CFC, HCFC, FC 혼합물의 기-액 상평형 상관관계 : 혼합규칙 평가

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Correlation of the Vapor-Liquid Equilibria of CFC, HCFC and FC mixtures : Critical Evaluation of Mixing Rules

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Introduction

Some of the most harmful chemicals with respect to ozone layer are chlorofluorocarbons(CFCs) which are extensively used for versatile applications such as refrigeration. An accurate description of the thermodynamic properties and phase equilibria of those compounds is very important for the application of their uses.

Theory

The Soave-Redlich-Kwong equation of state (SRK-EOS) [1] is used to model the vapor-liquid equilibria (VLE) of freon mixtures and its original form is

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

The mixture parameters a and b are derived from mixing rule

$$a = \sum_{j=1}^{n}\sum_{i=1}^{n} x_i x_j a_{ij}$$

$$b = \sum_{i=1}^{n} x_i b_i$$

For this fixed equation of state, a kind of mixing rules is introduced and calculated the optimized adjustable parameters. In this study the mixture parameters a's are closely examined by using the following three different types of mixing rules.

(i) the van der Waals one-fluid (OF) mixing rule
(ii) the Panagiotopoulos-Reid (P&R) mixing rule
(iii) the Modified Huron-Vidal second order (MHV2) mixing rule

In describing the phase equilibria using by the first and second mixing rules, they are needed by only EOS. But the third MHV2 includes the activity model, and thus additional calculation steps are needed. Any appropriate excess Gibbs energy model for VLE calculations can be adapted for the MHV2 model. In the present work we selected the NRTL model which is applicable to partially miscible as well as completely miscible systems. Using the fugacity coefficient calculated for each component in both liquid and vapor phases, the following VLE relationship is then applied to calculate the vapor phase composition :

$$y_i \phi_i^v = x_i \phi_i^l$$

Calculation of the interaction parameters

The VLE of eight different binary freon-freon mixtures were calculated over a

System	Temperature (Kelvin)	Pressure (bar)	Data Source
R134a/R143a	278 - 333	3.5 - 28.8	Kubota - Matsumoto
R12/R13	255 - 290	1.62 - 30.0	Mollerup - Fredenslund
R23/R13	199 - 273	1.5 - 27.5	Stein - Proust
R14/R13	199	1.5 - 15	Proust - Stein
R22/R142b	263 - 338	1.0 - 27.0	Kubota - Nojiri et al
R23/R22	273 - 353	7.15 - 53.95	Roth et al
R14/R23	145 - 283	0.2 - 51.3	Piacentini - Stein

Table 1. Data sources and temperature and pressure ranges of binary mixtures examined in this work

wide range of temperature and pressure with the SRK-EOS. Table 1 shows the various data sources used in this work. The acentric factor and critical properties of pure components were found in the literature [2]. The binary interaction parameters kij and the NRTL parameters α_{ij} and τ_{ij} were calculated from the experimental VLE data for each binary mixture with the IMSL optimization program at which the objective fuctions were to minimize the sum of the residuals.

Results and Discussion

Most of former works of describing the phase equilibria of freon mixtures were conducted by EOS only. In present work versatile mixing rules were introduced and the prediction and correlation ability of each appeared remarkably corresponding the polarity of component. The binary interaction parameters of eight freon-freon binary mixture systems and average absolute deviations (%AAD) for SRK-OF and SRK-P&R, and the NRTL molecular interaction energy parameters and nonrandomness parameter used in the SRK-MHV2 model are calculated. In general, the VLE values calculated from these models showed almost similar magnitude of deviations when compared with the experimental source data. It is therefore hard to say that a particular model is in better agreement than other models. The SRK-MHV2 model showed, however, good correlation abilities for all eight systems over the entire temperature and pressure ranges represented in Table 1. R23 was known as a relatively high polar compound [3]. In this work there were three mixtures containing R23 which have great nonideal behavior. The VLE results for an azeotropic R23/R13 system at a temperature of 224K are shown in Figure 1. For R23/R13, R23/R22, and R23/R14 mixtures the SRK-MHV2 appeared rather to be worse than the others. But itt should be considered that the SRK-MHV2 revealed a more important advantage than SRK-OF and SRK-P&R. It was the robustness of SRK-MHV2 in the fact that the calculated VLE values were less sensitive to the corresponding parameter variations. There was a knotty problem in running the calculation program. The susceptiblity of SRK-OF and SRK-P&R to the initial guessing values made a various kind of errors, and therefore the robustness. of SRK-MHV2 could be regarded as an powerful merit. In running the calculation program on the azeotropic system R23/R13, such an advantage was especially outstanding. For the three mixtures containing R23 which was considered quite a polar compound the SRK-P&R shows the best superiority. The interaction parameters calculated using the SRK-OF and the SRK-P&R could be positive or negative irregularly but the calculated parameters using the SRK-MHV2 were sustained within relatively tolerable variations over the whole temperature ranges in each system. Due to the robustness and consistency in parameters the SRK-MHV2 saved large efforts than SRK-OF and SRK-P&R. By Michelsen and Kistenmacher a problem, so-called "Michelsen-Kistenmacher syndrome", in the P&R model was evoked at mixtures containing very similar compounds [4] and it had been known that this syndrome occasionally turned up in multicomponent systems. In the present work any symptom of this syndrome was not shown. Although the P&R model has revealed a problem, it was successfully applied to binary polar mixtures. Most large non-ideal behavior among the investigated mixtures was appeared in the R23/R14 mixture and its *P-x-y* diagram at 172K was represented in Figure 2. In this figure the SRK-MHV2 showed the best correlation ability. regarding all these results, it is seen that the mixing rules have an effect on the fitting the phase equilibria, and totally the SRK-MHV2 showed the best one.

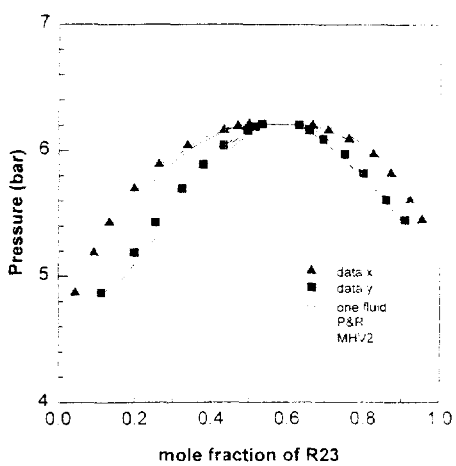

Figure 1. P-x-y diagram of R23/R13 mixture at 224K

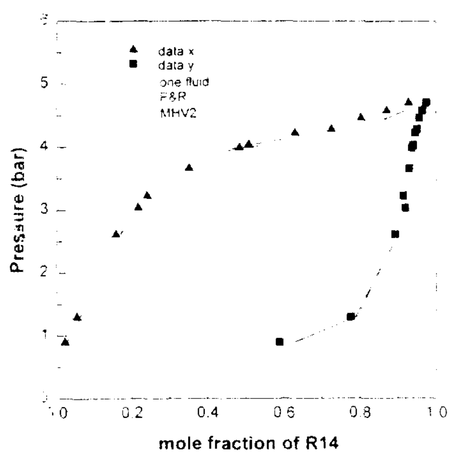

Figure 2. P-x-y diagram of R14/R23 mixture at 172 K

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