MAPPING BINARY LIQUID-VAPOR OR LIQUID-LIQUID-VAPOR EQUILIBRIA REGIONS, INCLUDING THE DIFFERENT AZEOTROPIC BEHAVIOURS, AS A FUNCTION OF THE NRTL BINARY PARAMETERS

Juan A. Reyes-Labarta, María del Mar Olaya and Antonio Marcilla

Department of Chemical Engineering, University of Alicante, Apdo. 99, Alicante (Spain)

http://iq.ua.es/gcef.htm

Introduction

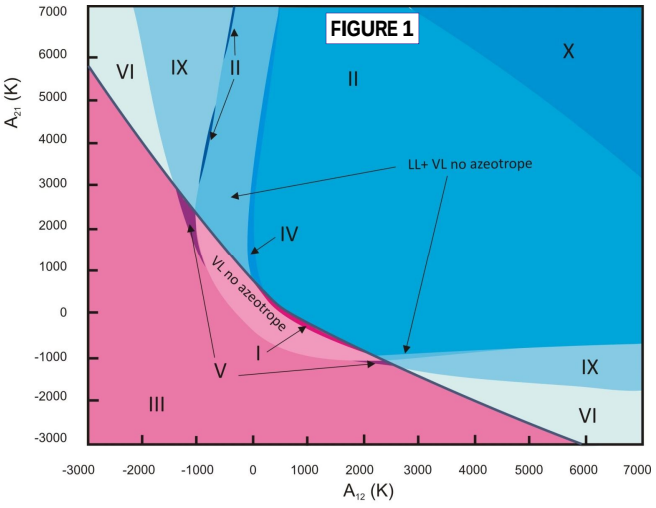
As it is very well known, the synthesis and design of separation processes requires the use of models to represent the phase equilibrium data, which involves the previous correlation of the experimental equilibrium data to obtain the values of the corresponding parameters. In previous works, we have studied the capabilities and limitations of the classical Gibbs energy of excess (G^E) models used in phase equilibrium data correlations, such as NRTL model, in representing the behaviour of different VL, LL and LLS equilibrium data [1-4]. In the present work, the relations between the binary parameters A_{ij} of the NRTL model and the existence of different equilibrium regions (i.e.: VL, LL or VLL), as well as the different possible azeotropic behaviours are analysed. The Gibbs energy of mixing (G^M) curve and the corresponding y-x and T-x,y diagrams along a matrix of A_{ij} parameters have been studied. The values for the A_{ij} parameters have been within the typical values obtained in experimental VLE and LLE data correlations.

Procedure

Results obtained obviously depend on the vapour pressure of the pure components, the total pressure as well as on the non-random parameter α in the NRTL model. In all the cases values of P=760 mmHg and α=0.2 have been used. Figure 1 shows as example the results obtained for a system where the boiling temperatures of the two pure components are around: 60 and 100 ºC. Different equilibrium regions can be observed showing the transition between different phase behaviours as a function of the interaction parameters values A_{ij} of the NRTL equation.

Therefore, depending on the Aij values, different equilibrium such as, LV without azeotropes, a homogeneous LV azeotrope (of minimum or maximum temperature), a heterogeneous azeotrope, 2 homogeneous azeotropes or even systems with two different LLE including 1 heterogeneous azeotrope, etc are obtained. The size and evolution of these regions depends on the boiling temperatures of the pure components studied. Regions with no azeotrope increase (decreasing the regions with homogeneous and heterogeneous azeotrope) with the difference of these temperatures. The knowledge of these types of behaviours would be of great interest in parameter optimization when correlating experimental equilibrium data to avoid typical convergence problems.

FIGURE 1



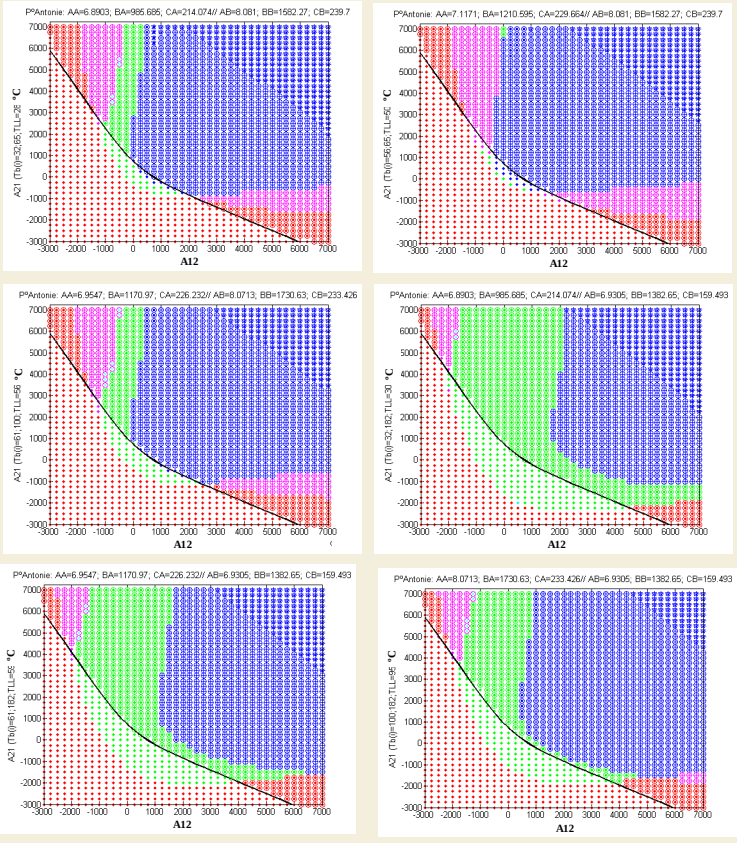
Legend:

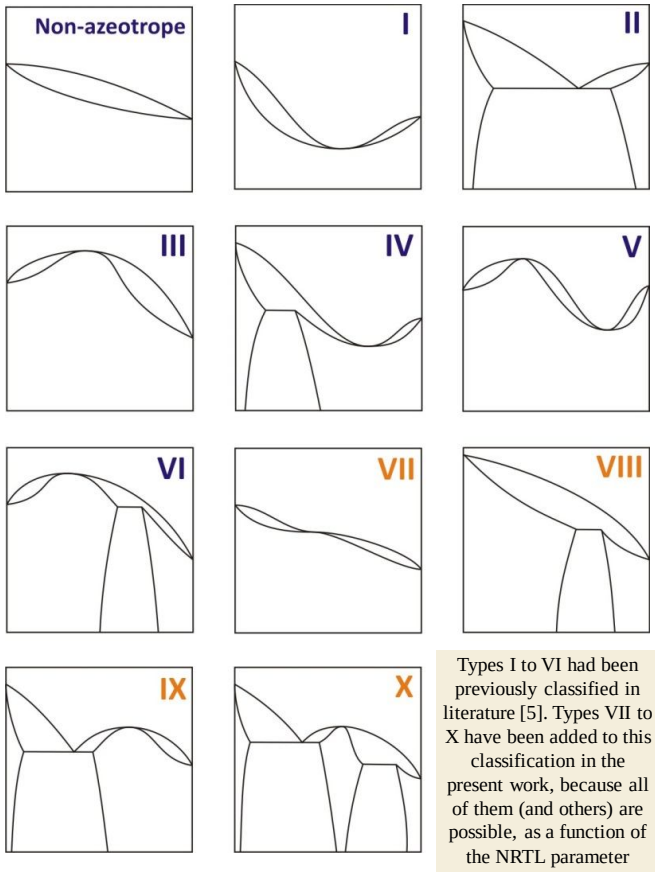
- LVE with 1 Tmax LV binary azeotrope
- LVE with 1 Tmin LV binary azeotrope
- LVE without binary azeotrope
- LVE with 2 binary azeotropes (Tmax and Tmin)
- LLE with 1LLV binary azeotrope (Tmin)
- 2 LLE and 1 LV binary azeotrope (Tmin)
- 2 LLE and 1 LLV binary azeotrope (Tmin)
- LLE and 1 Tmax LV binary azeotrope
- LLE and 1 Tmin LV binary azeotrope
- LLE and LVE without binary azeotrope
- LLE with 2 LV binary azeotropes (homogeneous)
- LLE with 1LV(Tmax) and 1LLV(Tmin) bin. azeot.
- LLE and 1 LLV(global) binary azeotrope (Tmin)
- Miscibility Boundary [Marcilla et al. 2010]

Numerical Examples

Figure 2 shows the results obtained for binary systems with different boiling temperatures of the pure components (from 32 to 182 ºC) at P=760 mmHg (indicated at the y axes) and the corresponding parameters of the Antoine's Equation for the vapour pressures are indicated in the title of each figure. It can be observed the different variety of behaviours that can be represented. These figures include the restrictions for the NRTL parameters values that correspond with total or partial miscibility in the liquid phase for each binary mixture (curve in black colour) [6].

FIGURE 2





Types I to VI had been previously classified in literature [5]. Types VII to X have been added to this classification in the present work, because all of them (and others) are possible, as a function of the NRTL parameter values.

Conclusions

The knowledge of the relations between the binary parameters Aij to reproduce different type of LL, LV or LLV equilibria can be very helpful in the correlation of experimental data in order to avoid false and incoherent solutions in the whole range of compositions and avoiding unnecessary iterations of non-consistent parameters.

References

[1] Marcilla, A; Olaya, M.M.; Serrano M.D.; Reyes-Labarta, J.A. Ind. Eng. Chem. Res. 2010, 49(20), 10100-10110.
[2] Marcilla, A.; Olaya, M.M.; Serrano, M.D.; Reyes-Labarta, J.A. Fluid Phase Equilib. 2010, 296(1), 15-24.
[3] Marcilla, A; Olaya, M.; Serrano M.D.; Velasco, R.; Reyes-Labarta, J.A. Fluid Phase Equilibria. 2009, 281, 87-95
[4] Reyes-Labarta, J.A; Olaya, M.; Velasco, R.; Serrano M.D.; Marcilla, A. Fluid Phase Equilibria. 2009, 278, 9-14.
[5] Gmehling, J.; Menke, J.; Krafczyk, J.; Fischer, Kai, Azeotropic Data. Ed. VHC, Germany, 1994.
[6] M.M. Olaya, A. Marcilla, M. D.Serrano , A. Botella, J.A. Reyes-Labarta, Ind. Eng. Chem. Res., vol.. 46 (21), pp. 7030-7037, 2007.