Journal of Zhejiang University SCIENCE
ISSN 1009-3095
http://www.zju.edu.cn/jzus
E-mail: jzus@zju.edu.cn

Extension of LCVM-type mixing rule to three-parameter equations of state for vapor-liquid equilibria of mixtures*

HAN Xiao-hong (韩晓红)[†], CHEN Guang-ming (陈光明)[†‡], WANG Qin (王 勤), CUI Xiao-long (崔晓龙)

(*Institute of Refrigeration and Cryogenics, Zhejiang University, Hangzhou 310027, China*)

[†]E-mail: hanxh@163.com; gmchen@zju.edu.cn

Received Apr. 9, 2005; revision accepted July 17, 2005

Abstract: In this paper, the LCVM mixing rule is extended to the multi-parameter equations of state by combining infinite-pressure and zero-pressure mixing rule models. The new LCVM-type mixing rule, coupled with Patel-Teja equation of state (EOS) is applied for vapor-liquid equilibria of different polar and non-polar systems in which the NRTL activity coefficient model is used to calculate the excess Gibbs free energy. The tested results agree well with existing experimental data within a wide range of temperatures and pressures. In comparison with the Van der Waals mixing rule, the new mixing rule gives much better correlations for the vapor-liquid equilibria of non-polar and polar systems.

Key words: Vapor-liquid equilibrium (VLE), Equation of state (EOS), Mixing rule, Activity coefficient model
doi:10.1631/jzus.2005.AS0017 **Document code:** A **CLC number:** O642.4; TQ013.1

INTRODUCTION

Vapor-liquid equilibrium (VLE) calculations often use activity coefficient models. Such approach is quite popular, mainly because of the availability of methods for predicting the activity coefficient models, like NRTL model (Renon and Prausnitz, 1968). However, it does not solve the problem of treating systems containing gaseous components and/or in the critical region. The EOS (equation of state) methods enjoy many potential advantages, such as the possibility of treating high pressures and the near-critical range and calculating a consistent set of phase properties. There is great progress in making full use of the merits of the two methods, and in using excess thermodynamic properties in combination with EOSs and activity coefficient models. Several classical based on excess free energy models mixing rules proposed in recent years combine the advantages due partially to equations of state and activity coefficient models for liquids to obtain better extrapolation at high temperatures and pressures and to achieve an accurate description of the composition of non-polar, polar and strong polar systems for VLE prediction. These mixing rules include HV (Huron and Vidal, 1979), MHV1 and MHV2 (Michelsen, 1990), PSRK (Holderbaum and Gmehling, 1991), LCVM (Boulouvalas *et al.*, 1994), HVOS (Orbey and Sandler, 1995). But most of them were proposed for two-parameter EOSs. There are very few reports on application of these excess free energy models to three-parameter EOSs (Yang *et al.*, 1997; Han *et al.*, 2005). Thus, with the rapid development of computer technology and the merits for three-parameter EOSs, the mixing rule proposed for two-parameter EOSs can be extended to three-parameter EOSs. Therefore, how to apply excess free energy type mixing rule to three-parameter EOSs to improve their prediction accuracy is worth investigating. The LCVM mixing rule with no theoretic but empirical base was originally developed by combing infinite-pressure and zero-pressure mixing models. This model provides reasonable results for highly asymmetric mixtures. In

---

[‡] Corresponding author

[*] Project (No. 50276054) supported by the National Natural Science Foundation of China

addition, LCVM mixing rule's parameter δ which influences the Flory-Huggins logarithmic term and the excess energy term make the model have relatively high accuracy for predicting highly asymmetric mixtures. In this paper, we extended the concept of LCVM-type mixing rule to three-parameter EOSs to correlate the VLE of mixtures. The correlated results agreed well with the experimental data over a wide range of temperatures and pressures.

DERIVATION OF LCVM-TYPE MIXING RULE

Taking Patel-Teja EOS (Patel and Teja, 1982) as an example, the new LCVM-type mixing rule for three-parameter EOSs was derived.

Patel-Teja equation of state

The Patel-Teja (P-T) equation of state is written as

$$p = RT/(v-b) - a/\left[v(v+b)+c(v-b)\right] \tag{1}$$

where p is the pressure, v is the molar volume, T is the absolute temperature, R is the universal gas constant, and a, b, c are the equation of state's dependent parameters, given as

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

$$b = \Omega_b R T_c / P_c \tag{3}$$

$$c = \Omega_c R T_c / P_c \tag{4}$$

where

$$\Omega_c = 1 - 3\xi_c \tag{5}$$

$$\Omega_a = 3\zeta_c^2 + 3(1-2\zeta_c)\Omega_b + \Omega_b^2 + 1 - 3\zeta_c \tag{6}$$

while Ω_b is the least value of the following equation

$$\Omega_b^3 + (2-3\zeta_c)\Omega_b^2 + 3\zeta_c^2\Omega_b - \zeta_c^3 = 0 \tag{7}$$

The temperature-dependent function $\alpha(T_r)$ is defined as

$$\begin{aligned}\alpha(T_r) = [1 + (0.452412 + 1.30932\omega \\ - 0.295937\omega^2)(1 - T_r^{0.5})]^2\end{aligned} \tag{8}$$

where ω is the acentric factor.

Derivation of the new LCVM-type mixing rule

Using the basic thermodynamic relations and Eq.(1), the excess Helmholtz free energy at constant temperature and pressure of component i is given by

$$\begin{aligned}\frac{A^E}{RT} = -\sum_i x_i \ln\left(\frac{Z_{\mathrm{m}}}{Z_i}\right) - \sum_i x_i \ln\left(\frac{1-b_{\mathrm{m}}/v_{\mathrm{m}}}{1-b_i/v_i}\right) \\ + \frac{a_{\mathrm{m}}}{b_{\mathrm{m}}RT}\lambda_{\mathrm{m}} - \sum_i x_i\left(\frac{a_i}{b_iRT}\right)\lambda_i\end{aligned} \tag{9}$$

where subscript 'm' means mixture.

Assuming $u_{\mathrm{m}0}=v_{\mathrm{m}}/b_{\mathrm{m}}\approx v_i/b_i=u_{i0}$, the expressions for the parameters λ_{i0} and $\lambda_{\mathrm{m}0}$ at zero pressure are obtained by Eq.(9) as

$$\begin{aligned}\lambda_{i0} = &\frac{1}{\sqrt{1+6\psi_{i0}+\psi_{i0}^2}} \\ &\times \ln\frac{u_{i0} + \left(\psi_{i0}+1+\sqrt{1+6\psi_{i0}+\psi_{i0}^2}\right)/2}{u_{i0} + \left(\psi_{i0}+1-\sqrt{1+6\psi_{i0}+\psi_{i0}^2}\right)/2}\end{aligned} \tag{10}$$

$$\begin{aligned}\lambda_{\mathrm{m}0} = &\frac{1}{\sqrt{1+6\psi_{\mathrm{m}0}+\psi_{\mathrm{m}0}^2}} \\ &\times \ln\frac{u_{\mathrm{m}0} + \left(1+\psi_{\mathrm{m}0}+\sqrt{1+6\psi_{\mathrm{m}0}+\psi_{\mathrm{m}0}^2}\right)/2}{u_{\mathrm{m}0} + \left(1+\psi_{\mathrm{m}0}-\sqrt{1+6\psi_{\mathrm{m}0}+\psi_{\mathrm{m}0}^2}\right)/2}\end{aligned} \tag{11}$$

where

$$\psi_{i0} = c_i / b_i \tag{12}$$

Taking the 2:1 geometric average of the Lorentz and Arithmetic rules (Sadus, 1993), the parameter $\psi_{\mathrm{m}0}$ can be expressed by the following combining rule as

$$\begin{aligned}\psi_{\mathrm{m}0} = \sum_i\sum_j\Big[x_ix_j\left(\left(\psi_{i0}^{1/3}+\psi_{j0}^{1/3}\right)/2\right)^2 \\ \times\left(\left(\psi_{i0}+\psi_{j0}\right)/2\right)^{1/3}\Big]\end{aligned} \tag{13}$$

At zero pressure, the optimum value $u_{i0}=u_{\mathrm{m}0}\approx 1.18$ obtained by Twu *et al.*(1998) and at infinite pressure, $u_{\mathrm{m}\infty}=v_{\mathrm{m}}/b_{\mathrm{m}}\approx v_i/b_i=u_{i\infty}=1$, while the expressions of $\lambda_{i\infty}$ and $\lambda_{\mathrm{m}\infty}$ can be obtained in the same form as given in Eqs.(10) and (11), by changing u_{i0} to $u_{i\infty}$ and $u_{\mathrm{m}0}$ to $u_{i\infty}$.

The formulation of the new mixing rule for parameter α ($=a/(bRT)$) is based on the concept of the LCVM mixing rule, that is, the parameter $\alpha_{\text{LCVM-M}}$ in the new mixing rule is expressed as a linear combination of α_{v} (HVOS mixing rule expression at infinite pressure) and α_{M} (MHV1 mixing rule expression at zero pressure), as given by

$$\alpha_{\text{LCVM-M}} = \delta\alpha_{\text{v}} + (1-\delta)\alpha_{\text{M}} \tag{14}$$

Using Eq.(9), the expressions of α_{v} and α_{M} are obtained as

$$\alpha_{\text{v}} = \sum_i \left(x_i \frac{\lambda_{i\infty}}{\lambda_{\text{m}\infty}} \frac{a_i}{b_i RT} \right) + \frac{1}{\lambda_{\text{m}\infty}} \left(\frac{A^{\text{E}}_{p\to\infty}}{RT} + \sum_i \left(x_i \ln \frac{b_{\text{m}}}{b_i} \right) \right) \tag{15}$$

$$\alpha_{\text{M}} = \sum_i \left(x_i \frac{\lambda_{i0}}{\lambda_{\text{m}0}} \frac{a_i}{b_i RT} \right) + \frac{1}{\lambda_{\text{m}0}} \left(\frac{A^{\text{E}}_{p\to 0}}{RT} + \sum_i \left(x_i \ln \frac{b_{\text{m}}}{b_i} \right) \right) \tag{16}$$

where superscript E is excess property.

Substituting Eqs.(15)~(16) into Eq.(14), yields

$$\begin{aligned} \frac{a_{\text{m}}}{b_{\text{m}} RT} &= \sum_i \left[x_i \left(\frac{\delta\lambda_{i\infty}}{\lambda_{\text{m}\infty}} + \frac{(1-\delta)\lambda_{i0}}{\lambda_{\text{m}0}} \right) \frac{a_i}{b_i RT} \right] \\ &\quad - \left(\frac{\delta}{\lambda_{\text{m}\infty}} + \frac{(1-\delta)}{\lambda_{\text{m}0}} \right) \frac{A^{\text{E}}_{\gamma}}{RT} \\ &\quad - \left(\frac{\delta}{\lambda_{\text{m}\infty}} + \frac{(1-\delta)}{\lambda_{\text{m}0}} \right) \sum_i \left[x_i \ln \left(\frac{b_{\text{m}}}{b_i} \right) \right] \end{aligned} \tag{17}$$

We chose EOS parameter b_{m} satisfying the two known boundary conditions, that is, at low pressures, the equation of state should produce a second virial coefficient which is quadratic in composition and at high densities, the equation of state should behave like an activity coefficient model. Therefore

$$B_{\text{m}} = b_{\text{m}} - \frac{a_{\text{m}}}{RT} = \sum_i \sum_j \left[x_i x_j (b - a/(RT))_{ij} \right] \tag{18}$$

while, for the parameter c_{m}, the following expression is adopted

$$c_{\text{m}} = (\psi_{\text{m}0} + \psi_{\text{m}\infty}) b_{\text{m}} / 2 \tag{19}$$

Thus, Eqs.(17)~(19), together with Eqs.(10)~(14), constitute a complete set of the new LCVM-type mixing rules. Here, the parameter δ [in Eq.(17)] determining the relative contribution of MHV1 and HVOS models, was obtained by fitting the bubble point pressures for a variety of binary mixtures at high and low pressures. We used δ=0.36, the same value used by Boukouvalas *et al*.(1994). The mixing rule uses two reference pressures, and has no basis in theory. But depending on the assumptions (Orbey and Sandler, 1995) that $A^{\text{E}}_{p\to\infty}$ and $A^{\text{E}}_{p\to 0}$ are identical, the parameters obtained from a liquid activity model at low pressure are directly usable for both pressures.

Fugacity coefficient

The general expression of the fugacity coefficient ϕ_i for a species in a mixture, needed for phase behavior calculations, is calculated from the expression below

$$RT \ln \phi_i = \int_v^{\infty} \left(\frac{\partial p}{\partial n_i} - \frac{RT}{v} \right) \mathrm{d}v - RT \ln z \tag{20}$$

The mixture fugacity coefficient ϕ_i of P-T EOS can be obtained by Eq.(1) and Eq.(20), as

$$\begin{aligned} \ln \phi_i &= \ln(Z-B) + \frac{1}{v-b} \left(\frac{\partial (n_T b_{\text{m}})}{\partial n_i} \right) \\ &\quad - \frac{L}{RT} \left(\frac{\frac{1}{n_T} \frac{\partial (n_T^2 a_{\text{m}})}{\partial n_i}}{K b_{\text{m}}} - \frac{a_m \left(\frac{\partial (n_T d_{\text{m}})}{\partial n_i} - \frac{\partial (n_T e_{\text{m}})}{\partial n_i} \right)}{(K b_{\text{m}})^2} \right) \\ &\quad - \left(\frac{a_{\text{m}}}{RT b_{\text{m}} K} \frac{\partial (n_T d_{\text{m}})}{\partial n_i} \left(\frac{1}{v - d_{\text{m}}} \right) - \frac{a_{\text{m}}}{RT b_{\text{m}} K} \frac{\partial (n_T e_{\text{m}})}{\partial n_i} \left(\frac{1}{v - e_{\text{m}}} \right) \right) \end{aligned} \tag{21}$$

where

$$L = \frac{1}{K b_{\text{m}}} \ln \left(\frac{2Z + [(b_{\text{m}} + c_{\text{m}}) + b_{\text{m}} K] p/(RT)}{2Z + [(b_{\text{m}} + c_{\text{m}}) - b_{\text{m}} K] p/(RT)} \right),$$

$$K = \sqrt{c_{\text{m}}^2 / b_{\text{m}}^2 + 6 c_{\text{m}} / b_{\text{m}} + 1}, \quad d_{\text{m}} = 0.5[-(b_{\text{m}} + c_{\text{m}}) + b_{\text{m}} K],$$

$$e_{\text{m}} = 0.5[-(b_{\text{m}} + c_{\text{m}}) - b_{\text{m}} K],$$

$$\frac{1}{n_T} \frac{\partial (n_T^2 a_{\text{m}})}{\partial n_i} = \frac{\frac{\partial (n_T \alpha)}{\partial n_i} + \left(\frac{a_{\text{m}}}{RT} - \frac{\partial n_T B_{\text{m}}}{\partial n_i} \right) E_2}{-E_2/(RT) - E_1}$$

$$\left[\text{with}\, E_1=1/(b_\mathrm{m}RT),\ E_2=-\frac{1}{b_\mathrm{m}}\left(\frac{a_\mathrm{m}}{b_\mathrm{m}RT}-\left(\frac{\delta}{\lambda_{\mathrm{m}\infty}}+\frac{(1-\delta)}{\lambda_{\mathrm{m}0}}\right)\right)\right],$$

$$\frac{\partial(n_T b_\mathrm{m})}{\partial n_i}=\frac{-\dfrac{\partial(n_T\alpha)}{RT\partial n_i}+\left(\dfrac{a_\mathrm{m}}{RT}-\dfrac{\partial n_T B_\mathrm{m}}{\partial n_i}\right)E_1}{E_1+E_2/(RT)},$$

$$\frac{\partial(n_T c_\mathrm{m})}{\partial n_i}=0.5\left(-\left(\frac{\partial(n_T\psi_{\mathrm{m}0})}{\partial n_i}+\frac{\partial(n_T\psi_{\mathrm{m}\infty})}{\partial n_i}\right)b_\mathrm{m}+(\psi_{\mathrm{m}0}+\psi_{\mathrm{m}\infty})\frac{\partial(n_T b_\mathrm{m})}{\partial n_i}\right),$$

$$\frac{\partial(n_T d_\mathrm{m})}{\partial n_i}=0.5\left(-\left(\frac{\partial(n_T b_\mathrm{m})}{\partial n_i}+\frac{\partial(n_T c_\mathrm{m})}{\partial n_i}\right)+\frac{b_\mathrm{m}\dfrac{\partial(n_T b_\mathrm{m})}{\partial n_i}+3b_\mathrm{m}\dfrac{\partial(n_T c_\mathrm{m})}{\partial n_i}+3c_\mathrm{m}\dfrac{\partial(n_T b_\mathrm{m})}{\partial n_i}+c_\mathrm{m}\dfrac{\partial(n_T c_\mathrm{m})}{\partial n_i}}{Kb_\mathrm{m}}\right),$$

$$\frac{\partial(n_T e_\mathrm{m})}{\partial n_i}=0.5\left(-\left(\frac{\partial(n_T b_\mathrm{m})}{\partial n_i}+\frac{\partial(n_T c_\mathrm{m})}{\partial n_i}\right)-\frac{b_\mathrm{m}\dfrac{\partial(n_T b_\mathrm{m})}{\partial n_i}+3b_\mathrm{m}\dfrac{\partial(n_T c_\mathrm{m})}{\partial n_i}+3c_\mathrm{m}\dfrac{\partial(n_T b_\mathrm{m})}{\partial n_i}+c_\mathrm{m}\dfrac{\partial(n_T c_\mathrm{m})}{\partial n_i}}{Kb_\mathrm{m}}\right).$$

NRTL model

The excess Gibbs energy calculated by using the NRTL local composition model, is

$$\frac{G^\mathrm{E}_{(T,P)}}{RT}=\sum_i x_i\sum_j\frac{x_j\exp\left(-\alpha_{j,i}\dfrac{\tau_{j,i}}{RT}\right)}{\sum_k x_k\exp\left(-\alpha_{k,i}\dfrac{\tau_{k,i}}{RT}\right)}\tau_{j,i} \tag{22}$$

while the relation between the activity coefficient and composition in the NRTL model is given by

$$\ln\gamma_i=\frac{\sum_j x_j\tau_{ji}G_{ji}}{\sum_k x_k G_{ki}}+\sum_j\frac{x_j G_{ij}}{\sum_k x_k G_{kj}}\left(\tau_{ij}-\frac{\sum_l x_l\tau_{lj}G_{lj}}{\sum_k x_k G_{kj}}\right) \tag{23}$$

where $G_{ji}=\exp(-a_{ji}\tau_{ji})$, $a_{ji}=a_{ij}$, $\tau_{i,i}=0$, $a_{i,i}=0$. $a_{j,i}$, $\tau_{j,i}$ and $\tau_{i,j}$ are adjustable parameters. The parameter a_{ji} is composition and temperature independent but is only a characteristic parameter of solution dependent, in other words, if $a_{ji}=0$, the solution is random, if $a_{ji}\neq 0$, the solution is not random. Renon and Prausnitz (1968) chose a_{ji} of 0.20~0.47 for different substances.

In the present paper, we chose $a_{j,i}=0.3$. While the parameters $\tau_{j,i}$ and $\tau_{i,j}$ are adjusted directly to VLE data, using the objective function through the following algorithm

$$OF=\sum_i^N\left((y_{1,\mathrm{exp}}-y_{1,\mathrm{cal}})_i^2+(y_{2,\mathrm{exp}}-y_{2,\mathrm{cal}})_i^2\right) \tag{24}$$

where subscripts 'exp' and 'cal' mean experimental value and calculated value, respectively.

RESULTS AND DISCUSSION

In Table 1, δp and Δy are the calculated average derivations of the pressure and vapor composition respectively

$$\delta p=1/N\sum_i\left|(p_\mathrm{cal}-p_\mathrm{exp})/p_\mathrm{exp}\right|_i \tag{25}$$

$$\Delta y=1/N\sum_i\left|y_\mathrm{cal}-y_\mathrm{exp}\right|_i \tag{26}$$

The new LCVM-type mixing rule, coupled with P-T EOS, was tested for VLE of nonpolar-nonpolar, nonpolar-polar and polar-polar systems, such as cryogenic mixtures of Ar-N_2, N_2-O_2, Methane-ethylene, refrigerant mixtures of R134a+R143a, R134a+R600a, Propylene+propane, R134a+R235fa, R600a+R235fa, R32+R227ea, R290+R600a and other mixtures of ethanol+water, methyl-acetate+ethyl -acetate, hydrogen sulfide+propane, in which the NRTL activity coefficient model is used to calculate the excess Gibbs free energy. The average absolute deviation (AAD) of vapor pressure obtained for P-T EOS with the new mixing rule and P-T EOS with the Van der Waals mixing rule is shown in Table 1 showing that over a wide range of temperature and pressure, using P-T EOS, combined with the Van der Waals mixing rule, yields large deviations for several systems, for example, ethanol+water, methanol+

Table 1 Correlation results for different systems using P-T EOS

System	Temp. ranges (K)	*N*	P-T+VDW mixing rule		P-T+the new LCVM-type mixing rule		Ref.
			δp (%)	Δy	δp (%)	Δy	
R143a+R134a	273.15~313.15	27	5.0231	0.0816	3.4460	0.0209	Lim *et al.*(2002)
R143a+R152a	303.15~313.15	12	6.0123	0.0563	2.9869	0.0217	
Ethanol+water	423.15~473.15	15	12.3598	0.0236	1.3892	0.0418	Niesen *et al.*(1986)
R134a+R600a	293.66~303.68	19	3.0498	0.0056	2.0878	0.0170	Bobbo *et al.*(1998)
R134a+R235fa	283.96~303.68	15	2.0023	0.0032	4.0637	0.0201	
R600a+R235fa	303.68	12	3.3897	0.0162	3.5820	0.0075	
Methanol+water	321.91~373.15	36	14.0261	0.0401	4.4058	0.0208	Mitsuho *et al.*(1986)
Acetone+water	298.15~423.15	22	12.3224	0.0456	5.3093	0.0190	
Carbon dioxide+ethylene	252.95	12	6.3215	0.0105	4.6863	0.0084	
Acetone+methanol	373.15~423.15	25	7.3215	0.0188	6.0683	0.0325	
Methanol+ TEGDME	293.15~393.15	36	11.3243	0.0325	5.8995	0.0152	
Propylene+propane	260.95~329.85	23	3.3029	0.0147	0.9456	0.0173	
Methane/ethylene	186.25~206.25	19	5.3021	0.0221	2.5860	0.0103	
Hydrogen sulfide+propane	243.15~288.15	19	10.3856	0.8020	1.4498	0.0189	
MTB+methyl-acetate	353.15~373.15	30	0.3243	0.0212	2.0477	0.0097	Lee *et al.*(1997)
Acetone+methyl-acetate	293.15~313.15	33	0.0626	0.0057	0.1777	0.0048	
methyl-acetate+ethyl-acetate	353.15~373.15	24	8.2535	0.0203	1.6193	0.0166	
N_2+O_2	70.15~77.65	30	3.6201	0.0103	3.8012	0.0170	Kagan *et al.*(1974)
R32+R227ea	283.20~323.21	21	8.3642	0.0364	5.2318	0.0198	Coquelet *et al.*(2003)
R290+R600a	253.15~323.15	36	3.2589	0.0213	1.1380	0.0198	Jong *et al.*(2004)

water, acetone+water, methanol+TEGDME, hydrogen sulfide+propane, while the results from the new LCVM-type mixing rule with P-T EOS is in good agreement with the existing experimental data, and shows much better agreement with data than the Van der Waals rule. Besides, the average derivations of pressure and composition are smaller, that is to say, the new LCVM-type mixing rule with P-T EOS gives much better correlations for VLE systems.

CONCLUSION

Though multi-parameter EOSs were not used widely in many calculations in the past, now with the development of computer technology, they can be widely used in view of their own merits. For mixtures, many mixing rules (e.g. the proposed G^E-type mixing rule in recent years) were proposed only for two-parameter EOSs, thus decreasing their applications in G^E-type mixing rules. Therefore, it is necessary to extend them to multi-parameter EOSs. In this paper, based on the experiment of LCVM mixing rule adapting to two-parameter EOSs, i.e. forming the linear combination of a_v at infinite pressure and a_M at zero pressure, it has been extended to the multi-parameter equations of state. In the new LCVM-type mixing rule adapting to the three-parameter EOSs, the reduced parameters λ_0 and λ_∞ were introduced. The parameter δ which determines the relative contributions of zero pressure and infinite pressure was obtained by fitting the bubble point pressures for a variety of binary mixtures at high and low pressures. In addition, the parameter b_m in the model satisfies the second virial coefficient boundary condition based on statistical mechanics. Although the new LCVM-type mixing rule has no basis in theory, it can use the activity coefficient model at low pressure. Coupled with Patel-Teja equation of state (EOS), it has been applied for vapor-liquid equilibria of different polar and non-polar systems in which the NRTL activity coefficient model is used to calculate the excess Gibbs free energy. The results showed that it could give out much better correlations for the VLE systems by comparison of the VDW mixing rule and P-T EOS.

References

Bobbo, S., Roman, S., Nicola, E., Alberto, B., 1998. A recirculation apparatus for vapor-liquid equilibrium measurements of refrigerants. Binary mixtures of R600a, R134a, R236fa. *Fluid Phase Equilibria*, **150-151**: 343-352.

Boulouvalas, C., Spiliotis, N., Coutsikos, P., Tzouvaras, N., 1994. Prediction of vapor-liquid equilibrium with LCVM model: A linear combination of the Huron-Vidal and Michelsen mixing rules coupled with the original UNIFAC and the t-mPR equation of state. *Fluid Phase Equilibria*, **92**:75-106.

Coquelet, C., Hong, D.N., Chareton, A., Baba-Ahmed, A., Richon, D., 2003. Vapor-liquid equilibrium data for the difluoromethane+1,1,1,2,3,3,3-heptafluoropropane system at temperatures from 283.2 to 343.38 K and pressures up to 4.5 MPa. *Int. J. of Refr.*, **26**:559-565.

Han, X.H., Wang, Q., Chen, G.M., Cui, X.L., 2005. Extension of Huron-type mixing rule to three-parameter Harmens-Knapp cubic equation of state. *Chemical Research in Chinese Universities*, **21**(3):209-212.

Holderbaum, T., Gmehling, J., 1991. PSRK: A group contribution equation of state based on UNFIAC. *Fluid Phase Equilibria*, **70**:251-265.

Huron, M., Vidal, J., 1979. New Mixing rules in simple equations of State for representing vapor-liquid equilibria of strongly non-ideal mixtures. *Fluid Phase Equilibria*, **3**:225-271.

Jong, S.L., Quang, N.H., Ji, Y.P., Lee, B.G., 2004. Measurement of vapor-liquid equilibria for the binary mixture of Propane (R-290)+Isobutane (R-600a). *J. Chem. Eng. Data*, **49**:192-198.

Kagan, B.B., Fulideman, B.M., Kafalafu, B.B., Guangshui, P.T., 1974. Vapor-liquid Equilibria Database (Version). Jiangtan Society Publishing Company, Tokyo, p.11-16.

Lee, M.J., Hsiao, C.C., Lin, H.M., 1997. Isothermal vapor-liquid equilibria for mixtures of methyl tetra-butyl ether, methyl acetate, and ethyl acetate. *Fluid Phase Equilibria*, **137**:193-207.

Lim, J.S., Park, J.Y., Lee, B.G., 2002. Phase equilibria of 1,1,1-trifluoroethane (HFC-143a)+1,1,1,2-tetrafluoroethane (HFC-134a), and +1,1-difluoroethane (HFC-152a) at 273.15, 293.15, 303.15, 313.15 K. *Fluid Phase Equilibria*, **193**:29-39.

Michelsen, M.L., 1990. A modified Huron-Vidal mixing rule for cubic equations of state. *Fluid Phase Equilibria*, **60**:213-219.

Mitsuho, H., Shuzo, O., Kunio, N., 1986. Computer Aided Data Book of Vapor-liquid Equilibria. Amsterdam and American Elsevier Publishing Company, New York.

Niesen, V., Palavra, A., Kidnay, A.J., Yesavage, V.F., 1986. An apparatus for vapor-liquid equilibrium at elevated temperatures and pressures and selected results and pressures and selection results for water-ethanol and methanol-ethanol systems. *Fluid Phase Equilibria*, **31**:283-298.

Orbey, H., Sandler, S.I., 1995. On the combination of equations of state and free energy models. *Fluid Phase Equilibria*, **111**:53-70.

Patel, N.C., Teja, A.S., 1982. A new cubic equation of state for fluids and fluid mixtures. *Chem. Eng. Sci.*, **37**:463-473

Renon, H., Prausnitz, J.M., 1968. Local composition in thermodynamic excess function for liquid mixture. *AIChE J.*, **14**:135-144.

Sadus, R.J., 1993. Influence of combining rules and molecular shape on the high pressure phase equilibria of binary fluid mixtures. *J. Phys. Chem.*, **97**:1985-1992.

Twu, C.H., Coon, J.E., Bluck, D., Tilton, B., Rowland, M., 1998. Connection between zero-pressure mixing rules and infinite-pressure mixing rules. *Fluid Phase Equilibria*, **153**:29-44.

Yang, T., Chen, G.J., Yan, W., Guo, T.M., 1997. Extension of the Wong-Sandler mixing rule to the three-parameter Patel-Teja equation of State: Application up to the near-critical region. *Chem. Eng. J.*, **67**:27-36.