다양한 혼합법칙을 통한 1,1,1,2-tetrafluoroethane) + propane의 기액평형

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Vapor-Liquid Equilibria for 1,1,1,2-tetrafluoroethane + propane with various mixing rules

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Introduction

Many mixtures of interest in the chemical industry exhibit strong nonideality, greater than that describable by regular solution theory. Models for describing and predicting the phase behaviour have been continuously developed. Among many models, a very attractive route for developing better mixing rules is to combine an EOS with activity coefficient models.[2]

In this study, we measured isothermal vapor-liquid equilibria for binary systems of 1,1,1,2-tetrafluoroethane (HFC-134a)+propane at 293.15, and 303.15 K. The experimental data were correlated with five mixing rules combined with the Peng-Robinson-Stryjek-Vera equation of state and the NRTL excess free energy model. These mixing rules are HV-O(Huron Vidal-Original), MHV1(Modified Huron-Vidal 1st order), MHV2(Modified Huron Vidal 2nd order), LCVM(Linear Combination of Huron Vidal and michelsen), and HVOS(Huron Vidal modified by Orbey and Sandler) models [1] and the NRTL parameters obtained by these mixing rules were presented.

Theory

The VLE experimental data were correlated with the Peng-Robinson-Stryjek-Vera (PRSV) equation of state. The Peng-Robinson-Stryjek-Vera (PRSV) equation of state expressed as follows.

The Peng-Robinson-Stryjek-Vera (PRSV) equation of state

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

$$a(T) = \left(0.457235 \frac{R^2 {T_C}^2}{P_C} \right) \alpha(T)$$

$$b = 0.077796 \frac{RT_C}{P_C}$$

Here, we use the temperature dependence of the α term proposed by Stryjek and Vera.

$$\alpha(T) = \left[1 + \kappa\left(1 - \sqrt{T/T_C}\right)\right]^2$$

$$\kappa = \kappa_0 + \kappa_1(1 + T_r^{0.5})(0.7 - T_r)$$

$$\kappa_0 = 0.378893 + 1.4897153\omega - 0.1713184\omega^2 + 0.0196554\omega^3$$

where the k_1 is specific constant for each pure compound. k_1 of the PRSV equation is obtained by fitting pure component saturation pressure(P^{vap}) versus temperature data. The stryjek-Vera modification of α takes care of the inaccuracies in temperature dependence of the term at low temperature.

These mixing rules have been developed that combine excess free-energy models (NRTL model in this study) with a cubic EOS (PRSV EOS in this study). Various mixing rules based on this concept are expressed as follows.[2]

Mixing rules

The Huron-Vidal (Original) Mixing Rules (HVO)

$$a = b\left[\sum xi\left(\frac{a_i}{b_i}\right) + \frac{G^{ex}{}_\gamma}{C^*}\right] \qquad b = \sum_i x_i b_i$$

The Modified Huron-Vidal 1st order Mixing Rules (MHV1)

$$\frac{G^{ex}{}_\gamma}{RT} = -\sum_i x_i \ln\left(\frac{b}{b_i}\right) + q_1\left(\frac{a}{bRT} - \sum_i x_i \frac{a_i}{b_i RT}\right) \qquad b = \sum_i x_i b_i$$

The Modified Huron-Vidal 2nd order Mixing Rules (MHV2)

$$q_1\left(\varepsilon - \sum_i x_i \varepsilon i\right) + q_2\left(\varepsilon^2 - \sum_i x_i \varepsilon_i^{\,2}\right) = \frac{G^{ex}{}_\gamma(T, x_i)}{RT} + \sum x_i \ln\left(\frac{b}{b_i}\right) \qquad b = \sum_i x_i b_i$$

The Linear Combination of Huron-Vidal and Michelsen Models (LCVM)

$$\frac{a}{bRT} = \left(\frac{\lambda}{C^*} + \frac{1-\lambda}{q_1}\right)\frac{G^{ex}{}_\gamma}{RT} + \frac{1-\lambda}{q_1}\sum_i x_i \ln\left(\frac{b}{b_i}\right) + \sum_i x_i \frac{a_i}{b_i RT} \qquad b = \sum_i x_i b_i$$

The Orbey-Sandler Modification of Huron-Vidal mixing rules (HVOS)

$$\frac{A^{ex}{}_{EOS}}{RT} = \frac{G^{ex}{}_\gamma}{RT} = -\sum_i x_i \ln\left(\frac{b}{b_i}\right) + C^*\left(\frac{a}{bRT}\right) - \sum_i x_i \frac{a_i}{b_i} \qquad b = \sum_i x_i b_i$$

Table 1. Optimum k_1 values of pure component in the PRSV equation of state

chemical	Temperature range (K)	k_1	Data source
HFC-134a	293.15~303.15	0.0020	REFPROP 6.0 [3]
propane	293.15~303.15	-0.0028	REFPROP 6.0 [3]

In this study we use the NRTL model as excess free-energy model and set the nonrandomness parameter, a_{ij}, equal to 0.3 for binary mixture studied here.

Results and discussion

The VLE of propane/HFC-134a system were predicted using various mixing rules combined with NRTL excess free energy model and the PRSV equation of state. k_1 of the pure components (propane and HFC-134a) in the range of 293.15~303.15 K were listed in Table 1 and all the binary parameters of the NRTL model with six mixing rules were listed in Table 2. These mixing rules combined with PRSV equation of state and an activity coefficient model (NRTL) for the G^{ex} term show very good correlations for the vapor-liquid equilibria of refrigerant mixtures. The AAD(%) of this system were listed in Table 3.

In this system, there exist azeotropes. The azeotropic points change with temperature and they were x_1 = 0.6207(mole fraction), P = 1.056 MPa at 293.15 K, and x_1 = 0.6798(mole fraction), P = 1.363 MPa at 303.15 K for propane/HFC-134a system, respectively.

Table 2. Values of NRTL parameters in PRSV EOS-G^{ex} (NRTL) model

	EOS-G^{ex} Model NRTL parameters				
	HV-O	MHV1	MHV2	LCVM	HVOS
			293.15 K		
A_{12}	873.071	781.450	719.099	802.098	902.367
A_{21}	477.268	316.038	308.565	368.332	450.572
P_{12}	1.498	1.341	1.234	1.376	1.549
P_{21}	0.819	0.524	0.529	0.6323	0.773
			303.15 K		
A_{12}	983.293	1216.083	1091.167	1270.654	980.960
A_{21}	349.234	-11.656	5.995	19.073	350.491
P_{12}	1.632	2.018	1.811	2.109	1.628
P_{21}	0.579	-0.019	0.010	0.031	0.581

* The unit of A_{12} and A_{21} is cal/mol and P_{12}(A_{12}=RT) and P_{21}(A_{21}=RT) is dimensionless

Table 3. AAD(%) of P by various mixing rules

	HV-O	MHV1	MHV2	LCVM	HVOS
		AAD-y(%)			
293.15 K	1.283	1.537	1.762	1.428	1.337
303.15 K	2.014	3.620	4.003	1.988	1.988
		AAD-P(%)			
293.15 K	1.100	1.154	1.256	1.136	1.093
303.15 K	0.733	1.499	1.788	0.740	0.740

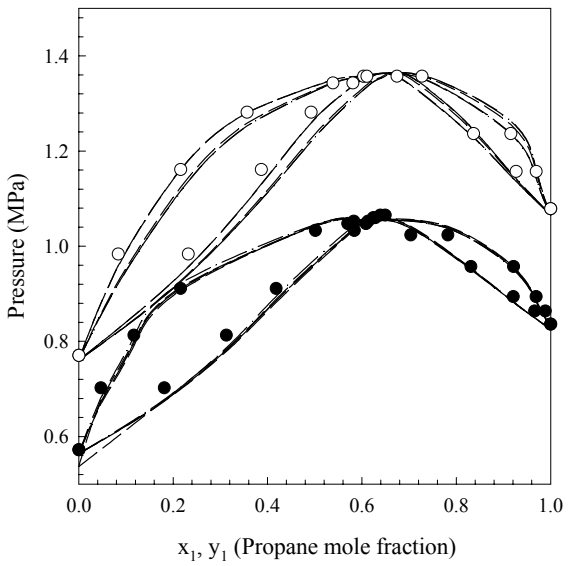

Figure 1. VLE prediction curve for propane + HFC-134a system using the NRTL model with PRSV EOS-Gex models. (●); exp. at 293.15 K, (○); exp. at 303.15 K, (- -); HV-O model, (---); MHV1 model, (-···-); MHV2 model, (——);LCVM model, (···); HVOS model

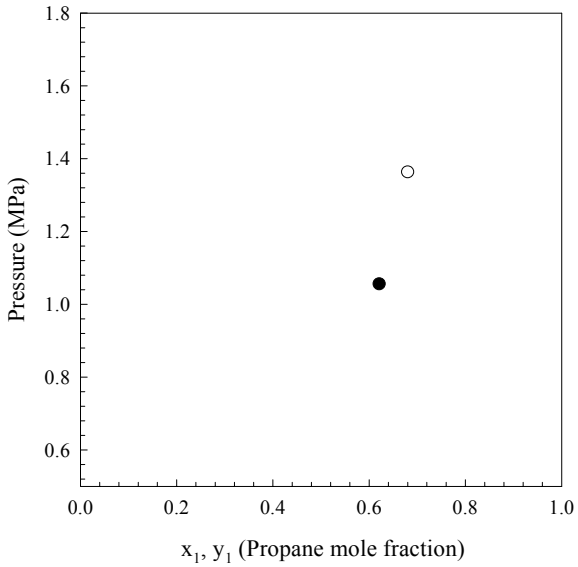

Figure 2. The azeotropic composition with pressure for propane + HFC-134a system, (●); exp. at 293.15 K, (○); exp. at 303.15 K.

Literature Cited

1. D. S. H., Wong and S. I., Sandler, *AIChE J.*, 38(5), 671-680, (1992)
2. H. Orbey., S. I. Sandler., "Modeling Vapor-Liquid Equilibria-cubic equation of state and their mixing rules", 19-74, (1998)
3. M. Huber, J. Gallagher, M. O. McLinden, G. Morrison, "Thermodynamic Properties of Refrigerants and Refrigerant Mixtures Database(REFPROP) V.5.0", NIST, (1996)