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Using the NRTL model with the Vidal equation of state EOS-q^E formulation for vapor/liquid equilibrium calculations

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ABSTRACT

In this work Vidal equation of state formulation (EOS-q^E) was evaluated for vapor/liquid equilibria (VLE) isothermal calculations of binary and ternary mixtures, using NRTL model with 2 and 3 parameters for q^E representation in the low to high pressure range, resulting at least as convenient and accurate in application as the gamma/phi formulation and Redlich–Kister expansion; and better than using Huron/Vidal and Wong/Sandler mixing rules EOS-G^E formulation. Compared with referenced models, satisfactory predictions of VLE at temperatures different than that, at what correlation was obtained. Finally, isobaric VLE was correlated in the experimental error precision range.

1. Introduction

VLE data is fundamental for separation process design, operation, evaluation and optimization. Obtaining VLE data using EOS with PHI–PHI scheme has been object of plenty of research work, which has been reviewed by many authors like Valderrama, J.O. [1]. A big portion of this research has been related with the composition dependence of the EOS parameters, for which no general theory is known. Previously, Urdaneta, M.R., et al. [2] evaluated successfully the EOS-q^E Vidal, J. [3] modeling scheme using the Redlich, O., et al. [4] expansion with 4-parameters (4PRK) and Wilson model for q^E representation, for VLE isothermal calculations of binary and ternary mixtures in the low to high pressure range and isobaric VLE correlation. Following the same research strategy and mathematical basement described in our previous article [2] in this work was evaluated NRTL model [5] with 2 and 3 parameters (2PNRTL and 3PNRTL) for q^E representation of EOS-q^E formulation, with results at least as convenient and accurate in application as the gamma/phi formulation and better than using Huron/Vidal (HV) [6] and Wong/Sandler (WS) [7] mixing rules EOS-G^E formulation.

2. The Vidal EOS-q^E formulation using the NRTL model

The following Eq. (1) gives the NRTL expression for q^E in phase Pi:

$$(q^E)^{=\pi} z_1 z_2 \left(\frac{\tau_{12} G_{12}}{z_2 + z_1 G_{12}} + \frac{\tau_{21} G_{21}}{z_1 + z_2 G_{21}} \right) \quad (1)$$

where, $z_i = x_i$ or y_i; $\tau_{12} = \Delta g_{12}/RT$; $\tau_{21} = \Delta g_{12}/RT$; $G_{12} = \exp(-\alpha_{12}\tau_{12})$; $G_{21} = \exp(-\alpha_{21}\tau_{21})$ Using the generalized phase superscript π (= v or l), q^π becomes:

$$q^\pi = z_1 z_2 \left(\frac{\tau_{12} G_{12}}{z_2 + z_1 G_{12}} + \frac{\tau_{21} G_{21}}{z_1 + z_2 G_{21}} \right) + z_1 q_1 + z_2 q_2 \quad (2)$$

$$A^\pi = \frac{(q^E)^\pi}{z_1 z_2} = \left(\frac{\tau_{12} G_{12}}{z_2 + z_1 G_{12}} + \frac{\tau_{21} G_{21}}{z_1 + z_2 G_{21}} \right) \quad (3)$$

Here, any other solution model may be used for $(q^E)^\pi$, as 4-parameter Redlich–Kister expansion used by Urdaneta et al. [2] resulting their expression: $A^\pi = A_0 + A_1(z_1 - z_2) + A_2(z_1 - z_2)^2 + A_3(z_1 - z_2)^3$.

Also,

$$\beta^\pi = \frac{(z_1 b_1 + z_2 b_2)P}{RT} \quad (4)$$

Eq. (5) may now be solved for Z^l and Z^v. The partial excess parameters $(\bar{q}_i^E)^\pi$ of Eq. (6) and (7) are given by Van Ness and Abbott [8]:

$$Z^{\pi^3} + u_1 Z^{\pi^2} + u_2 Z^\pi + u_3 = 0 \quad (5)$$

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b	parameter in cubic equation of state
nC6	n-hexane
q	equation-of-state parameter
q_i	equation-of-state parameter for pure species i
$\bar{q}_i$	partial equation-of-state parameter parameter
q^{E}	excess equation-of-state parameter. $q^{\pi} = (q^{E})^{\pi} + \sum_i x_i q_i$;
$\bar{q}_i^{E}$	partial excess equation-of-state parameter; Eqs. (6) and (7)
u_1, u_2, u_3	composite parameters for Peng/Robinson equation; Eq. (5)
x_i	mole fraction of species i in liquid phase
y_i	mole fraction of species i in vapor phase
z_i	generic mole fraction = x_i or y_i
3PNRTL, 2PNRTL	3-parameter and 2-parameter NRTL equations, respectively
4PRK, 3PRK, 2PRK	4-parameter, 3-parameter and 2-parameter Redlich/Kister equations, respectively
A_0, A_1, A_2, A_3	parameters in the Redlich/Kister equation
CO_2	carbon-dioxide
DEK	diethyl-ketone
G^{E}	excess Gibbs energy
MTBE	Methyl *tert*-butyl ether
P	absolute pressure
P_i^{sat}	saturation vapor pressure of species i
R	universal gas constant
T	absolute temperature
Δg_{ij}	temperature independent constants of τ_{ij} parameters of NRTL local solution model
Z	compressibility factor [$Z = PV/(RT)$]
$\hat{f}_i$	fugacity of species i in solution

Greek letters

α	(or α_{12}), τ_{12}, τ_{21} parameters in NRTL equation
β	equation-of-state parameter
γ_i	activity coefficient of species i in solution
δ	defines a difference between a calculated and experimental property
$\hat{\phi}_i$	fugacity coefficient for species i in solution
π	phase superscript meaning vapor ($\pi = v$) or liquid ($\pi = l$)

Subscripts

i, j	identify a species

where:

$$u_1 = \beta^{\pi} - 1 \quad u_2 = (q^{\pi} - 3\beta^{\pi} - 2)\beta^{\pi} \quad u_3 = (1 + \beta^{\pi} - q^{\pi})\beta^{\pi 2}$$

As in our previous work [2], in this one it is used the Peng-Robinson EOS [9] improved by Stryjek and Vera [10]:

$$(\bar{q}_1^{E})^{\pi} = z_2^2 \left[\tau_{21} \left(\frac{G_{21}}{z_1 + z_2 G_{21}} \right)^2 + \frac{\tau_{12} G_{12}}{(z_2 + z_1 G_{12})^2} \right] \tag{6}$$

$$(\bar{q}_2^{E})^{\pi} = z_1^2 \left[\tau_{12} \left(\frac{G_{12}}{z_2 + z_1 G_{12}} \right)^2 + \frac{\tau_{21} G_{21}}{(z_1 + z_2 G_{21})^2} \right] \tag{7}$$

The Eq. (8) yields the partial parameters $\bar{q}_i^{\pi}$:

$$\bar{q}_i^{\pi} = (\bar{q}_i^{E})^{\pi} + q_i \tag{8}$$

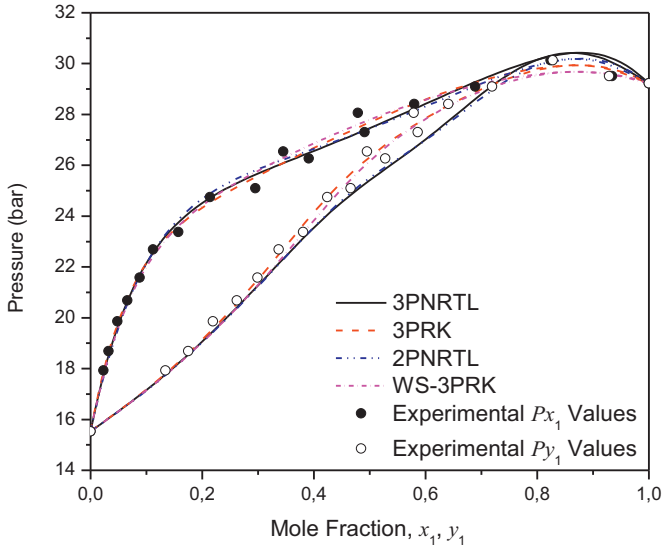

Fig. 1. Experimental values [30] and correlated *Pxy* curves for ethanol(1)/H_2O(2) at 200 °C using PRSV EOS with q^{E} given by 3PRK, 3P and 2PNRTL, and WS-3PRK models with parameters fitted to *Px* data.

Fugacity coefficients $\hat{\phi}_i^{l}$ *and* $\hat{\phi}_i^{v}$, can now be calculated from Eq. (9):

$$\ln \hat{\phi}_i^{\pi} = \frac{b_i}{b^{\pi}}(Z^{\pi} - 1) - \ln(Z^{\pi} - \beta^{\pi}) - \bar{q}_i^{\pi} I^{\pi} \tag{9}$$

where, $I^{\pi} = 1/\sigma - \epsilon \ln\left(z^{\pi} + \sigma\beta^{\pi}/z^{\pi} + \epsilon\beta^{\pi}\right)$ and for PR EOS used in this work, $\epsilon = 1 - \sqrt{2}$ and $\sigma = 1 + \sqrt{2}$. Eq. (9) leads through Eq. (10) to values of P and vapor-phase mole fractions:

$$x_i \hat{\phi}_i^{l} = y_i \hat{\phi}_i^{v} (i = 1, 2, \ldots, N) \tag{10}$$

Eq. (10) comes from VLE fundamental condition, $\hat{f}_i^{l} = \hat{f}_i^{v}$ and $\hat{f}_i^{\pi} = x_i \hat{\phi}_i^{\pi} P$

3. Correlation of data of binary systems

In the present work was used the same iterative algorithm outlined in Fig. 1 of our previous work [2] of VLE formulations for BUBL P calculations, but adapted for 2 and 3 parameters NRTL model. The initial guess values required for P and vapor composition may be experimental. Alternatively, P may usually be taken as the x_i-weighted sum of the pure-species vapor pressures, with y_1 from Raoult's law assumption.

Parameters for NRTL correlating equation for $(q^{E})^{l}$ were found by a fitting procedure based on P–x_1 data to minimize the sum of squares of the pressure residuals, i.e., the differences between experimental and calculated values of P. This is in direct analogy to Barker's method [11] for the evaluation of parameters in expressions for G^{E}. This procedure was applied with the 2PNRTL and 3PNRTL models, to fit 34 binary P–x_1 data sets at 50 °C [12–20] for first 19 data sets (Group A) evaluated in our previous work [2] and 15 additional data sets (Group B) in the 45–85 °C range [11,22–30] evaluated in this work.

Results for the PR EOS pure and binary 4PRK parameters are shown in Tables 1 and 2 for Group B data set. Table 1 presents experimental vapor pressures, q_i values, and b_i values.

Table 2 gives values of the 4PRK parameters for the calculation of $(q^{E})^{l}$, obtained by regression of the P–x_1 of Group B data sets (4PRK parameters of Group A data appear in our previous work [2]) Also