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Development of a Criterion for Azeotrope Prediction of Binary Refrigerant Mixtures

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Abstract−A simple criterion for binary azeotrope formation of refrigerant mixtures based on the regular solution theory was developed and applied to several refrigerant mixtures. This criterion requires no complex calculation and can be easily applied when vapor pressure and saturated density data of pure components are available. It was proven that the formation of an azeotrope could be well predicted with this criterion for the mixtures we studied.

Key words: Criteria, Azeotrope, Prediction, Refrigerant, Regular Solution

INTRODUCTION

Hydrochlorofluorocarbons (HCFCs) or hydrofluorocarbons (HFCs) have been used as alternative refrigerants. Since each material has pros and cons as refrigerant, use of mixtures has been considered to compensate for defects. For example, HFC-134a and HFC-32 have excellent properties as refrigerant and little harmful effect on the environment, but they also have disadvantages such as poor compatibility with lubricants or flammability. There are several criteria for selecting the components of a refrigerant mixture. First, thermodynamic properties like heat of vaporization and vapor pressure should be considered. Whether it is azeotrope mixture or not can be another criterion. Azeotropic mixtures have advantages as refrigerants because they tend to behave like a pure compound in a refrigerator. So, it would be very useful to be able to predict whether a mixture would form an azeotrope or not.

There have been many studies on the azeotrope formation. Ewell [1944] established a qualitative criterion of azeotrope formation. He divided materials into five classes and summarized the type of phase behavior for each binary pair. Eduljee and Tiwari [1976] set quantitative criteria of azeotrope formation. They just related the possibility of azeotrope formation to the difference of normal boiling point temperature, so their criteria have prediction ability. In addition, many researchers have studied the isothermal condition of azeotrope formation [Kim and Kang, 1995; Kim, 1999]. Prigogine and Defay [1954] found an isothermal criterion for azeotrope formation in regular solutions using a Margules type activity coefficient model. They have also stated that their method could easily be applied with other activity coefficient models. Stephan and Wagner [1985] have performed a similar study applying the Wilson's activity coefficient model. But their criteria are useful only when the activity coefficients between binary pairs fitted to experimental data are available. In this work, we tried to develop a criterion for azeotrope formation that can be used without fitted activity coefficient. The possibility of azeotrope formation is explained here with the pure components vapor pressures and the solubility parameter in regular solution theory.

THEORY

1. Derivation of the Criterion

HCFCs and HFCs including one or two carbon atoms are usually used as alternative refrigerants. They have similar molecular sizes and shapes. Also, the phase behavior of their mixture appears to be ideal in many cases. Lee and Sun [1993] noticed that the vapor-liquid equilibria of refrigerant mixtures could be calculated accurately with a simple cubic equation of state, and it implies to some extent that strong interactions representing non-ideal behavior do not exist between these materials. Ewell has pointed that halocarbon-halocarbon mixtures always show positive deviations from Raoults law.

From the above, it is expected that refrigerant mixtures will show the phase behavior of regular solution. A simple criterion of azeotrope formation can be derived based on the regular solution assumption. Activity coefficient of each component in binary mixture is expressed in the regular solution theory by

$$\mathrm{RT}\ \ln\gamma_1=\nu_1\Phi_2^2[\delta_1-\delta_2]^2 \tag{1a}$$

$$\mathrm{RT}\ \ln\gamma_2=\nu_2\Phi_1^2[\delta_1-\delta_2]^2 \tag{1b}$$

From modified Raoult's law and azeotropic condition where vapor composition is equal to liquid composition, the following equation is obtained.

$$\frac{P_2^{sat}}{P_1^{sat}}=\frac{\gamma_1}{\gamma_2} \tag{2}$$

Combining Eq. (1) and Eq.(2), we have

$$\ln\frac{P_2^{sat}}{P_1^{sat}}=\frac{1}{\mathrm{RT}}(\delta_1-\delta_2)^2(\nu_1\Phi_2^2-\nu_2\Phi_1^2) \tag{3}$$

Φ_1 is the volume fraction of component 1 and has a value between 0 and 1. The quantity of $\nu_1\Phi_2^2-\nu_2\Phi_1^2$ increases or decreases monotonically as Φ_1 varies. We can construct a criterion of azeotrope formation by putting 0 and 1 to Φ_1.

Thus, we get

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[‡] This paper is dedicated to Professor Wha Young Lee on the occasion of his retirement from Seoul National University

$$-\frac{v_2}{RT}(\delta_1-\delta_2)^2 \le \ln\frac{P_2^{sat}}{P_1^{sat}} \le \frac{v_1}{RT}(\delta_1-\delta_2)^2 \qquad (4)$$

Azeotropy is a phenomenon that arises when the nonideality of the mixture is great enough to overcome the vapor pressure difference of the components. Square of the solubility parameter difference represents the nonideality of mixture. From the criterion derived in this work, we can forecast the formation of azeotrope in a more quantitative manner.

2. Application of the Criterion

The criterion derived in this work was tested for several binary refrigerant mixtures. We applied this criterion to mixtures whose vapor-liquid equilibria are well known. To apply the criterion, the vapor pressure and saturated liquid density data of pure components are needed. The heat of vaporization required in the calculation of the solubility parameter was determined from the Clausius-Clapeyron equation.

The availabilty of the criteria was tested for both azeotropic and non-azeotropic mixtures. HFC-152a/CFC-12 is one of the well-known azeotropic mixtures and it forms azeotropic point over a wide temperature range. Fig. 1 displays the result of application of the criterion to this mixture. The solid curve represents 'ln P_2^{sat}/P_1^{sat}', and the dashed lines represent lower and upper boundaries calculated from Eq. (4). It means that if the solid curve exists between the two dashed lines, the mixture is likely to form azeotrope. The solid symbols represent the results of former experiments where azeotrope has been observed [Pennington and Reed, 1950; Hinrichsen, 1969].

Fig. 2 represent the results of application to another azeotropic mixture HFC-134a/CFC-12. Kleiber [1994] measured the phase equilibria for this system and found an azeotrope. As can be seen from the figure, predictions and experimental results agree well with each other. HFC-134a/CFC-12 mixture forms an azeotrope in a narrow temperature range according to this figure. There are some mixtures that show azeotropic behavior at only limited temperature range, and HFC-134a/CFC-12 is an example. Simple criteria that make use of only pure components property not reflecting actual system's condition-temperature or pressure- are likely to fail in prediction of such systems. In case the difference between the normal boiling temperature of each component is very small, such criteria generally lead to prediction of azeotrope, but it is often proven to be wrong. HCFC-124/HCFC-142b system is a non-azeotropic mixture at room temperature in spite of the fact that the normal boiling point temperature difference of HCFC-124 and HCFC-142b is as small as 0.4 K. The criterion derived in this work was applied to this system

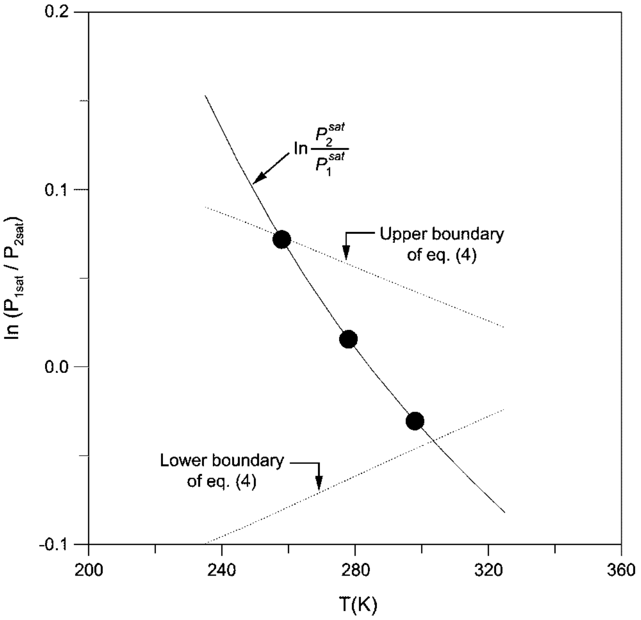
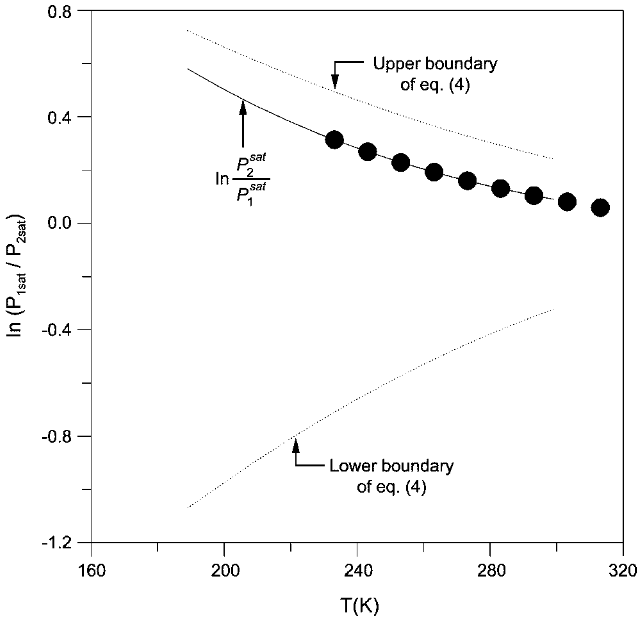


Fig. 2. Application of the criterion of azeotrope formation to HFC-134a/CFC-12 system.



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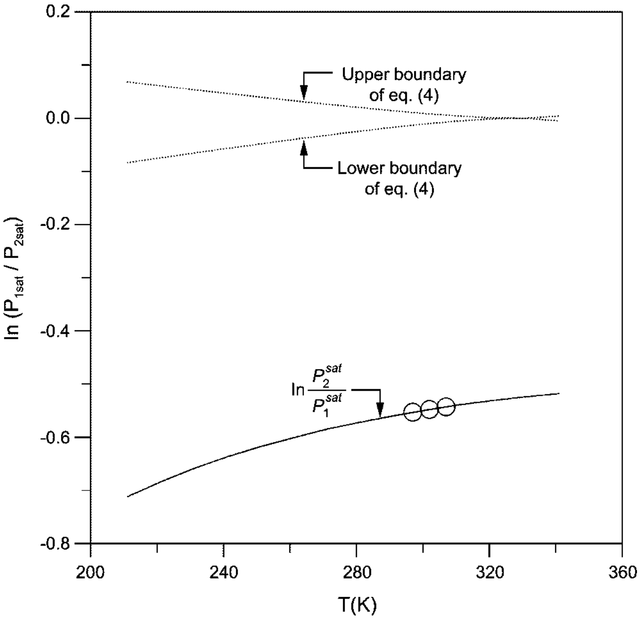

Fig. 3. Application of the criterion of azeotrope formation to HCFC-124/HCFC-142b system.

and the result is shown in Fig. 3. In this figure, the open symbols represent the result of experiment where azeotrope was not seen [Lee et al., 1996].

From the above examples, we ascertained that our new criteria work correctly when predicting the azeotropic behavior of binary refrigerant mixtures.

CONCLUSION

A new criterion of azeotrope formation was developed based on the regular solution theory and applied to several refrigerant mixtures. This criterion predicted correctly the azeotropic and non-azeotropic behaviors of several refrigerant mixtures which other existing criteria have failed to predict.

If we summarize the advantages of the criteria derived in this work:

1. It has a prediction ability without fitted parameters obtained from experiments.
2. It reflects the dependence on actual thermophysical conditions of mixtures.
3. It does not need complicated thermodynamic calculation like the equation of state.

Because this criterion has been simply derived based on the assumption that all the refrigerant mixtures are basically regular solutions, there are surely some mixtures that cannot be predicted correctly with this criterion. However, this criterion will be very useful when we have to select an unknown alternative refrigerant mixture.

NOMENCLATURE

P^{sat} : saturation pressure [bar]
T : temperature [K]
R : gas constant [J/mol K]
ν : saturated volume [cm^3/mol]
Φ : volume fraction
δ : solubility parameter [$(J/cm^3)^{0.5}$]

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