the system butanol (1) acetic acid (2) water (3) at 298.15 K with the RMSD as 0.005.

Table 1. The NRTL parameters correlated for two typical systems

τ_{ij}	$j = 1$	2	3
	Chloroform (1)–methanol (2)–water (3) at 298.15 K		
$i = 1$	0.0000	-0.1928×10^3	0.4776×10^3
2	0.2199×10^3	0.0000	0.1173×10^3
3	0.1772×10^4	-0.3215×10^3	0.0000
	Chloroform (1)–ethanol (2)–water (3) at 298.15 K		
$i = 1$	0.0000	0.1086×10^4	0.1117×10^4
2	-0.5241×10^3	0.0000	-0.1590×10^3
3	0.1879×10^4	0.4766×10^3	0.0000

acetate–methanol–water; hexane–ethanol–water; ethyl acetate–ethanol–water; butanol–acetic acid–water. The root-mean square deviation of mole fractions for all components in these systems is 0.006, 0.008, 0.006, 0.008, 0.015, 0.011, 0.010, 0.005, and mean RMSD for all systems is 0.009. For the first two systems, the parameters fitted in this work are listed in Table 1, and calculation data are also compared with experimental data in Table 2.

The results show that the NRTL equation with the parameters in this work could be used to predict phase split composition for solvent systems widely used in CCC.

Table 2. Liquid–liquid equilibrium data (mole fraction) of chloroform–methanol–water at 298.15 K

x_1^{exp}	x_1^{cal}	x_2^{exp}	x_2^{cal}	x_3^{exp}	x_3^{cal}
		Chloroform-rich phase			
0.9203	0.9270	0.0376	0.0290	0.0421	0.0440
0.8849	0.8901	0.0737	0.0622	0.0414	0.0477
0.8677	0.8548	0.0913	0.0935	0.0410	0.0516
0.8089	0.8055	0.1319	0.1368	0.0592	0.0578
0.7395	0.7398	0.1850	0.1929	0.0755	0.0673
0.6362	0.6430	0.2755	0.2723	0.0883	0.0848
		Water-rich phase			
0.0036	0.0017	0.0402	0.0487	0.9562	0.9497
0.0051	0.0031	0.0879	0.0993	0.9071	0.8976
0.0068	0.0051	0.1448	0.1434	0.8484	0.8515
0.0102	0.0088	0.2038	0.1994	0.7860	0.7918
0.0157	0.0160	0.2733	0.2654	0.7110	0.7186
0.0275	0.0318	0.3468	0.3486	0.6257	0.6196

CONCLUSIONS

Liquid–liquid equilibrium data of eight typical solvent systems used in CCC are correlated and predicted using a molecular thermodynamic model NRTL. The parameters in the model are regressed only with the special system considered. Detailed comparison with experimental data shows that LLE of these systems can be predicted with greatly improved accuracy.

NOMENCLATURE

γ_i	activity coefficient of component *i*
τ_{ij}	interaction parameters between *i* and *j*
G_{ij}	interaction energy between *i* and *j*
x_i	mole fraction of component *i*
α_{ij}	non-random parameter between *i* and *j*
a_{ij}	temperature independent interaction parameter between *i* and *j*
b_{ij}	temperature dependent interaction parameter between *i* and *j*
T	temperature (K)
exp	superscript for experimental data
cal	superscript for calculated data

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