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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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Abstract—The vapor-liquid equilibrium data of the binary CFC, HCFC, and FC mixtures were correlated with the Soave-Redlich-Kwong equation of state incorporated with some types of mixing rules; the conventional one fluid, Panagiotopoulos-Reid and modified Huron-Vidal second order mixing rules. The Panagiotopoulos-Reid mixing rule showed the superiority to the other models in predicting the VLE of freon mixtures with low errors. The modified Huron-Vidal second order model showed good convergence ability, which was due to its robustness to parameter variation.

Key words: *CFC, HCFC, FC, Vapor-liquid Equilibria, Mixing Rule*

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. Many countries have decided to freeze the use of CFCs by replacing them with hydrochlorofluorocarbons (HCFCs) and finally stop their production until the end of 1995, and thus substitutes that would have similar physical and chemical properties to CFCs should be invented to cope with this situation. An accurate description of the thermodynamic properties and phase equilibria of those compounds is very important for the application of their uses. Some works have been conducted to correlate the phase behavior of mixtures of CFCs, HCFCs, FCs and hydrocarbons with several empirical equations of state [Asselineau et al., 1978; Fransson and Vamling, 1993; Platzer and Maurer, 1993; Abu-Eishah, 1991]. Most of these were treated with the binary interaction parameters of the conventional mixing rule, which were considered to be temperature dependent.

In this work, the Soave-Redlich-Kwong equation of state (SRK-EOS) is used to model the vapor-liquid equilibria of freon mixtures. Several mixing rules incorporated with the SRK-EOS were used in order to determined the corresponding binary interaction parameters. The overall percentage average absolute deviations between known data and calulated results are listed to compare which rule shows the best agreement in fitting procedure.

THEORY

The SRK-EOS [Soave, 1972] in its original form is

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

$$a(T)=0.4274\alpha(T)R^2T_c^2/P_c \tag{2}$$

$$b=0.08664RT_c/P_c \tag{3}$$

$$\alpha(T)=\{1+m(1-T_r^{0.5})\}^2 \tag{4}$$

$$m=0.480+1.574\omega-0.176\omega^2 \tag{5}$$

and the mixture parameters a and b are derived from mixing rule

$$a=\sum_{j=1}^{n}\sum_{i=1}^{n} x_ix_ja_{ij} \tag{6}$$

$$b=\sum_{i=1}^{n} x_ib_i \tag{7}$$

In this study the mixture parameter a's are closely examined by using the following three different types of mixing rules.

(i) the van der Waal one-fluid (OF) mixing rule

$$a_{ij}=(a_ia_j)^{0.5}(1-k_{ij}) \tag{8}$$

(ii) the Panagiotopoulos-Reid (P&R) mixing rule [Panagiotopoulos and Reid, 1986]

$$a_{ij}=(a_ia_j)^{0.5}[1-k_{ij}+(k_{ij}-k_{ji})x_i] \tag{9}$$

(iii) the Modified Huron-Vidal second order (MHV2) mixing rule [Michelson, 1990]

In 1979 Huron and Vidal proposed a new method for deriving mixing rule which is connected to the excess Gibbs energy model [Huron and Vidal, 1979]

$$g^E=RT[\ln_{\varphi}-\sum_{i=1}^{n} x_i\ln_{\varphi_i}] \tag{10}$$

where φ and φ_i are the fugacity coefficients of the solution mixture and pure component i, respectively. The modified formula of this mixing rule using SRK-EOS and a reference zero pressure has the following explicit form

$$q_1\left(\alpha-\sum_{i=1}^{n} x_i\alpha_i\right)+q_2\left(a^2-\Sigma x_i\alpha_i^2\right)=\frac{g^E}{RT}+\sum_{i=1}^{n} x_i\ln\left(\frac{b}{b_i}\right) \tag{11}$$

where $\alpha=a/bRT$ and $\alpha_i=a_i/b_iRT$. The recommended values of q_1 and q_2 for the MHV2 are −0.487 and −0.0047, respectively.

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

System	Temperature (Kelvin)	Pressure (bar)	Data source
R134a+R143a	278-333	3.5-28.8	Kubota-Matsumoto [1993]
R12+R13	255-290	1.62-30.0	Mollerup and Fredenslund [1976]
R23+R13	199-273	1.5-27.5	Stein and Proust [1971]
R14+R13	199	1.5-15	Proust and Stein [1979]
R22+R142b	263-338	1.0-27.0	Kubota-Nojiri et al. [1990]
R23+R22	273-353	7.15-53.95	Roth et al. [1992]
R14+R23	145-283	0.2-51.3	Piacentini and Stein [1967]

The fugacity coefficient for the SRK-MHV2 is given by

$$\ln\varphi_i = \ln\left[\frac{RT}{P(v-b)}\right] + \left(\frac{1}{v-b} - \frac{\alpha}{v+b}\right)b_i - \ln\left(\frac{v+b}{v}\right)\left[\frac{\partial(n\alpha)}{\partial n_i}\right]_{T,P,n_j} \quad (12)$$

The composition derivative of nα in MHV2 can be calculated from each mixing rule and is given by

$$\left[\frac{\partial(n\alpha)}{\partial n_i}\right]_{T,P,n_j} = \frac{1}{q_1 + 2\alpha q_2}\left[q_1\alpha_i + q_2(\alpha^2 + \alpha_i^2) + \ln\gamma_i + \ln\left(\frac{b}{b_i}\right) + \frac{b}{b_i} - 1\right] \quad (13)$$

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 [Renon and Prausnitz, 1968] which is applicable to partially miscible as well as completely miscible systems [Prausnitz et al., 1986]. 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:

$$y_i\hat{\varphi}_i^v = x_i\hat{\varphi}_i^l \quad (14)$$

In the previous work, we applied several mixing rules to the high-pressure phase equilibria and used the UNIQUAC for an appropriate excess Gibbs energy model [Yoon et al., 1993].

CALCULATION OF THE INTERACTION PARAMETERS

The VLE of eight different binary freon-freon mixtures were

Table 2. Binary interaction parameters for one fluid and P&R mixing rules, and NRTL interaction energy parameters for MHV2 mixing rule and %AADs

System	Temp. (K)	One fluid		P&R			MHV2			
		k_{12}	%AAD	k_{12}	k_{21}	%AAD	α_{12}	τ_{12}	τ_{21}	%AAD
R143a+ R134a	278.15	0.005	0.707	0.0084	0.0165	1.002	0.345	25.134	5.048	0.84
	288.15	−0.0003	0.722	−0.0004	0.0116	0.639	0.265	7.072	8.495	0.66
	303.15	0.0015	0.750	0.0113	0.0050	0.520	0.306	9.052	10.323	0.71
	318.15	0.0026	0.821	0.0172	0.0012	0.654	0.264	11.351	8.089	0.87
	333.15	−0.0003	0.766	0.003	0.0095	0.949	0.422	5.818	6.426	0.78
R12+R13	255	0.0292	1.148	0.0387	0.0231	0.983	0.271	40.933	41.430	1.06
	290	0.0359	1.031	0.0565	0.0291	0.758	0.354	44.856	45.205	0.94
R23+R13	273.09	0.1048	1.657	0.1195	0.0945	0.496	0.389	94.960	95.094	0.763
	224.61	0.1075	2.043	0.1167	0.0996	1.290	0.361	125.008	120.000	1.096
R14+R13	199.8	0.0293	0.748	0.0384	0.0201	0.695	0.351	23.026	42.235	0.673
R22+ R142b	263.15	0.0079	1.192	0.0187	0.0045	1.171	0.450	2.982	6.183	0.997
	273.15	0.0052	0.631	0.00003	0.0076	0.547	0.30	1.191	−0.387	0.468
	283.15	0.0127	0.778	0.0238	0.0086	0.703	0.236	6.066	8.962	0.69
	293.15	0.0118	0.726	0.0129	0.0110	0.722	0.239	6.065	8.961	0.54
	313.15	0.0034	0.860	0.0126	−0.0015	0.719	0.280	−4.010	−4.310	0.82
	338.15	0.0035	0.426	0.0016	0.0050	0.402	0.30	−5.089	−5.088	0.48
R23+R22	273.15	0.0250	0.395	0.0259	0.0249	0.394	0.292	21.772	30.862	0.36
	293.15	0.0164	0.267	0.0230	0.0106	0.171	0.237	16.672	20.226	0.31
	303.15	0.0180	0.268	0.0163	0.0197	0.254	0.274	16.553	20.681	0.24
	323.15	0.0214	0.581	0.0034	0.0383	0.201	0.209	16.585	20.740	0.63
	343.15	0.0278	0.466	0.0154	0.0544	0.343	0.305	21.336	27.288	0.62
	353.15	0.0288	0.266	0.0207	0.0767	0.215	0.388	16.343	20.278	0.38
R14+R23	145.15	0.0981	6.425	0.0454	0.1247	4.665	0.34	278.045	93.466	4.80
	172.04	0.1273	3.373	0.0863	0.1309	1.778	0.29	250.03	85.442	1.21
	199.81	0.1326	1.395	0.0997	0.1393	0.918	0.29	221.027	79.427	0.57
	224.81	0.1302	1.308	0.0983	0.1512	0.626	0.42	211.192	78.577	0.46
	255.37	0.1384	1.280	0.1104	0.1719	0.676	0.38	211.757	56.648	0.97
	283.15	0.1506	0.304	0.1389	0.2305	0.283	0.30	211.757	56.577	0.33
R22+ R134a	343.81	0.0146	1.255	0.0105	0.0178	1.160	0.283	11.676	11.650	1.490
	356.15	0.0166	0.710	0.0105	0.0191	0.390	0.371	10.805	14.585	0.751
	369.15	0.0208	0.337	0.0181	0.0229	0.344	0.292	19.140	10.342	0.318
	370.15	0.0241	0.371	0.0299	0.0164	0.372	0.262	21.529	18.603	0.324
	372.12	0.0335	0.246	0.0360	0.0206	0.218	0.233	21.553	21.593	0.145

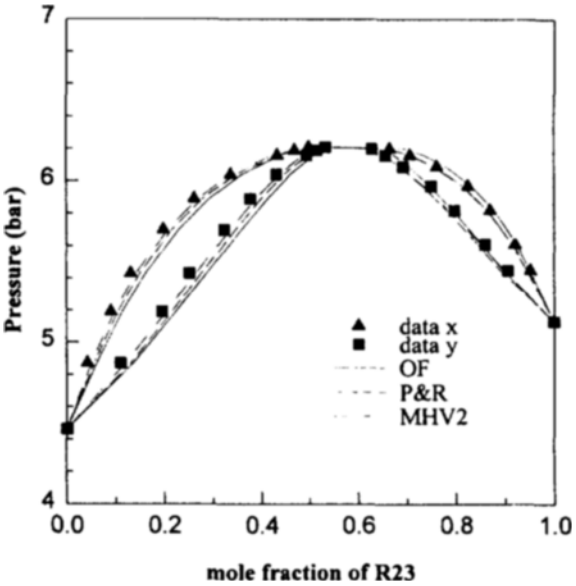

Fig. 1. P-x-y diagram of R23/R13 mixture at 273K.

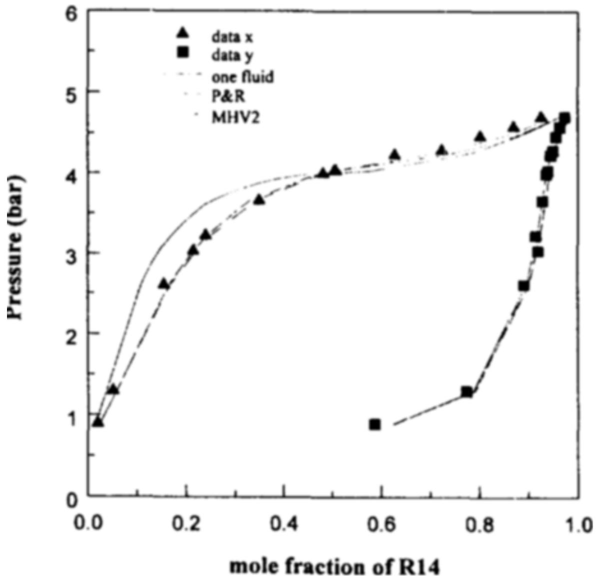

Fig. 2. P-x-y diagram of R14/R23 mixture at 172K.

calculated over a 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 [Fransson and Vamling, 1993]. The binary interaction parameters k_{ij} and the NRTL parameters α_{ij} and τ_{ij} were optimized from the experimental VLE data for each binary mixture using the nonlinear programming with constraints at which the objective functions were to minimize the sum of the residuals.

$$\Delta x = \sum_{i=1}^{n} \frac{|x_{exp} - x_{cal}|}{n}, \quad \Delta y = \sum_{i=1}^{n} \frac{|y_{exp} - y_{cal}|}{n} \tag{15}$$

$$F = \sum_{i=1}^{n} \frac{\Delta x + \Delta y}{2} = \mathrm{AAD} \tag{16}$$

where n is the number of data.

RESULTS AND DISCUSSION

The examined binary systems were compared with three different types of models ; SRK-OF, SRK-P&R, and SRK-MHV2. The binary interaction parameters of eight freon-freon binary mixture systems and average absolute deviations (%AAD) for the SRK-OF and the SRK-P&R, and the NRTL molecular interaction energy parameters and nonrandomness parameter used in the SRK-MHV2 model are listed in Table 2. 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. But the conventional OF mixing model showed somewhat larger errors than the others. The SRK-P&R and SRK-MHV2 models showed good correlation abilities for all eight systems over the entire temperature and pressure ranges represented in Table 1.

Most freons were known as polar compounds and according to the literature [Blindenbach et al., 1994], R23 was a relatively higher one among those examined in the present study. In this work there were three mixtures containing R23, that is R23/R13, R23/R22, and R23/R14, which have great nonideal behavior. For these mixtures the SRK-P&R showed the superiority. The VLE results for an azeotropic R23/R13 system at a temperature of 273K are shown in Figure 1. In running the calculation program there was a knotty problem. The susceptibility of SRK-OF and SRK-P&R to the initial guessing values made errors, that is, those might not approach to the global optimum point, depending on initial point. So if the superiority of the SRK-P&R would be utilized sufficiently and it should not fall into the singular point, the initial guessing values should be chosen carefully. But for the SRK-MHV2 this problem didn't happen. It found the optimum point easily regardless of initial value. Therefore the SRK-MHV2 saved large efforts during calculation stage. For the azeotropic system R23/R13 such an advantage was especially outstanding. Thus it could be regarded as a powerful merit that the SRK-MHV 2 was less sensitive to the corresponding parameter variations. 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.

By Michelsen and Kistenmacher a problem, so-called "Michelsen-Kistenmacher syndrome", in the P&R model was evoked at mixtures containing very similar components [Michelsen and Kistenmacher, 1990] 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 such a problem, it was successfully applied to binary polar mixtures in this study. The largest nonideal behavior among the investigated mixtures 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.

CONCLUSIONS

The experimental VLE data for the eight binary systems were investigated with the SRK-EOS incorporated with the OF, P&R,

and MHV2 models. The agreement between the calculated and the experimental VLE values was generally satisfactory for all three different mixing rules. Among those the P&R mixing rule was found to have stronger predictability with calculated interaction parameters to these examined freon binary mixture systems. The SRK-MHV2 also showed good correlation ability, but less than the SRK-P&R. The difference in %AAD values between the P&R and the MHV2 model was trivial, and thus in the point of utility of a model it could be said that SRK-MHV2 is also recommended. The SRK-MHV2 model showed good convergence ability, which is absolutely needed to calculate the VLE, because of its robustness to parameter variation.

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NOMENCLATURE

a : parameter in the equation of state
b : parameter in the equation of state
g^E : excess Gibbs free energy
k : binary interaction parameter in the one-fluid and the Panagiotopoulos-Reid mixing rule
n : number of moles and number of data
P : pressure [bar]
q_1, q_2 : constants of the Modified Huron Vidal mixing rule
R : gas constant [J/mol]
T : temperature [K]
v : molar volume
x : mole fraction in liquid phase
y : mole fraction in vapor phase

Greek Letters

α : equation of state parameter, $\alpha = a/bRT$, and nonrandomness parameter of the NRTL equation
γ : activity coefficient
φ : fugacity coefficient
τ : interaction energy parameter of the NRTL equation of state, $\tau_{ij} = (g_{ij} - g_{jj})/RT$
ω : acentric factor

Superscripts

* : reference zero pressure value
$\hat{}$: molar property
l : liquid phase
v : vapor phase

Subscripts

c : critical property
r : reduced property
i, j : molecular species

Abbreviations

R12 : dichlorodifluoromethane (CCl_2F_2)
R13 : chlorotrifluoromethane ($CClF_3$)
R14 : tetrafluoromethane (CF_4)
R22 : chlorodifluoromethane ($CHClF_2$)
R23 : trifluoromethane (CHF_3)
R134a : 1,1,1,2-tetrafluoroethane (CH_2FCF_3)
R142b : 1-chloro-1,1-difluoroethane (CH_3CClF_2)
R143a : 1,1,1-trifluoroethane (CH_3CF_3)

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