ON THE USE OF THE NRTL METHOD

FOR CALCULATION OF LIQUID – LIQUID

EQUILIBRIA IN TERNARY SYSTEMS

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Abstract

Application of the NRTL method to experimental data obtained on several systems at different temperatures shows that the energy parameter set that minimizes the objective function at a given temperature, T_1, can be used for estimating phase compositions at other T values without serious error. It is concluded that this approach should be preferred to the use of interpolated or extrapolated g_{ij} values.
Keywords: Thermodynamics – Liquid-liquid equilibria - NRTL method

Resumen

La aplicación del método NRTL para ajustar curvas de equilibrio líquido – líquido en varios sistemas a distintas temperaturas muestra que, para estimar las composiciones de equilibrio a una temperatura arbitraria T, es preferible emplear el conjunto de parámetros de energía obtenidos al ajustar los datos obtenidos a una temperatura dada antes que utilizar valores de los g_{ij} interpolados o extrapolados de las series obtenidas.
Palabras clave: Termodinámica; equikibrio líquido-líquido; método NRTL.

Introduction

Prediction of thermodynamic properties in liquid mixtures is of great importance for the chemical engineer. Among the different approaches that have been proposed in order to achieve this goal, the *Non-Ramdom Two Liquid* method (NRTL) [1] is still one of the most frequently employed options. However, and as we have already pointed out previously [2], the original predictive goal of this method has been replaced by ex-post calculation of the fitting parameters that best correlate experimental data.

In Reference 2 particular attention was devoted to the fact that, when a system is experimentally studied at different temperatures, the fitting parameters that result when the usual calculation techniques are applied do not show a cogent behaviour and, in fact, it is not possible to obtain fitting parameters at an arbitrary temperature value by interpolating or extrapolating from the calculated values.

In this work, we further explore the behaviour of the NRTL equations in the case of three component mixtures showing liquid – liquid phase equilibria.

The NRTL method

The basic equation of the method stems out from an essentially heuristic approach that combines a modification of the quasi – chemical theory of Guggenheim [3] with the model of Scott [4]. In this approach a binary solution, **1-2**, is considered as a mixture of two types of cell: one centered in a molecule of species **1** and the other in a molecule of species **2**. A non-random distribution results that is described in terms of local mole fractions:

$$x_{21}/x_{11} = (x_2/x_1) \exp[-\alpha_{12}(g_{21} - g_{11})/RT] \tag{1}$$

where x_{21} and x_{11} are, respectively, the mole fractions of components **2** and **1** in the neighborhood of molecule **1**, g_{21} and g_{11} are the Gibbs energies of interaction for the 2-1 and 1-1 pairs and α_{12} is a characteristic constant of the mixture. Calculation of Gibbs excess energies yields:

$$\ln \gamma_j = x_i^2 \{ [\tau_{ij} G_{ij}^2/(x_j + x_i G_{ij})^2] + [\tau_{ji} G_{j1}/(x_i + x_j G_{ji})^2] \} \tag{2}$$

where

$$\tau_{ij} = (g_{ij} - g_{jj})/RT \tag{3}$$

and

$$G_{ij} = \exp\left(-\alpha_{ij}\tau_{ij}\right) \tag{4}$$

with these equations and employing experimental data from liquid – vapour and liquid – liquid equilibria of binary systems the α_{ij} and $(g_{ij} - g_{jj})$ values can be obtained.

The extension of the NRTL approach to multicomponent systems is based on the usual assumption that only pair interactions can be considered and, hence, activity coefficients for the different species in a given phase can be written as:

$$\ln \gamma_j = (\Sigma_j \tau_{ji} G_{ji} x_j / \Sigma_k G_{ki} x_k) + \Sigma_j\{(x_j G_{ij} / \Sigma_k x_k G_{kj})[\tau_{ij} - (\Sigma_l x_l \tau_{lj} G_{lj} / \Sigma_k x_k G_{kj})]\} \tag{5}$$

Thus, the method allows to make predictions on phase compositions for liquid – liquid equilibria in ternary systems employing energy parameters obtained experimentally from phase equilibria in binary systems.

However, almost all published papers dealing with experimental determination of liquid – liquid equilibria in ternary systems do not apply the NRTL approach in order to verify its predictive capability but, instead, the method is employed for calculating the τ_{ij} values that minimize an objective function like:

$$[\Sigma_{k=1}\Sigma_{j=1,2}\Sigma_{i=1\text{-}3}\,(x_{ijk} - x^{*}_{ijk})^2]^{1/2} \cdot N^{-1} \tag{6}$$

where x_{ijk} is the experimental mole fraction of component **i** in the **j** phase for the **k**th tie line, x^{*}_{ijk} is the corrresponding calculated value and N is the number of experimental tie lines.

As we have shown in previous work [2], the interaction parameter obtained for a given pair of species is neither independent of the nature of the third component nor of the temperature at which the experimental data set was obtained. Moreover, the observed change in the interaction parameters does not show a cogent behaviour with, for instance, changes in aliphatic chain length of a component or temperature variation. Hence, an estimation of energy parameters for a given mixture made by interpolation or extrapolation of previously obtained values is a very risky choice.

In this respect it is not surprising that the nature of molecule **3** affect the interaction between molecules **1** and **2.** However, the apparently chaotic variation of energy parameters with temperature is somewhat baffling and, consequently, we decided to carry out further work in studying this particular behaviour.

Calculations and discussion

In order to further examine the output of the NRTL method when applied to liquid – liquid equilibria in ternary systems at varying temperature literature data were chosen for systems that widely differ in their chemical characteristics. Thus, data from the following ternary mixtures were considered:

a) heptadecane + propylbenzene + N-methyl-2-pyrrolidone (NMP) at 298.15 K, 308.15 K, 318.15 K and 328.15 K [5].
b) limonene + ethanol + water at 293.15 K, 303.15 K, 313.15 K and 323.15 K [6].
c) methyl tert-butyl ether (MTBE) + 1-hexanol + water at 288.15 K, 298.15 K and 308.15 K [7].

   d) methyl propyl ketone (MPK) + propanoic acid + water at 298.15 K, 308.15 K, 318.15 K
      and 328.15 K [8].
   e) benzonitrile + propanone + water at 298.15 K, 303.15 K, 308.15 K, 313.15 K and
      318.15 K [9].

     In Tables 1 – 5 the g_{ij} values obtained for the five systems when the objective function
of Eqn. (6) is minimized for each temperature are displayed together with the g_{ij} obtained
when data at all temperatures are employed in a single minimization process. In all cases the
steepest descent method was employed with α = 0.3 and, since the relevant parameters in the
calculations are the τ_{ij} values, all values are referred to $g_{11} = 0$. It is clear from these results
that the variation of the g_{ij} values with temperature is not regular and, hence, it is impossible
to obtain the fitting parameters at an intermediate temperature by interpolation. Also, it is
readily seen that the results obtained when data at all temperatures are simultaneously
employed in the minimization process fit very poorly with experimental data.

Table 1: Fitting parameters for the NRTL approach for the system heptadecane (1) +
propylbenzene (2) + NMP (3) calculated from data in Ref. [5].

T / K	g_{12}	g_{13}	g_{22}	g_{23}	g_{33}
298.15	2746	8435	-9665	3876	3256
308.15	2262	8623	-12594	3854	4122
318.15	3472	10630	-9136	4300	-12740
328.15	3494	10342	-9512	4495	-12211
All data	2954	8156	-1540	4540	3540

Table 2: Fitting parameters for the NRTL approach for the system limonene (1) + ethanol (2)
+ water (3) calculated from data in Ref. [6].

T / K	g_{12}	g_{13}	g_{22}	g_{23}	g_{33}
293.15	10924	28789	598	14137	-2557
303.15	12804	27668	-24258	17281	-4871
313.15	15439	28986	-20965	19900	-2703
323.15	14901	29967	-18660	19730	1855
All data	11581	23922	6144	15542	13548

Table 3: Fitting parameters for the NRTL approach for the system MTBE (1) + 1-hexanol (2) + water (3) calculated from data in Ref. [7].

T / K	g_{12}	g_{13}	g_{22}	g_{23}	g_{33}
288.15	108610	10310	31730	46000	9590
298.15	129970	12230	-1480	14350	-14820
308.15	98245	12869	27025	42362	12503
All data	25981	22333	-3053	15227	18449

Table 4: Fitting parameters for the NRTL approach for the system water (1) + propanoic acid (2) + MPK (3) calculated from data in Ref. [8].

T / K	g_{12}	g_{13}	g_{22}	g_{23}	g_{33}
298.15	-5908	9136	-28657	-3314	-404
308.15	-6555	14239	-29496	2828	3680
318.15	-6952	10726	-31211	-2194	196
328.15	-7243	10926	-32490	-2438	363
All data	29931	7339	6122	6485	-3294

Table 5: Fitting parameters for the NRTL approach for the system water (1) + benzonitrile (2) + propanone (3) calculated from data in Ref. [9].

T / K	g_{12}	g_{13}	g_{22}	g_{23}	g_{33}
298.15	7439.3	695.4	-7126.2	-4432.2	-3850.8
303.15	8029.1	-346	-6459.4	-5737.2	-7336.7
308.15	7730.4	-881	-6947.1	-6571.1	-8735.2
313.15	7440.1	-1086	-6850.6	-7239.7	-9179.1
318.15	7253	-1482	-6354	-7540	-10583
All data	1511	10556	-11272	81	2405

Now, a quick inspection of Eqns. (5) and (6), which depend on the τ_{ij} and the α_{ij}, indicates that the objective function must have a number of local minima. The immediate

question that arises is how good will be the correlation at a given temperature, T_1, if the parameters obtained by looking for the absolute minimum in Eqn. (6) at another temperature, T_2, are employed. We have performed these calculations and the results are summarized in Tables 6 – 10. In Figures 1 – 5 some of the resulting ternary diagrams are shown.

Table 6: Objective functions defined by Eqn. (6) at different temperatures obtained with the g_{ij} sets calculated at T(g_{ij}) for the system heptadecane + propylbenzene + NMP.

| T(g_{ij})/K	O.F.(298.15 K)	O.F.(308.15 K)	O.F.(318.15 K)	O.F.(328.15 K)
298.15	0.0035	0.0079	0.0073	0.0069
308.15	0.0083	0.0054	0.0065	0.0067
318.15	0.0066	0.0058	0.0061	0.0049
328.15	0.0075	0.0055	0.0064	0.0057
All data	0.0089	0.0133	0.0173	0.03500

Table 7: Objective functions defined by Eqn. (6) at different temperatures obtained with the g_{ij} sets calculated at T(g_{ij}) for the system limone + ethanol + water.

| T(g_{ij})/K	O.F.(293.15 K)	O.F.(303.15 K)	O.F.(313.15 K)	O.F.(323.15 K)
293.15	0.0238	0.0226	0.0241	0.0239
303.15	0.0256	0.0231	0.0253	0.0234
313.15	0.0254	0.0234	0.0238	0.0214
323.15	0.0257	0.0239	0.0234	0.0214
All data	0.1398	0.0941	0.1299	0.1278

Table 8: Objective functions defined by Eqn. (6) at different temperatures obtained with the g_{ij} sets calculated at T(g_{ij}) for the system MTBE + 1-hexanol + water.

T(g_{ij})/K	O.F.(288.15 K)	O.F.(298.15 K)	O.F.(308.15 K)
288.25	0.0188	0,0181	0.0154
298.25	0.0122	0.0156	0.0135
308.15	0.0170	0.0160	0.0138
All data	0.8095	0.8148	0.6960

Table 9: Objective functions defined by Eqn. (6) at different temperatures obtained with the g_{ij} sets calculated at T(g_{ij}) for the system MPK + propanoic acid + water.

T(g_{ij})/K	O.F.(298.15 K)	O.F.(308.15 K)	O.F.(318.15 K)	O.F.(328.15 K)
298.15	0.0143	0.0176	0.0198	0.0192
308.15	0.0153	0.0154	0.0189	0.0194
318.15	0.0144	0.0151	0.0175	0.0183
328.15	0.0148	0.0154	0.0170	0.0165
All data	0.3820	0.4447	0.4248	0.4352

Table 10: Objective functions defined by Eqn. (6) at different temperatures obtained with the g_{ij} sets calculated at T(g_{ij}) for the system benzonitrile + propanone + water.

T(gij)/K	O.F. (298.15 K)	O.F. (303.15 K)	O.F. (308.15 K)	O.F. (313.15 K)	O.F .(318.15 K)
298.15	0.0129	0.0223	0.0224	0.0258	0.0275
303.15	0.0192	0.0109	0.0107	0.0152	0.0232
308.15	0.0169	0.0081	0.0091	0.0127	0.0220
313.15	0.0215	0.0099	0.0118	0.0097	0.0160
318.15	0.0228	0.0139	0.0149	0.0130	0.0135
All data	0.1726	0.1562	0.1504	0.1419	0.1305

The obtained results indicate that the objective function values that result for the different systems studied remain within the same order of magnitude when the energy parameter set calculated at a given temperature is changed by the parameter set obtained at other temperature. Moreover, in some cases, and as a consequence of experimental uncertainties, a better objective function value results when the parameter set obtained at a different temperature is employed.
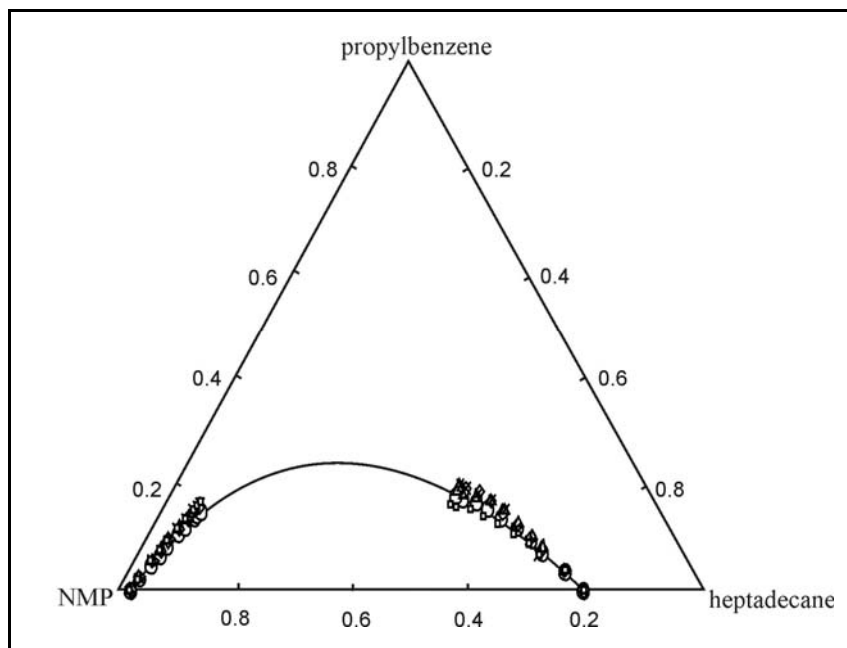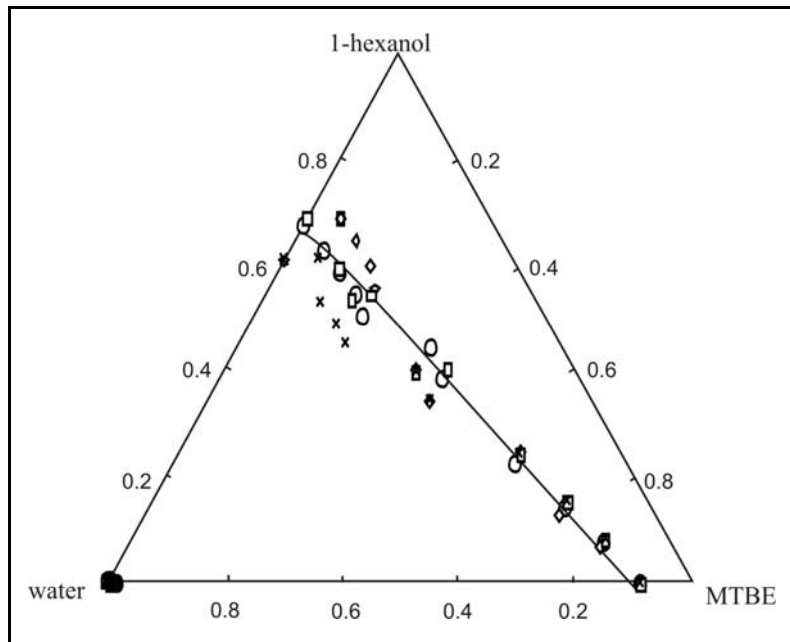
Figure 1: Experimental (o and solid curve) and calculated phase compositions for the {heptadecane + propylbenzene + NMP} system [5] at 328.15 K, employing the g_{ij} values that minimize the objective function of Eqn. (6) at the indicated temperature: □, 298.15 K; ✕, 308.15 K; △, 318.15 K; ◇, 328.15 K.
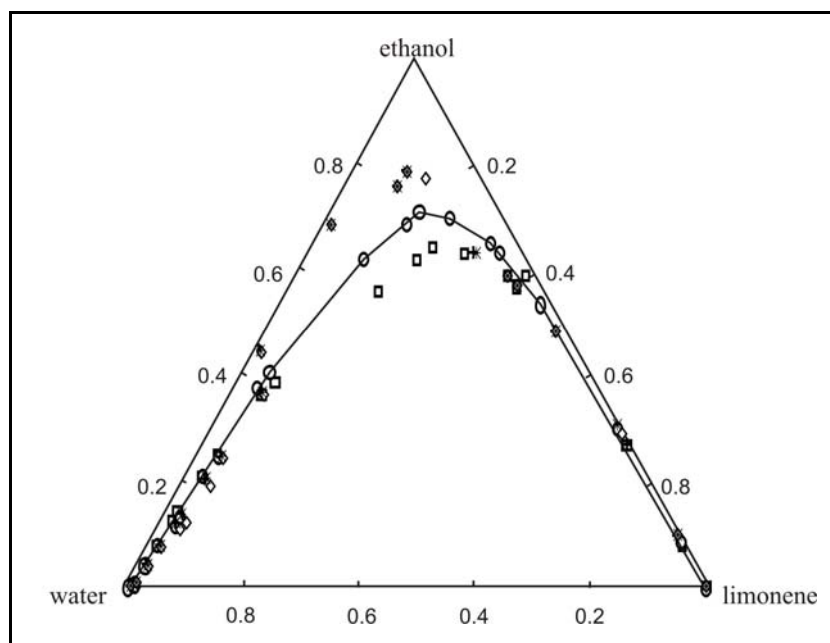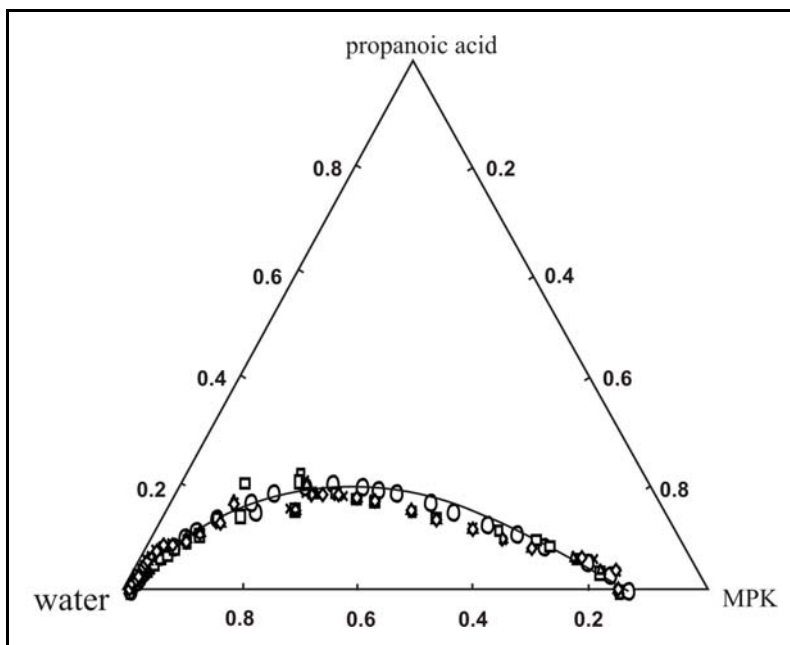

Figure 2: Experimental (o and solid curve) and calculated phase compositions for the {limonene + ethanol + water} system [6] at 293.15 K, employing the g_{ij} values that minimize the objective function of Eqn. (6) at the indicated temperature: □, 293.15 K; ✚, 303.15 K; ✳, 313.15 K; ◇, 323.15 K.
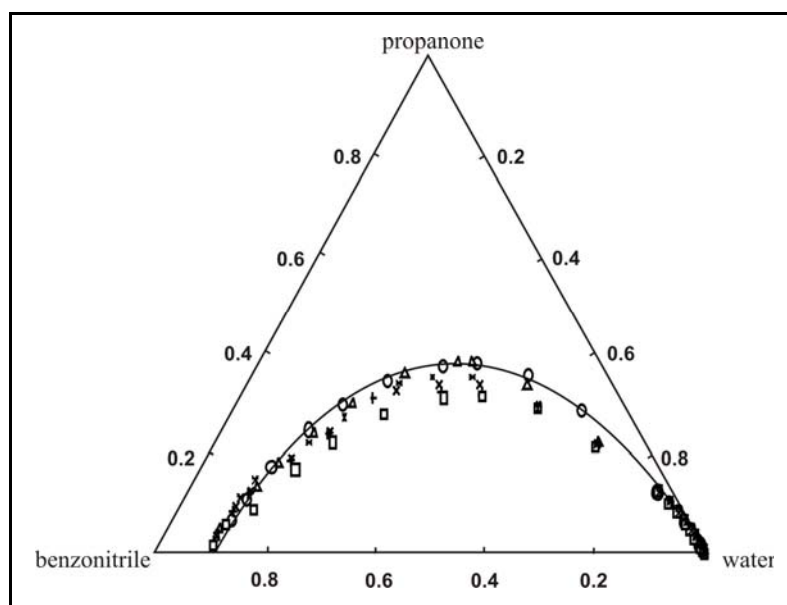
Figure 3: Experimental (o and solid curve) and calculated phase compositions for the {MTBE + 1-hexanol + water} system [7] at 288.15 K, employing the g_{ij} values that minimize the objective function of Eqn. (6) at the indicated temperature: □, 288.15 K; □, 298.15 K; ✕, 308.15 K

Figure 4: Experimental (o and solid curve) and calculated phase compositions for the {MPK + propanoic acid + water} system [8] at 298.15 K, employing the g_{ij} values that minimize the objective function of Eqn. (6) at the indicated temperature: □, 298.15 K; ✕, 308.15 K; △, 318.15 K; ◇, 328.15 K.

Figure 5: Experimental (o and solid curve) and calculated phase compositions for the {benzonitrile + propanone + water} system [9] at 318.15 K, employing the g_{ij} values that minimize the objective function of Eqn. (6) at the indicated temperature: □, 298.15 K; +, 303.15 K; ✕, 308.15 K; ✱, 313.15 K; △, 318.15 K.

By the other hand, and looking at Figures 1 – 5 it is clear that the shape of the curves is maintained when energy parameters obtained at temperatures different from the experimental one are employed and that larger quantitative differences are observed near the plait point zone but, nevertheless, the results are acceptable for prediction purposes.

The final conclusions are:

a) if data are available at a given temperature, T_1, for the liquid – liquid equilibrium of a ternary system, compositions at T_2 can be safely estimated employing the energy parameter set obtained from the experimental values.

b) if data are available at several temperatures and estimations are needed at a different thermal condition any of the energy parameter sets should be used rather than employing extrapolated or interpolated g_{ij} values.

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