

2 성분계 혼합물인 propane (R290) 과 butane(R600)의 VLE 데이터 측정

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Vapor-Liquid Equilibrium for the binary mixture of propane (R290) +butane (R600)

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Introduction

CFC alternative refrigerants have been developed for many years. Recently some of them are commercialized and replaced with old ones. Following the tendency of the world, the Korean government recommends installing non-CFCs facilities. Light hydrocarbons can be one of the alternative refrigerants. Although light hydrocarbons are toxic, flammable, and explosive, they are expected alternatives because they are rather cheap, plentiful and environmentally benign chemicals. Also they have low GWP. In this work, VLE data for binary mixture of butane + propane at five equally spaced temperatures between 273.15 and 323.15K were measured by using a circulation-type equilibrium apparatus. The experimental data were correlated with the Peng-Robinson equation of state[1]used the Wong-Sandler mixing rule[2] with combine NRTL excess Gibbs free energy model. Almost all the calculated values with this model give a good agreement with the experimental data and these systems exhibit near azeotropes.

Theory

1. Vapor-Liquid Equilibrium

The definition of the fugacity of a species in solution is parallel to the definition of the pure species fugacity.

$$\mu_i^{ig} = \Gamma_i(T) + RT \ln y_i P \quad (1)$$

For species i in a mixture of real gases or in a solution of liquids, the equation analogous to (1), the ideal-gas expression, is:

$$\mu_i \equiv \Gamma_i(T) + RT \ln \hat{f}_i \quad (2)$$

Where \hat{f}_i is the fugacity of species i in solution, replacing the partial pressure $y_i P$. This definition of \hat{f}_i does not make it a partial molar property, and it is therefore identified by a circumflex rather than by an over bar.

A direct application of this definition indicates its potential utility.

$$\mu_i^\alpha = \mu_i^\beta = \dots = \mu_i^\pi \quad (i = 1, 2, \dots, N) \quad (3)$$

Equation (3) is the fundamental criterion for phase equilibrium. Since all phases in equilibrium, are at the same temperature, an alternative and equally general criterion follows immediately from (2).

$$\hat{f}_i^\alpha = \hat{f}_i^\beta = \dots = \hat{f}_i^\pi \quad (i = 1, 2, \dots, N) \quad (4)$$

Thus, multiple phases at the same T and P are in equilibrium when the fugacity of each constituent species is the same in all phases [3].

Apparatus and Procedure

The vapor-liquid equilibrium apparatus used in this work was a circulation-type one in which both liquid and vapor phases were re-circulated continuously. The equilibrium cell is a type-316 stainless steel vessel within an inner volume of about 85 cm³. In its middle part, two Pyrex glass windows of 20-mm thickness were installed before and behind so that the liquid level, mixing and circulating behaviors, and critical phenomena could be observed by the back light during operation. A stirrer, rotated at variable speeds by an external magnet, was used to accelerate the attainment of the equilibrium state and to reduce concentration gradients in both phases [4]

Experiments for a binary system were performed by the following procedures. The system was first evacuated to remove all inert gases. A certain amount of butane was supplied to the cell, and then the temperature of the entire system was held constant by controlling the temperature of the water bath. After the desired temperature was attained, the pressure of the pure component was measured. A certain amount of propane was introduced into the cell from a sample reservoir. The mixture in the cell was stirred continuously with the magnetic stirrer for over one hour. Both the vapor and liquid phases were re-circulated by the dual-head circulation pump until an equilibrium state was established. After equilibration, the pressure in the equilibrium cell was measured and then vapor and liquid samples

were with-drawn from the recycling lines by the vapor and liquid sampling valves, respectively. The compositions of the samples were measured by immediately injecting them into the GC, which was connected online to vapor and liquid sampling valves.

Result and discussion

The average deviation ($|\Delta P/P| \%$) between measured and calculated values from the data of REFPROP 6.01 is 0.133% for propane and 0.005% for butane. Fig 1. shows the comparison of measured and calculated values with the PR EOS for propane + butane at (273.15, 283.15, 293.15, 303.15, 313.15 and 323.15)K. The average values of AAD- P and AAD- y were 0.303% and 0.021 for the PR EOS. The PR EOS based results are shown in Fig 2 and 3. From these figures and the low average deviations of P and y , we conclude that the calculated values using the PR EOS gives good agreement with the experimental data. This mixture exhibited no azeotrope.

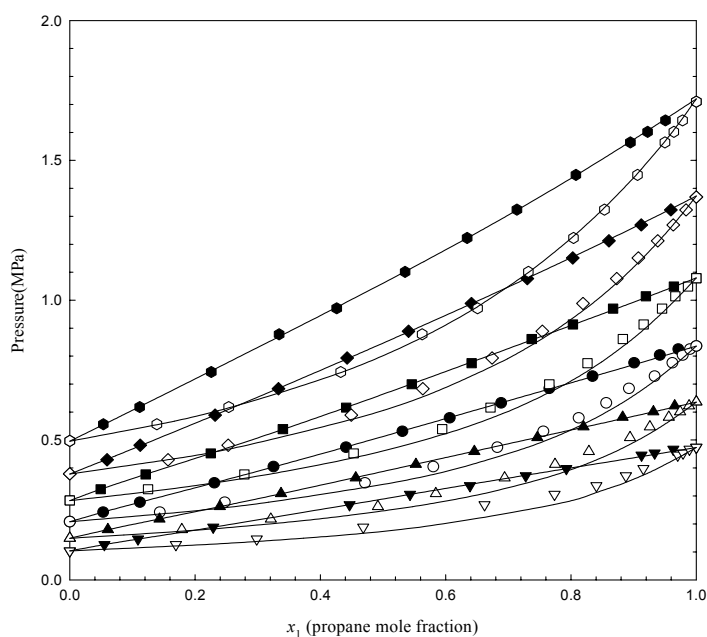
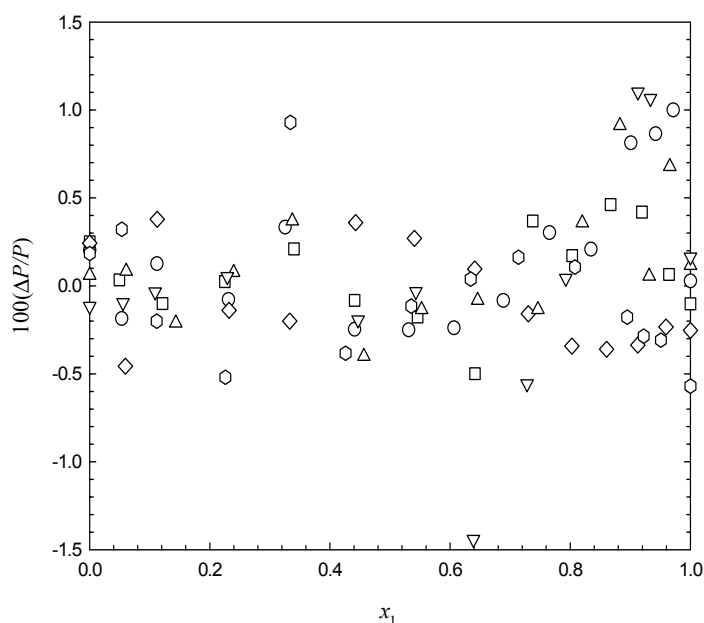


Fig.1. P - x - y diagram for the propane + butane system. Experimental data at 273.15(∇); 283.15 (\triangle); 293.15 (\circ); 303.15 (\square); 313.15 (\diamond); 323.15 (\hexagon) calculated with PR-EOS using W-S mixing (—).

Fig.2. Deviation of pressure for the system propane (1) + butane (2) from the PR- EOS using W-S mixing rule.



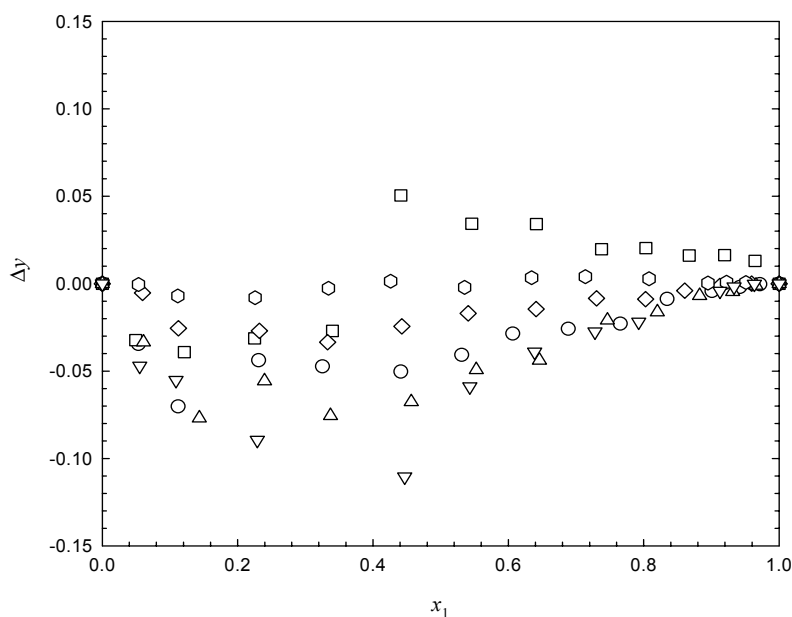


Fig.3. Deviation of vapor composition for the system propane (1) + butane (2) from the PR EOS using W-S mixing rule.

Conclusion

The VLE data for binary systems of propane + butane were measured at four temperatures between (273.15 and 323.15)K using a circulation-type equilibrium apparatus. The experimental data were correlated with the PR EOS using the Wong-Sandler mixing rules. Calculated results with these equations have given satisfactory results in comparison with the experimental data. It was found that this mixture did not show azeotropic behavior over this range of temperature.

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