NRTL PARAMETERS FOR SOME TYPE I AND II TERNARY SYSTEMS

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summary

Difficulties associated with the phase equilibrium data correlations, such as convergence, objective function definition, initial parameters value dependence, and existence of multiple or metastable solutions, make difficult the correlation of the experimental liquid-liquid equilibrium data for some systems.

In this paper, a robust algorithm proposed by the authors, has been used to correlate 11 ternary systems that have not been previously correlated in the DECHEMA Chemistry Data Series [1] or, if they were, results were inconsistent with the number of miscible pairs in the system (Figure 1). A good representation of the LLE data for all the systems has been achieved using the NRTL model.

correlation procedure

For the specific calculation of the LLE, the isoactivity criterion has been applied using the Newton-Raphson method. In addition:

1. A procedure [2] based on the second derivative of the Gibbs energy of mixing function (g^M), that takes advantage of the topological information related to surface curvature changes, is used to eliminate most of the problems arising from multiple solution roots and the need for smart initial guesses.
2. An adaptation of the vector method is used [3] when Newton-Raphson method fails to converge.
3. A polynomial relation between the NRTL parameters Aij, deduced elsewhere [4], has also been used to ensure correct phase behaviour among all the binary subsystems involved in the ternary systems.

The Simplex Flexible method was used as the optimization tool for the calculation of the NRTL parameters Aij which minimize the composition objective function.

Moreover, in order to check the consistency of the NRTL parameters obtained, in the whole range of compositions, a stability test based on the topological analysis of the g^M surface has been carried out (Figure 2).

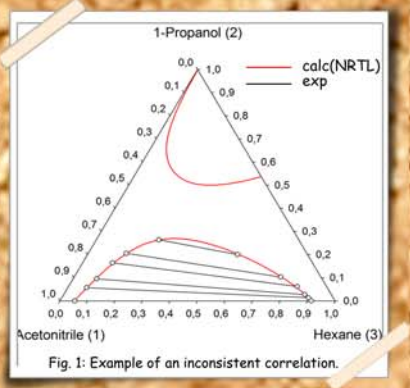


Fig. 1: Example of an inconsistent correlation.

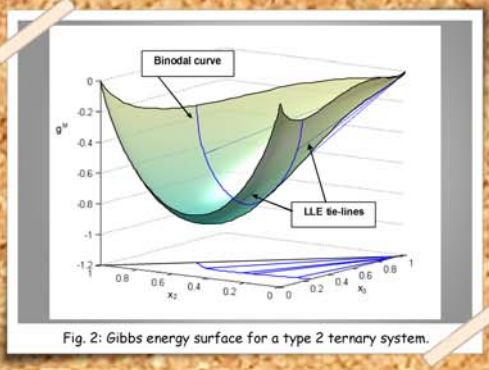
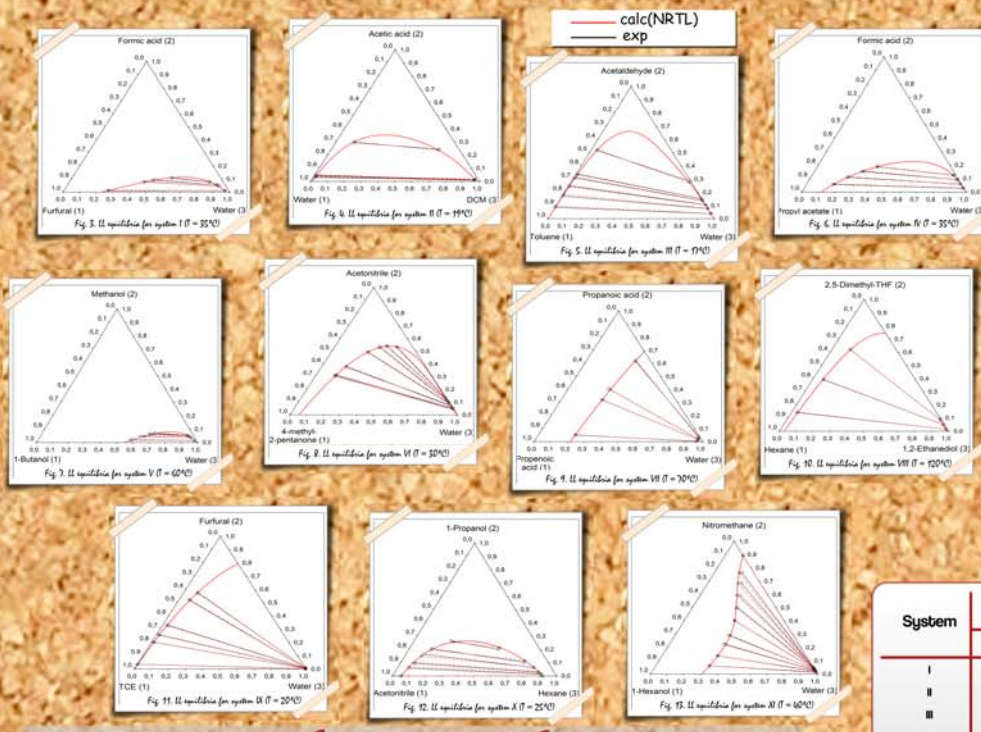


Fig. 2: Gibbs energy surface for a type 2 ternary system.



results & discussion

Results for 11 ternary systems are shown in Figures 3 to 13. NRTL parameters and the calculated standard deviations for each system are provided in the table shown below.

It can be seen that, using an appropriate correlation algorithm, many problems related to phase equilibria correlations can be overcome.

System	NRTL binary parameters: A_{ij} (K) and α_{ij}									Standard deviation
	A_{12}	A_{21}	α_{12}	A_{13}	A_{31}	α_{13}	A_{23}	A_{32}	α_{23}	
I	923.06	-495.40	0.2	31123	1229.5	0.2	413.32	-1050.4	0.2	0.40
II	-1774.3	-443.71	0.2	1184.9	620.46	0.2	-218.50	-4549.3	0.3	0.22
III	46110	25.387	0.2	1936.0	3344.7	0.2	575.25	-62.729	0.2	0.48
IV	-15191	-466.97	0.2	236.20	2344.3	0.2	-604.97	-11841	0.2	0.36
V	-1876.2	-299.16	0.3	-136.97	1680.0	0.3	-18733	-2713.7	0.2	0.67
VI	-19.814	268.88	0.2	404.31	1606.5	0.2	-39.552	78235	0.2	0.43
VII	53.359	-192.31	0.2	119.86	1114.2	0.2	-3.5836	1170.4	0.2	0.37
VIII	-463.68	851.53	0.2	773.45	1516.9	0.2	338.47	725.07	0.2	0.23
IX	1400.6	-610.03	0.2	1355.0	1671.4	0.2	62.823	1130.8	0.2	0.25
X	-255.45	-598.71	0.2	671.58	425.70	0.2	428.77	-71918	0.2	0.86
XI	645.07	-30.321	0.2	-89.209	2689.8	0.2	403.03	690.99	0.2	0.75

references & acknowledgements

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