

Improvement of Accuracy of the Multicomponent Vapor–Liquid Equilibria Prediction for the Purpose of Separation Process Modelling

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A method for the prediction of vapor–liquid equilibrium data of multicomponent systems utilizing binary and ternary vapor–liquid information is presented. The dependences of the activity coefficients on the liquid mixture composition are expressed by the excess molar Gibbs energy equation (G^E equation: NRTL, UNIQUAC, Wilson, Redlich – Kister) extended by the universal ternary contribution including the influence of ternary interactions of molecules of the multicomponent mixture. Binary parameters of the G^E equations are original, obtained independently from the binary equilibrium data of the corresponding binary subsystems; parameters of the universal ternary contribution were evaluated from the ternary VLE data. The advantage of this method is the possibility to relatively accurately predict VLE of multi-component systems using only the original binary and the corresponding ternary parameters without the knowledge on the multi-component equilibrium.

It was prepared a new electronic database of the ternary contribution parameters. The database consists of the sets of ternary parameters of G^E equations, such as NRTL, UNIQUAC, Wilson and Redlich – Kister, evaluated for approximately 100 ternary VLE systems of different chemical character. Original binary parameters of G^E equations, experimental VLE data of the ternary systems and binary subsystems were taken from the VLE Data Collection DECHEMA. The aim of this database is to provide access to ternary parameters and to improve the prediction of multi-component vapor–liquid, liquid–liquid and vapor–liquid–liquid equilibria essential for the separation equipment design.

1. Introduction

Design of industrial separation equipment and estimation of optimum operation conditions of such equipment requires a lot of information about the nature of systems to be separated. Quality of the design calculations is especially sensitive to the reliability of thermodynamic data describing the separated mixture equilibrium.

Selection of correct experimental data and their thermodynamic processing, i.e. their representation in the form of equations describing the variation of excess Gibbs energy or activity coefficients with the mixture composition ($G^E = f(x)$; $\gamma_i = f(x)$), seems to be crucial for the description of multiphase multi-component equilibria. Numerous authors were engaged in thermodynamic processing of equilibrium data. In the literature either monographic collections (Wichterle et al., 1993) or databases (Gmehling et al., 1979-2000;

Hirata et al., 1977; Hála et al., 1968) could be found containing vapor-liquid and liquid-liquid equilibrium data of mostly binary systems together with “simplified” thermodynamic description in the form of commonly used classical (Van Laar, Margules, etc) and non-classical (NRTL, Wilson, UNIQUAC, etc.) G^E equations (Novák et al., 1987). Databases provide binary parameters of the above-mentioned equations, which could be employed in the prediction of multi-component multiphase equilibria during the modelling of separation processes and equipment with simulation engines (e.g. HYSYS and ASPEN+ software employing the DECHEMA database). The principal question is the quality of prediction of multi-component multiphase equilibria based solely on binary equilibrium data and what influence on the quality of distillation column design has the inaccuracy of equilibrium prediction. By reviewing the studies concerned with the description of multi-component equilibria, it could be found that the quantitative agreement between experimental and predicted multi-component equilibria is only lightly probable, if the prediction is based on the excess Gibbs energy expressions employing parameters obtained from the binary equilibrium data only. In order to improve the prediction quality, also ternary equilibrium information should be included. One of the possible ways is the introduction of ternary terms into the original G^E models. Interesting and simple is the approach of our former colleagues Surovy et al. (1982) who introduced the so called universal ternary contribution.

2. Theory

The authors (Surovy et al., 1982) supposed that the difference between the measured value of excess Gibbs energy in a ternary mixture, G^E , and the value calculated on basis of binary equilibrium data, G_b^E , is caused by the ternary intermolecular interactions. This difference could be expressed in form of McLaurin expansion

$$\Delta_l G^E / RT = (G^E / RT) - (G_b^E / RT) = x_1 x_2 x_3 (E_1 x_1 + E_2 x_2 + E_3 x_3). \quad (1)$$

Ternary contribution to the activity coefficient of the component 1, $\Delta_l \ln \gamma_1$, is expressed by the relation (1) as follows

$$\Delta_l \ln \gamma_1 = x_2 x_3 [E_1 x_1 (2 - 3x_1) + E_2 x_2 (1 - 3x_1) + E_3 x_3 (1 - 3x_1)]. \quad (2)$$

This expression comprises three ternary parameters, E_i , and it could be used together with any of the G^E equations (such as NRTL, UNIQUAC, Wilson, Redlich - Kister). Therefore, the expanded G^E models include binary parameters evaluated from independent binary equilibrium data and the ternary contribution parameters, which are obtained from the ternary information.

The ternary contribution has been successfully extended also for quaternary liquid-liquid equilibrium system (Graczova et al., 1992). It was supposed that the value of excess Gibbs energy in a quaternary mixture is liquid given by the sum of the value calculated using the corresponding binary parameters, G_b^E , and the ternary contribution $\Delta_l G^E$. Taking into account, that the probability of intermolecular interactions with the number of molecules involved decreases exponentially, quaternary interactions were omitted. Ternary contribution to the excess Gibbs energy of a four-component system was obtained by summing up the ternary contributions of corresponding four ternary subsystems of the original system

$$\begin{aligned}
\Delta_l G^E / RT = & x_1 x_2 x_3 (E_{14} x_1 + E_{24} x_2 + E_{34} x_3) + \\
& + x_1 x_2 x_4 (E_{13} x_1 + E_{23} x_2 + E_{43} x_4) + \\
& + x_1 x_3 x_4 (E_{12} x_1 + E_{32} x_3 + E_{42} x_4) + \\
& + x_2 x_3 x_4 (E_{21} x_2 + E_{31} x_3 + E_{41} x_4)
\end{aligned} \quad (3)$$

and the ternary contribution to the component 1 activity coefficient of a quaternary system, $(\Delta_l \ln \gamma_1)_q$, could be expressed in the following form

$$\begin{aligned}
(\Delta_l \ln \gamma_1)_q = & x_2 x_3 [E_{14} x_1 (2 - 3x_1) + E_{24} x_2 (1 - 3x_1) + E_{34} x_3 (1 - 3x_1)] + \\
& + x_3 x_4 [E_{12} x_1 (2 - 3x_1) + E_{32} x_3 (1 - 3x_1) + E_{42} x_4 (1 - 3x_1)] + \\
& + x_2 x_4 [E_{13} x_1 (2 - 3x_1) + E_{23} x_2 (1 - 3x_1) + E_{43} x_4 (1 - 3x_1)] - \\
& - 3x_2 x_3 x_4 (E_{21} x_2 + E_{31} x_3 + E_{41} x_4).
\end{aligned} \quad (4)$$

The activity coefficient of component 1 in a four-component mixture, γ_1 , is given as a sum of the activity coefficient calculated by the original G^E equation employing binary parameters, γ_{1b} , and the ternary contribution $(\Delta_l \ln \gamma_1)_q$

$$\ln \gamma_1 = \ln \gamma_{1b} + (\Delta_l \ln \gamma_1)_q. \quad (5)$$

An analogous procedure is used to calculate activity coefficients of components of five- and multicomponent systems.

Advantage of this strategy is a low CPU demand, possibility to employ the original binary G^E model parameters and parameters of the ternary contribution also for other multicomponent systems comprising the corresponding binary and ternary subsystems.

This assumption was verified employing four four-component liquid-liquid extraction systems of the type aliphatic hydrocarbon – aromatic hydrocarbon – mixed solvent (Graciová and Surový, 1992; Graciová et al., 2002a,b, 2008a). Therefore, refining of the description of vapor-liquid as well as vapor-liquid-liquid multi-component equilibria using the ternary contribution seems to be very interesting also from the viewpoint of distillation modelling (classical, azeotropic, extractive, and also reactive). Refining of the multi-component equilibrium description could influence also distillation columns design, which is one of the goals of this research project.

3. Evaluation of ternary contribution parameters

Parameters of the universal ternary contribution, E_i , were evaluated from the ternary VLE data via minimization of the objective function, F , by the simplex method. For the sets of ternary P - x , y data the following form of objective function was used

$$F = \sum_i \sum_n (y_i - y_{\text{calc},i})^2 + \sum_n \left(\frac{P - P_{\text{calc}}}{P} \right)^2 \quad n = 1, 2, \dots, N; \quad i = 1, 2, 3. \quad (6)$$

P and P_{calc} are experimental and calculated total pressures; y_i and $y_{\text{calc},i}$ are experimental and calculated mole fractions of the i -th component in the vapor phase. Assuming ideal behavior

of vapor and real behavior of liquid phases the total pressure P_{calc} and mole fraction $y_{\text{calc},i}$ were calculated using the relations

$$P_{\text{calc}} = x_1\gamma_1P_1^\circ + x_2\gamma_2P_2^\circ + x_3\gamma_3P_3^\circ \quad (7)$$

$$y_{\text{calc},i} = \frac{x_i\gamma_iP_i^\circ}{P_{\text{calc}}} \quad i = 1, 2, 3 \quad (8)$$

γ_i being the activity coefficient and P_i° saturated vapor pressure of the component i .

4. Results and discussion

In this study, for thermodynamic description of the multicomponent VLE data, the G^E equations extended by the universal ternary contribution were chosen. This procedure was applied to about 100 ternary and tree quaternary VLE systems. Original NRTL, UNIQUAC, Wilson equation parameters for the corresponding binary subsystems were chosen from the VLE Data Collection DECHEMA (Gmehling et al., 1979-2000). The binary parameters of the Redlich – Kister equation were evaluated independently from isothermal P - x,y (resp. P - x , x - y) binary data; the sets of ternary contribution parameters of G^E equations were evaluated from the ternary VLE data, taken from the same source.

Visualisation of results (in the form of 2D and 3D diagrams) was done by an original program made in Matlab. Ternary parameters evaluated from the ternary equilibrium data are summarised in an **electronic database** in the form of a spreadsheet containing parameters of pure components, binary and ternary parameters of G^E equations, residues of mole fractions and pressures, as well as 2D and 3D diagrams of these ternary systems. The electronic database and its MENU will be presented in our conference contribution. For illustration, we took one ternary system out of the 100 ternaries, included in the database, system acetone(1) – ethanol(2) – hexane(3), $t = 55$ °C (Figure 1).

Results of the ternary VLE correlations using original binary parameters and parameters of ternary contribution of all G^E equations show (Gracová et al., 2006, 2007, 2008c, 2008d) that the use of universal ternary contribution improves significantly the thermodynamic description of the ternary vapor–liquid equilibria even using the original binary parameters. Mean deviation of the total pressure decreased on average by about 3 times for the all chosen ternary systems. Less important effect was observed when comparing the mean deviation of the component mole fractions (approximately 1.4 times lower mean deviation for the whole data set). The correlation results are even better than the direct fitting of the ternary VLE data for about 2/3 of all chosen ternary systems. This method allows correctly describing VLE of the ternary systems even if the amount of experimental equilibrium points is insufficient or just incomplete VLE data (e.g. P - x , only) are available.

A method for the prediction of isothermal vapor - liquid equilibrium data of VLE quaternary systems utilizing binary and ternary vapor – liquid information only has been successfully used (Gracová et al., 2005, 2008b, 2008e). The method was applied to predict VLE of the three isothermal quaternary systems: hexane(1) – benzene(2) – cyclohexane(3) – N-methylpyrrolidone(4), $t = 69.7$ °C; ethanol(1) – chloroform(2) – acetone(3) – hexane(4), $t = 55$ °C and 2-butanone(1) – croton aldehyde(2) – toluene(3) – 2-ethoxyethanol(4), $t = 57$ °C. For illustration, the results of the quaternary VLE prediction are shown for the second

quaternary system ethanol(1) – chloroform(2) – acetone(3) – hexane(4), $t = 55\text{ }^{\circ}\text{C}$ in Figure 2, in the form of comparative 2D P - x,y plots.

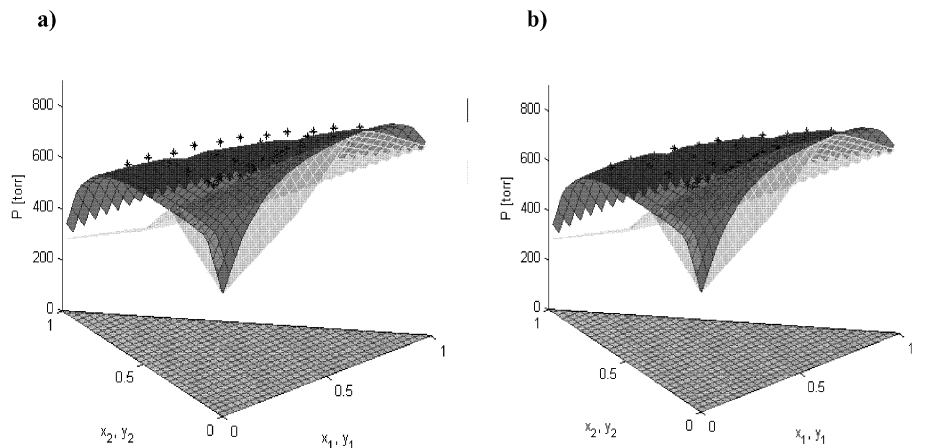


Figure 1 Comparative 3D diagrams, isothermal P - x,y diagrams of the ternary system acetone(1) – ethanol(2) – hexane(3), $t = 55\text{ }^{\circ}\text{C}$; a) predicted from the binary equilibrium data, b) correlated by the NRTL equation extended with the ternary contribution parameters. + experimental data; \blacksquare $P_{cal} = f(x)$ and \square $P_{cal} = f(y_{cal})$ calculated data.

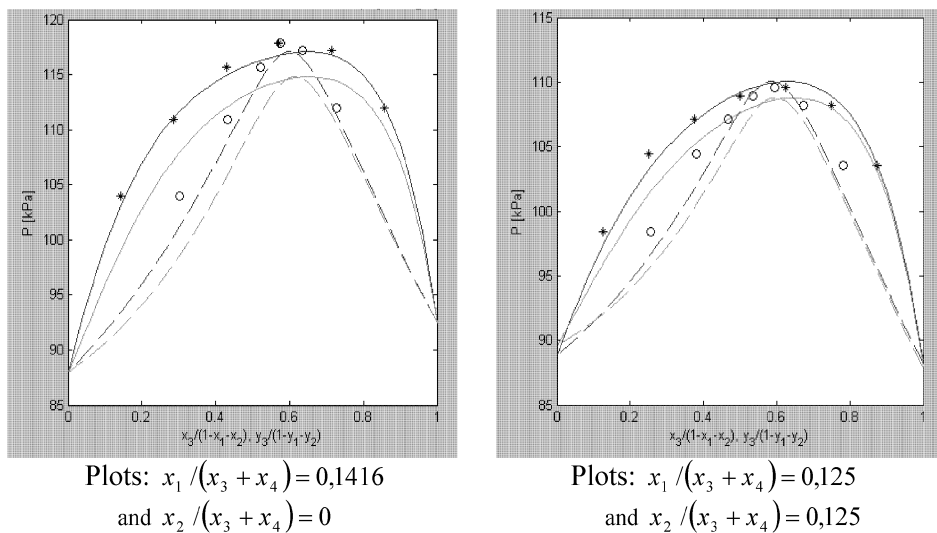


Figure 2 Comparative 2D P - x,y plots for the quaternary VLE system of ethanol(1) – chloroform(2) – acetone(3) – hexane(4), $t = 55\text{ }^{\circ}$. +, o experimental points; green lines – VLE data prediction with original binary parameters of the NRTL equation, blue lines – prediction of VLE data with binary and ternary NRTL parameters.

5. Conclusion

A simple procedure for the thermodynamic description of multi-component multiphase equilibria based on binary and ternary equilibrium data and its use for the purpose of distillation columns modeling is presented. Open electronic database of the contribution parameters was prepared to provide access to the ternary parameters aimed to improve the prediction of multi-component vapor–liquid, liquid–liquid and vapor–liquid–liquid equilibria essential for the separation equipment design. The database is being continuously supplemented by the parameters for further ternary systems and it will be available at the web page of our institution. The use of ternary contribution parameters was illustrated on the prediction of vapor–liquid equilibrium of quaternary systems.

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