Explicit Equation to Calculate the Liquid-Vapour Equilibrium for Ternary Azeotropic and Non Azeotropic Systems

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In many cases, it is interesting to have the possibility of using explicit equation to calculate or reproduce the phase equilibrium compositions, particularly when dealing with optimization algorithms to simulate or design separation processes or their industrial equipment such as distillation and extraction columns, etc. [1-4].

In the present work, we present a new set of equations that can reproduce the VLE very accurately for azeotropic and non azeotropic ternary systems:

\[
\begin{align*}
YY_1 &= \frac{x_1}{a_1x_1 + b_1x_2 + c_1x_3} \\
YY_2 &= \frac{x_2}{a_2x_1 + b_2x_2 + c_2x_3} \\
YY_3 &= \frac{x_3}{a_3x_1 + b_3x_2 + c_3x_3} \\
y_1 &= \frac{YY_1}{YY_1 + YY_2 + YY_3} \\
y_2 &= \frac{YY_2}{YY_1 + YY_2 + YY_3} \\
y_3 &= \frac{YY_3}{YY_1 + YY_2 + YY_3}
\end{align*}
\]

where \(x_i\) and \(y_i\) are the composition of the conjugated liquid and vapour phases in equilibrium, and the subscript \(i\) refers to the different component of the mixture.

We can observe that these equations have 9 correlation parameters (\(a_i, b_i, c_i\)), which have to be positive. They can be used to reproduce the equilibrium of the followings systems yielding a very good results comparing with classical thermodynamic models as NRTL:

- 2-butanol + 2-butanone + water at 600 mmHg (33 points)
- 2-butanol + 2-propanol + water at 760 mmHg (17 points)
- acetone + 2-butanone + water at 760 mmHg (37 points)
- 2-propanol + diisopropylamine + water at 760 mmHg (26 points)
- 2-propanol + water + toluene at 760 mmHg (34 points)
- water + 1-propanol + 1-butanol at 762 mmHg (16 points)
- ethanol + water + chlorobenzene at 760 mmHg (25 points)
- dietilether + ethanol + water at 2156,30 mmHg (39 points)
- dichloromethane + 2-butanone + water at 750 mmHg (25 points)

In this point it is important to remark that the proposed equations avoid the iterations in the equilibrium calculation steps inside the complex algorithm of design and simulation of separation processes, or even in the calculation of the distillation boundaries of azeotropic ternary systems.

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References

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1. Proposed equations

A new set of explicit equations capable of reproducing the VLE very accurately for both azotropic and non azotropic ternary systems are

\[ y_i = \sum_{j=1}^{n} \frac{x_j}{y_j} \]

Where: \( x_j \) and \( y_j \) are the composition of the conjugates L and V phases i and j respectively.

For the calculation of the vapor composition \( y_i \) from the known composition of the liquid \( x_i \), \( i \) and \( j \) represent the 9 correlation parameters of eqs. (1), \( \alpha_i \geq 0 \), \( \beta_i \), \( \gamma_i \), \( \delta_i \), and \( \zeta_i \), where \( n \) is the number of experimental lines.

The suggested procedure allows calculating the vapor composition \( y_i \) from the known composition of the liquid \( x_i \) and can be used in azoetric and non-azoetric systems (Fig.1 and 2).

In order to validate the goodness of the proposed equations, the following 12 systems from the Data Collection of DECHEMA Data Series have been correlated and compared with the results obtained with the NRTL model:

1. Toluene + 2-hexanone + 2-butanone
2. Toluene + 2-pentanone + 2-butanone
3. Toluene + 2-pentanone + 2-hexanone
4. Toluene + 2-pentanone + 2-butanone
5. Toluene + 2-pentanone + 2-hexanone
6. Toluene + 2-pentanone + 2-butanone
7. Toluene + 2-pentanone + 2-hexanone
8. Toluene + 2-pentanone + 2-butanone
9. Toluene + 2-pentanone + 2-hexanone
10. Toluene + 2-pentanone + 2-butanone
11. Toluene + 2-pentanone + 2-hexanone
12. Toluene + 2-pentanone + 2-butanone

2. Results and discussion

Table 1 shows the parameters \( \alpha_i, \beta_i, \gamma_i, \delta_i, \) and \( \zeta_i \) (the 9 correlation parameters of eqs. 1 and 2) used to calculate the LVE \( y_i \) and \( T_i \). The table also shows the \( \alpha_i, \beta_i, \gamma_i, \delta_i, \) and \( \zeta_i \) obtained with the suggested equations in comparison with NRTL. \( N \) is the number of experimental lines.

Results obtained show that the proposed equations yield good results compared with NRTL. Figure 3 illustrates the capability of the proposed equations for systems 1 and 3.

3. Conclusions

It can be concluded from the results obtained that the proposed equations yield very good results compared with the commonly used thermodynamic models such as NRTL, showing similar deviations. What is more important, the proposed equations are explicit and thus avoid the iterations in the equilibrium calculations. Consequently, they may greatly simplify the algorithms of design and simulation of separation processes and the calculation of the distillation boundaries of azotropes.

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References: