Precise correlation of propylene-propane system and its analysis of relative volatility

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A B S T R A C T

In this research, a prediction method for the vapor-liquid equilibrium compositions of the propylene-propane mixture by the combined use of the COSMO-RS method and the Peng-Robinson equation of state is examined. Employing the van der Waals (VdW) mixing rule, the average deviations from this method for both the pressures and vapor phase compositions are no more than 0.62% and 0.75%, respectively. The average deviations for the relative volatility and tray efficiency are 0.93% and 5.52%, respectively. This method successfully describes the relative volatility of this system is not only related to the temperature but also dependent on the propylene mole fraction at low temperatures and high propylene concentrations. The density, excess molar volume and surface tension data are listed. The calculations explain the irregular phenomenon of the relative volatility. The results show that the non-ideality of this system comes from the dispersions between the components dominates the bulk liquid properties at low temperatures and high propylene concentrations.

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1. Introduction

The separation of light olefins such as propylene + propane is very important to the petrochemical sector. Due to the close boiling points and lower relative volatilities of this system, obtaining high-purity propylene (>99.5 mol%) based on traditional rectification processes is quite difficult. Conventional propylene/propane separation technologies are based on distillation process in columns more than 150 trays which leads to high capital investment and operational cost. Therefore, it is particularly critical to accurately predict the vapor-liquid equilibrium properties of this system. Significant efforts have been made to find the suitable correlation for their vapor-liquid equilibrium data. Quang [1] et al. reported experimental isothermal vapor-liquid equilibrium (VLE) data for this mixture from 273.15 to 313.15 K. The data were correlated with the Peng-Robinson equation of state (PR-EOS) combined with the Wong-Sandler mixing rule. This correlation indicated that the values of the average deviations of the pressure (*AAD%-P*) varied within 0.06–0.15%, and the average deviations of the vapor phase composition (*AAD%-y*) varied within 0.51–1.30%; Manley and Swift [2] reported experimental VLE data from −20 to 100 °F. The method

they chose to correlate the data and calculate the relative volatilities included a rigorous form of the isothermal general coexistence equation. The relative volatilities had an estimated probable error of ±0.005 units. Laurance and Swift [3] reported experimental VLE data from 100 to 160 °F. By using the method described by Manley and Swift [2], they found that the application of the general coexistence equation was mostly sensitive to the accuracy of the vapor pressure data. The vapor pressure data had an estimated probable error of ±0.1%. Howat and Swift [4] sorted out 216 unique data points, of which approximately 30% were based on total pressure measurements. The data were correlated with the Redlich-Kwong equation of state (RK-EOS) combined with the Wilson equation, and the *AAD%-P* was 0.45%. Hakuta [5,6] et al. investigated isothermal VLE data of this mixture at low temperatures ranging from 0 to −100 °C, and the data were thermodynamically consistent with the RK-EOS. Harmens [7] presented VLE data for this mixture from 230 to 350 K. The data were correlated with a perturbed hard-sphere equation of state, adapted specially to the saturation properties of propylene and propane. In summary, although the prediction of VLE data for this system can meet the accuracy requirements in the thermodynamic range, when applied to the field of engineering, it resulted in the huge deviations of the prediction of the theoretical plate number of propylene distillation column. This would lead to a great deal of uncertainty in predicting the tray efficiency. The effect of these inaccuracies on design can be

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extremely critical [8].

Vision 2020 [9] published by AIChE strives toward developing accurate tray efficiency calculations and improving accurate relative volatility calculations that occupy the most important areas for the future of the distillation process. The overall column efficiency is one of the various definitions of the tray efficiency, which is often used as the most classic one. The overall column efficiency is defined by:

$$E_{oc} = N_T/N_a \tag{1}$$

where N_T is the number of theoretical trays in the column, N_a is the number of actual trays in the column.

There is currently no particularly accurate method for predicting the E_{oc}. The key point of it is when applying the experimental VLE data to industrial calculation, the prediction errors of N_T will be inevitably enlarged. If the prediction of N_T is not accurate enough, the accuracy of the prediction of the E_{oc} cannot be guaranteed. In this situation, to develop the accurate method for predicting the N_T, it is very necessary to improve the accuracy of relative volatility calculation. This is especially important for close boiling points systems.

Kister [10] has also noted that errors come from the relative volatility is the most underrated factor that affect the tray efficiency prediction. As shown in Fig. 1, when the relative volatilities are very low ($\alpha < 1.2$), small errors in the relative volatility correlation have a huge impact on the tray efficiency prediction (the calculation of N_T). For instance, at a relative volatility of 1.05, a −4% error in the relative volatility correlation predicts a tray efficiency that is 75%–85% higher than its true value. Since the propylene distillation column is often condensed with the water, the column is operated in a pressurized condition with the pressure of the top column nearly 20–22 atm. In this case, the relative volatility of the top column is around 1.03 and the relative volatility of the overall column is around 1.05. The effect of VLE errors on the column design will be greatly magnified in the calculation of N_T.

For this purpose, it is very meaningful to develop an accurate thermodynamic correlation method for the VLE data. This accurate method needs to have at least two features:

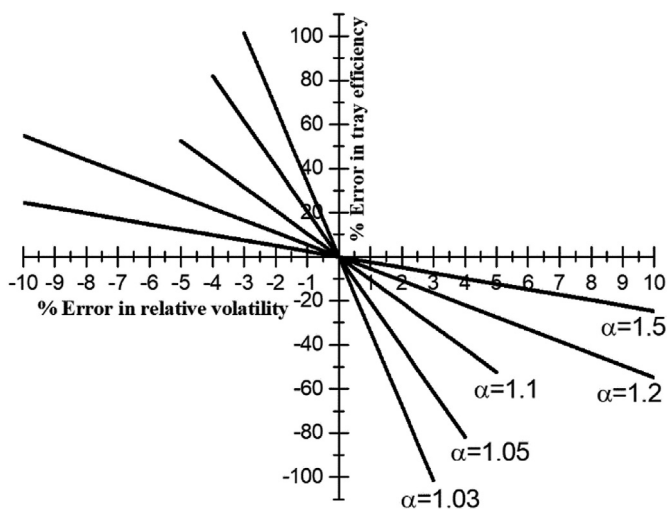1. The relative volatility calculated by the method should have the characteristic is not only related to the temperature but also dependent on the propylene mole fraction. Then the method can achieve the accurate requirements by describing the non-ideality of this system.
2. The deviations in the tray efficiency (E) caused by the deviations in the relative volatility should be as low as possible.

The purpose of this work is to develop an improved method for predicting the VLE properties of a binary mixture of propylene-propane for the basis of developing technologies to minimize the deviations in E_{oc} prediction. The prediction deviations of the commonly used methods are listed in Table 1 for the purpose of comparison. It indicates that the SRK-EOS and PR-EOS (in Aspen Plus V8.6 program) give the best results (the average deviations in the relative volatility are less than 1%). The only way to minimize the deviations based on the traditional empirical equation of state is to adjust the attraction parameter a with temperature, but it seems neither easy to operate nor can be applied generally to most situations (high temperature and pressure situation). The best way to get a suitable correlation for this system is to choose a straight forward process, which requires the fewer parameters the better.

Since its first publication in 1995, the quantum chemically based conductor-like screening model for realistic solvation (COSMO-RS) has been developed as a widely accepted and independent method for fluid phase equilibrium simulations [12,13]. Numerous studies [14–18] have been accomplished in order to compute the activity coefficients for VLE calculations. However, when using the theory to predict the VLE data of many systems, the prediction accuracies stay relatively crude. Therefore, it is one of the most important directions that the theory needs to be further developed to improve the prediction accuracy of various types of physical properties. It is also helpful for applying the molecular modeling from academic research to industry engineering.

The VLE data for the propylene + propane mixture at various temperatures have been previously reported by a few authors [1–7,19–21]. The VLE data are usually estimated using thermodynamic models based on the fundamental phase equilibrium criteria for equalizing the chemical potential in both phases [22]. This process is based on the gamma(γ)-phi(ϕ) calculation method,

Fig. 1. Direct effect of the errors in the relative volatility on the errors in the tray efficiency.

Table 1
The prediction deviations for the binary mixture of Propylene(1)+Propane(2) using different models.

Equation	T (K)	AAD%-P[a]	AAD%-y_1[b]	AAD%-α[c]	AAD%-E[d]
SRK	230–350	1.02	0.34	0.83	5.98
PR	230–350	0.42	0.36	0.86	6.10
PRWS	230–350	0.41	0.40	1.04	7.33
UNIFAC	230–350	1.58	1.46	2.66	20.71
UNIFAC-DMD	230–350	1.27	1.18	2.07	14.88
UNIQUAC	230–350	1.01	2.43	6.55	54.47
UNIQUAC-RK	230–350	1.10	1.26	3.23	21.63
BWR-Le	230–350	1.38	1.50	3.15	19.81
RK-WILSON[e]	230–350	0.21	2.20	4.55	39.60
SAFT	230–350	2.57	1.14	2.60	19.24
PC-SAFT	230–350	0.45	0.58	1.28	8.05
Lee-Kesler-Plocker	230–350	0.38	0.76	1.46	10.49

Reference Data [7].

[a] $AAD\% - P = \dfrac{1}{N}\sum_{i=1}^{N} 100 \left| \dfrac{p_{i,ref} - p_{i,cal}}{p_{i,ref}} \right|$

[b] $AAD\% - y_i = \dfrac{1}{N}\sum_{i=1}^{N} 100 \left| \dfrac{y_{i,ref} - y_{i,cal}}{y_{i,ref}} \right|$

[c] $AAD\% - \alpha = \dfrac{1}{N}\sum_{i=1}^{N} 100 \left| \dfrac{\alpha_{i,ref} - \alpha_{i,cal}}{\alpha_{i,ref}} \right|$

[d] $AAD\% - E = \left| -\dfrac{AAD\% - \alpha}{\ln \alpha} \right|$ (According to Reference [10]).

[e] Reference [4].