Calculation of NARM's Equilibrium with Peng-Robinson Equation of State

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The liquid molar volumes of nonazeotropic refrigerant mixtures (NARM), calculated with Peng Robinson (PR) equation, were compared with vapor–liquid equilibrium experimental data in this paper. Provided with co-reaction coefficient $k_i$, the discrepancies of liquid molar volume data for R22+R114 and R22+R142b using PR equation are 7.7% and 8.1%, respectively. When HBT (Hankinson-Brobst-Thomson) equation was joined with PR equation, the deviations are reduced to less than 1.5% for both R22+R114 and R22+R142b.

Keywords: equation of state, vapor-liquid equilibrium, nonazetropic refrigerant mixtures.

Introduction

There are mainly two well-known methods for the calculation of fluid phase equilibrium, the method of using equation of state (EOS) or activity coefficient. The later needs a plenty of vapor-liquid equilibrium experimental data in order to regress the calculating model’s parameters (such as non-random two liquid equation, (NRTL) etc). All means to describe thermodynamic properties are theoretically founded with the equation of state. If the EOS is suitable for the entire thermodynamic surface, all properties can be calculated by EOS. According to phase law, there are only two independent variables for binary systems.

When vapor and liquid are in equilibrium:

$$
\hat{f}_i^L = \hat{f}_i^V \\
\phi_i^L x_i P = \phi_i^V y_i P
$$

If there is a EOS which is suitable for both gas and liquid, the integral from $V_L$ (liquid phase) to $V_v$ (gas phase) can be performed, i.e., the fluid phase equilibrium can be calculated with equation (1) to (3) and EOS. The solution logic can be found in reference [1]. The PR equation of state is used widely because of its trustiness and simplicity.

PR equation is written as:

$$
P = \frac{RT}{v-b} \left( \frac{\partial P}{\partial n_i} \right)_{T,V,x_i(0)} dV - RT \ln Z
$$

$$
a(T) = a(T_c) \alpha(T, \Theta)
$$

$$
b(T) = b(T_c)
$$

$$
a(T_c) = 0.45724 R^2 T_c^2 / P_c
$$

$$
b(T_c) = 0.07780RT_c / P_c
$$

$$
\alpha^{0.5} = 1 + k(1 - T_r^{0.5})
$$

$$
k = 0.37464 + 1.54226\Theta - 0.26992\Theta^2
$$

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For mixtures, the mixing rule is written as:

\[
\begin{align*}
    a &= \sum \sum x_i x_j a_{ij} \\
    b &= \sum x_i b_i \\
    a_{ij} &= (1 - k_{ij}) \sqrt{a_j a_i}
\end{align*}
\]

The computing accuracy of the PR equation is satisfactory for gas phase, but not the same for liquid (especially for liquid molar volume) even though co-reaction coefficient \(k_{ij}\) are correlated from experimental data. The VLE experimental data and \(k_{ij}\) (R22+R114, R22+R142b) can be found in reference [2]. Comparing calculated liquid molar volumes with experimental values, the results are shown in Fig.1 and Fig.2. It can be seen that there are large discrepancies in molar volume calculation. This paper is to provide a method for molar volume calculation, which can reduce the error.

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\text{Fig. 1 Calculated and experimental[2] liquid molar volumes for R22+R114 system, } T=298.1K; \quad T=323.0K; \quad T=348.3K; \quad T=372.5K
\]

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\text{Fig. 2 Calculated and experimental[2] liquid molar volumes for R22+R42b system, } T=298.2K; \quad T=322.8K; \quad T=348.3K; \quad T=372.5K
\]

**Improvement Aiming at PVTx experiment data regression**

When equation of state is used to describe nonazeotropic refrigerant mixtures, it is important to have both excellent equation and appropriate mixing rule. For the sake of high computing accuracy, efforts should be made in both sides. While the equation and mixing rule are determined, the focus may be concentrated on co-reaction coefficient \(k_{ij}\). In fact, the computing errors even for liquid molar volume could be very small if every experimental point has its own \(k_{ij}\). Thus, the computing accuracy may be improved if \(k_{ij}\) is treated as a function of temperature \(T\) and concentrations of mixtures \(x_i\), \(k_{ij}=k(T,x)\). Whereas, the mixing procedure is so complex that the function almost can not be deduced theoretically. \(k_{ij}\) are regressed mostly from experimental VLE data and they are considered in common method as constant for a certain temperature range or a polynomial function of temperature. The key