The NRTL-PRA group contribution EoS for the simultaneous prediction of LLE, VLE and $h^E$ of hydrocarbon mixtures with associating compounds

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The goal of this study is to propose a modification of the NRTL-PR EoS for the prediction of phase equilibria and excess enthalpies in mixtures containing methanol with hydrocarbons; indeed, with these systems, the original equation is confronted to many difficulties arising from the simultaneous prediction of liquid-liquid equilibria together with vapor-liquid and enthalpy data. For this purpose, an additional term is included in the EoS excess Gibbs energy, $g_E$, of the Peng-Robinson equation to account for the self-association of methanol. The resulting NRTL-PRA EoS is successfully used for the prediction of both liquid-liquid and vapor-liquid equilibria, as well as excess enthalpies, in mixtures of methanol with hydrocarbons, light gases and associating compounds. Results are comparable to those obtained with other predictive EoS (VTPR and SAFT), but with the main advantage to predict all thermodynamic properties with a simple cubic equation.

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1. Introduction

Formation of gas hydrates is a major problem in offshore petroleum exploitations since it can lead to pipeline obstructions with heavy consequences; this problem is commonly prevented by injecting an inhibitor, mostly methanol. Therefore an accurate prediction of phase equilibria in mixtures containing methanol with hydrocarbons is of great interest for petroleum industry. The major difficulty arises from the simultaneous representation of liquid-liquid (LLE) data together with vapor-liquid equilibria (VLE) and excess enthalpies ($h^E$). Up to now, two approaches were considered by chemical engineers to solve this problem: first, the predictive cubic VTPR EoS [1], even if it is known to provide “not very satisfactory” liquid-liquid predictions; second, the CPA [2] and SAFT type equations (PC-SAFT [2–5], GC-PC-SAFT [6], SAFT-γ Mie [7], GCA [8]), even if none of these models gives information about the representation of excess enthalpies $h^E$ and if few of them (GC-PC-SAFT, SAFT-γ Mie and GCA EoS) are totally predictive.

The present work is based on the NRTL-PR EoS [9,10] previously developed in the “EoS/$g^E$” formalism [11] by using the generalized NRTL Gibbs energy [12] for the EoS excess Gibbs energy, $g_E$, coupled with the Peng-Robinson equation of state [13]. The NRTL-PR EoS is both: quite simple, since it remains a cubic EoS, and totally predictive, thanks to interaction energy parameters estimated through group contributions. As was shown in Refs. [9] and [10], it provides very good results for VLE and $h^E$ of hydrocarbon mixtures, but also for VLE and LLE of systems including associating compounds, namely water or ethylene glycol, with hydrocarbons.

However, for water-hydrocarbon or ethylene glycol-hydrocarbon mixtures, the main success of the NRTL-PR modeling, using only asymmetrical group interaction parameters between components $K$ and $L$ ($\Gamma_{KL} \neq \Gamma_{LK}$), is due to the fact that experimental data concern only one kind of phase equilibria (VLE or LLE). This statement is illustrated in Fig. 1 which represents, for the methanol-hexane system, the variation of the EoS excess Gibbs energy with respect to temperature; as for most of binary methanol-paraffin mixtures, the LLE and VLE diagrams are rather symmetric, so that Fig. 1 only reports the evolution of $g_E^{\text{EoS}}/RT$ for equimolar mixtures ($x_1 = 0.5$). For this type of mixtures, it is also well known that demixings observed in the LLE domain satisfy the following condition: $g_E^{\text{EoS}}(x_1 = 0.5)/RT > 0.5$; Fig. 1a, which represents the variation of this function with parameters determined from LLE data only, shows that, in this domain, namely for $T < 308 \text{K}$...
for methanol-hexane, \( g_{E_{\text{EOS}}}^{E}/RT \) is actually greater than 0.5; however, this modeling predicts, in the VLE domain, a “too fast decrease” of the excess function compared to the evolution expected in Fig. 1b, when parameters are determined from VLE data only.

As suggested by the above analysis, the modeling of methanol-hydrocarbon systems which requires the simultaneous representation of LLE and VLE should be more complex. For this purpose, a modification of the NRTL-PR equation is proposed in the present paper. The new EoS, named NRTL-PRA (NRTL-PR with Association) includes an additional term in the EoS excess Gibbs energy of the Peng-Robinson equation to account for the self-association of methanol; the generalized NRTL model being especially adapted to the prediction of liquid phase equilibria (as indicated by its name « Non Random Two Liquids »), the purpose of this additional term is mainly the improvement of predicted VLE and excess enthalpies \( h_{E} \). Thus, always for the system methanol-hexane, the new equation is applied to the prediction of phase equilibria and excess enthalpies of mixtures containing methanol with paraffins, cycloalkanes, aromatics, permanent gases, water and ethylene glycol. It is first compared with the original NRTL-PR EoS, in order to validate the behavior of both equations previously described in Fig. 1 for the methanol-hexane system. The NRTL-PRA group contribution EoS is then applied to the prediction of phase equilibria and excess enthalpies of mixtures containing methanol with paraffins, cycloalkanes, aromatics, permanent gases, water and ethylene glycol. We show that results obtained with the proposed EoS are comparable to those provided by the two other literature predictive EoS, but with the main advantage to predict all thermodynamic properties with a simple cubic equation.

**2. The NRTL-PRA EoS**

The equation is based on the Peng-Robinson equation of state [13]:

\[
P = \frac{RT}{\nu - b} - \frac{a}{\nu^2 + 2bv - b^2}
\]

in which the covolume \( b \) is calculated by \( b = \sum x_i b_i \) and the attractive term \( a \) is estimated in the EoS/g^E formalism using the generalized reference state [14]:

\[
\alpha = \frac{a}{bRT} = \sum_i x_i \frac{a_i b_i}{b_i RT} - \frac{1}{0.53} \left[ \frac{g_{\text{EOS}}^{E}}{RT} \right]
\]

with:

\[
g_{\text{EOS}}^{E} = g^{E} - RT \sum_i x_i \ln \frac{r_i}{r}
\]

where, \( r_i \) is the volume area factor.

In Eq. (3), the excess Gibbs energy \( g^{E} \) is expressed with the generalized NRTL model [12] modified, by means of the term \( g_{\text{EOS}}^{E} \), to take account of the self-association of methanol.

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