Propylene 과 HFC-134a 2 성분계 혼합물의 상평형

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Vapor-liquid equilibria for the binary mixture of propylene and HFC-134a

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Introduction

For nearly sixty years, CFCs have been widely used as solvents, foam blowing agents, aerosols and specially refrigerants due to their preeminent properties. However, they have been being regulated internationally because of their high ozone depletion potential (ODP) and global warming potential (GWP). In consequence, lots of research have been done to find the suitable replacement for CFCs. Initial alternatives included some HCFCs, but they will be also phased out internationally in a few years because their ozone depletion potentials and global warming potentials are in relative high levels though less than those of CFCs. HFCs, which have zero ODPs, were proposed as promising replacements for CFCs and HCFCs. Unfortunately, HFCs were revealed to have significant global warming potentials and have been included in the basket of green house gases to be regulated by Kyoto Protocol 1997. In the future, the using and production of HFCs will be reduced and it required environmentally benign chemicals to amend for that reduced quantity of HFCs.

In recent years, the utilization of hydrocarbons such as propane, n-butane, iso-butane, propylene, etc. as effective refrigerants is believed as an alternative solution because these hydrocarbons are environmentally benign chemicals (due to their zero ODPs and near zero GWPs) and have many outstanding properties. Moreover, they are common components of natural gas, so they are cheap and plentiful. Their flammability has caused some concerns but can be reduced by using the mixture of hydrocarbon and HFC in optimal composition.

In this work, mixture of propylene/HFC-134a was considered. By using an equilibrium apparatus, VLE data of this mixture, which are very important basic information in evaluating the performance refrigeration cycles and in determining optimal composition of mixture, were measured at five equally spaces temperatures between 273.15 and 313.15K. The experimental data were correlated with the Peng-Robinson equation of state [2] using the Wong-Sandler mixing rules.

Experimental

The procedure and apparatus of VLE measurement were expressed in previous papers [1,3] in detail.

Theory

The VLE data were corrected with the Peng-Robinson (PR) equation of state, which is expressed as follows:

$$P=\frac{RT}{v-b}-\frac{a(T)}{v(v+b)+b(v-b)} \tag{1}$$

$$a(T)=\left(0.457235\frac{R^2T_c^2}{P_c}\right)\alpha(T) \tag{2}$$

$$\alpha(T)=\left[1+k\left(1-\sqrt{T/T_c}\right)\right]^2 \tag{3}$$

$$b=0.077796\frac{RT_c}{P_c} \tag{4}$$

$$k=0.37464+1.54226\omega-0.26992\omega^2 \tag{5}$$

where a is a function of temperature, b is constant, k is a constant characteristic of each substance, ω is the acentric factor, P (in MPa) is the pressure, P_c (in MPa) is the critical pressure, T (in K) is the absolute temperature, T_c (in K) is the critical temperature, T_r is the reduced temperature. The Wong-Sandler mixing rule was used in this work to obtain equation-of-state parameters for a mixture from those of the pure components. This mixing rule for a cubic equation of state can be written:

$$b_m=\frac{\sum_i\sum_j x_ix_j(b-a/RT)_{ij}}{\left(1-A_\infty^E/CRT-\sum_i x_ia_i/RTb_i\right)} \tag{6}$$

with $$(b-a/RT)_{ij}=\frac{1}{2}\left[(b-a/RT)_i+(b-a/RT)_j\right](1-k_{ij}) \tag{7}$$

and $$\frac{a_m}{b_m}=\sum_i x_i\frac{a_i}{b_i}+\frac{A_\infty^E}{C} \tag{8}$$

where C is a numerical constant equal to $\ln\left(\sqrt{2}-1\right)/\sqrt{2}$ for the Peng-Robinson equation [2] used in this work. Also, A_∞^E is an excess Helmholtz free energy at infinite pressure that can be equated to a low-pressure excess Gibbs free energy [8]; in this study we use the NRTL model [9] given by

$$\frac{A_\infty^E}{RT}=\sum_i x_i\frac{\sum_j x_jG_{ji}\tau_{ji}}{\sum_k x_kG_{ki}} \tag{9}$$

with $$G_{ji}=exp\left(-\alpha_{ij}\tau_{ji}\right) \qquad and \qquad \tau_{ij}=A_{ij}/(RT) \tag{10}$$

where G_{ij} is the local composition factor for the NRTL model, τ_{ij} is the NRTL model binary interaction parameter, $A_{ij}=(g_{ij}-g_{jj})$, where g_{ij} is an interaction energy parameter of the *i-j* component, α_{ij} is a nonrandomness parameter, and R is the universal gas constant (8.314 $J.K^{-1}mol^{-1}$). The parameters of these equations were obtained by minimizing the following objective function:

$$objective\ \ function = \frac{1}{N}\sum_{j=1}^{N}\left[\left(\frac{P_{j,exp} - P_{j,cal}}{P_{j,exp}}\right)x100\right]^2 \tag{11}$$

where N is the number of experimental points, P_{exp} and P_{cal} are the experimental and calculated pressure, respectively.

Results and discussion

The VLE data measured at 273.15, 283.15, 293.15, 303.15 and 313.15 K for the mixture of propylene/HFC-134a are shown in Figure 1. It was found that this mixture showed azeotropic behavior in this range of temperature from 273.15 to 313.15K. These experimental data were correlated with Peng-Robinson equation of state using the Wong-Sandler mixing rules. The interaction parameter (f_{12}), NRTL parameters (A_{12}, A_{21}) and the average deviation of pressure and vapor phase composition between experimental and calculated data by at various temperatures are listed in Table 1. The deviations of vapor phase composition and pressure of the experimental data from the correlated value using the Peng-Robinson equation of state with the Wong-Sandler mixing rules in each point are shown in Figure 2 and Figure 3. It indicates that in the temperature range from 273.15 to 313.15K, the values of AD-P(%) and AD-y by PR equation of state varied within 0.11 - 0.43% and 0.0045 - 0.0094 respectively. All values are relatively low and acceptable. In other way, the Peng-Robinson equation of state using the Wong-Sandler mixing rules gives a good agreement with the experimental data.

Table 1. Interaction parameter (f_{12}), NRTL parameters and average deviations (AD) of vapor phase composition and pressure

Temperature (K)	Interaction parameter, f_{12}	NRTL parameters		Average deviation	
		A_{12}	A_{21}	AD-P(%)	AD-y
273.15	-0.3128	1.1545	2.7003	0.4326	0.0051
283.15	0.0146	0.2193	1.9369	0.2712	0.0094
293.15	-0.0067	0.3539	1.7473	0.1616	0.0045
303.15	0.1785	-0.1569	1.4044	0.1136	0.0077
313.15	0.1896	-0.2683	1.4356	0.2680	0.0079

Conclusion

Measurements of VLE for the mixture of propylene/HFC-134a at five equally spaces between 273.15 and 313.15K were carried out by using a circulation-type equilibrium apparatus. It was found that this mixture showed azeotropic behavior in this range of temperature. Experimental azeotropic points of this mixture at 273.15, 283.15, 293.15, 303.15 and 313.15K were measured approximately. The Peng-Robinson equation of state with the Wong-Sandler mixing rule has a good agreement with experimental data in the range of temperatures between 273.15 and 303.15K and expectantly applied to other ranges but it needs some further experiments to confirm.

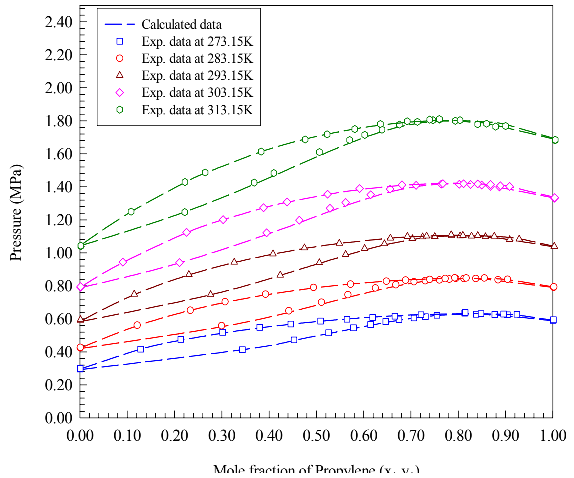

Figure 1. P-x-y diagram for the mixture of HFC-134a + propylene at various temperatures

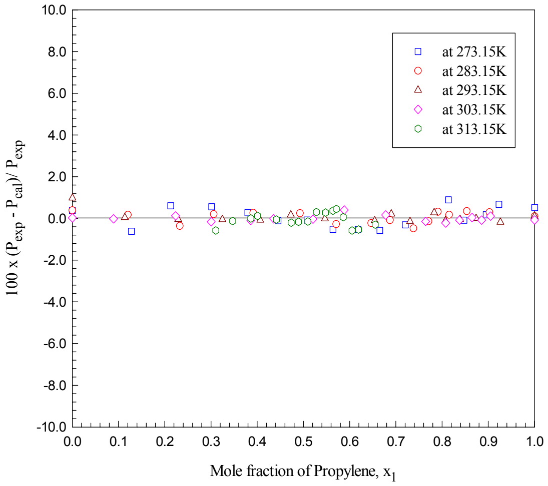

Figure 2. Deviation of pressure for the mixture of propylene + HFC-134a at various temperatures

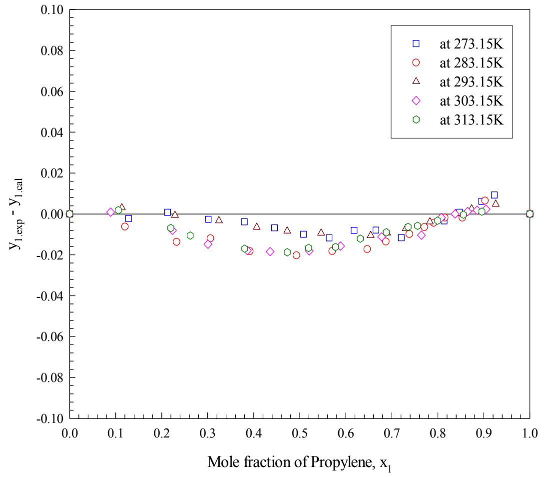

Figure 3. Deviation of vapor phase composition for the mixture of propylene (1) + HFC-134a(2)

Literature Cited

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