



## Short communication

Improper matching of solvation energy components in  $G^{\text{ex}}$ -based mixing rules

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## ABSTRACT

The physical significance of terms in two excess Gibbs free energy ( $G^{\text{ex}}$ )-based mixing rules, the modified Huron–Vidal (MHV1) and Wong–Sandler (WS) mixing rule, are examined through the use of solvation free energy. It is found that these mixing rules are in fact matching the charging contributions of solvation in an equation of state (EOS) to the complete solvation free energy in a liquid activity coefficient model (LM). The cavity contributions in the EOS are canceled as a result of the constant liquid molar volume to molecular volume ratio. The underlying idea of  $G^{\text{ex}}$ -based mixing rules that the EOS should behave like a LM at some limiting condition breaks down due to such an improper matching of solvation free energy components.

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## 1. Introduction

Excess Gibbs free energy ( $G^{\text{ex}}$ )-based mixing rules, such as the Huron–Vidal [1], the modified Huron–Vidal (MHV1) [2], and the Wong–Sandler (WS) [3] mixing rules, have attracted much attention for use in determination of the interaction parameters in cubic equations of state. Unlike conventional mixing rules in which the mixture parameters are obtained from “mixing” those of its components with certain composition dependence,  $G^{\text{ex}}$ -based mixing rules require the parameters to be determined at certain physically significant conditions. For example, the modified Huron–Vidal mixing rule requires that the liquid phase  $G^{\text{ex}}$  from an EOS to be the same as that from a liquid activity coefficient model (LM) at zero pressure.

The  $G^{\text{ex}}$ -based mixing rules provide a wonderful opportunity for making mixture VLE predictions over a wide range of temperature and pressure when combined with a predictive liquid model, such as UNIFAC [4,5], COSMO-RS [6–9], or COSMO-SAC [10,11]. However, it has been noted [11] that the combined model is often less accurate than the LM alone (assuming ideal vapor phase). In this communication, we show that one reason for the inferior behavior of the combined method is the assumption of equal ratio of liquid molar volume and the volume parameter in the EOS. By expressing  $G^{\text{ex}}$  in terms of solvation free energy, it is revealed that the cavity contributions of solvation from the EOS are cancelled as a result of

such an assumption. As a consequence, there is a mismatching of terms between those from the EOS and from the LM. We show that such a mismatching of free energy could have a significant effect on the VLE prediction especially when the volume parameters of the mixture components are very different.

## 2. The solvation properties from the Peng–Robinson equation of state

The solvation free energy  $\Delta G^{\text{*sol}}$  is the free energy change accompanied with a hypothetical process of transferring a solute molecule from a fixed position in an ideal gas to a fixed position in the fluid under constant temperature  $T$  and pressure  $P$ . It is a common practice [12–14] to decompose the solvation free energy into an attractive, referred to as charging  $\Delta G^{\text{*chg}}$ , and a repulsive, referred to as cavity  $\Delta G^{\text{*cav}}$ , contribution:

$$\Delta G^{\text{*sol}}(T, P, \underline{x}) = \Delta G^{\text{*chg}} + \Delta G^{\text{*cav}} \quad (1)$$

where the notation  $\underline{x}$  indicates that the fluid is a mixture with a certain composition. It can be shown [14,15] that the fugacity is related to the solvation free energy as

$$\ln \frac{f(T, P, \underline{x})}{P} = \frac{\Delta G^{\text{*sol}}}{RT} - \ln z \quad (2)$$

where  $z = PV/RT$  is the compressibility factor of the fluid. Note that in Eq. (2) we treat the mixture as a pseudo pure fluid. Additionally, since the solvation free energy is evaluated with the solute being fixed at some location in the fluid, it is different from the fugacity, which corresponds to the regular chemical potential, by the

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liberation free energy (the term  $RT \ln z$ ), i.e., the free energy gained when the solute is allowed to move [16].

With Eq. (2) the excess Gibbs free energy can readily be expressed in terms of the solvation free energy as

$$\frac{G^{\text{ex}}}{RT} = f(T, P, x) - \sum_i x_i f_i = \frac{\Delta G^{\text{*sol}}}{RT} - \sum_i x_i \frac{\Delta G_i^{\text{*sol}}}{RT} + \sum_i x_i \ln \frac{z_i}{z} \quad (3)$$

where we have used subscript  $i$  to denote the property of a pure fluid ( $f_i, z_i, \Delta G_i^{\text{*sol}}$ ), except that  $x_i$  is the mole fraction of component  $i$  in the mixture.

The molar solvation free energy can be determined from any EOS through the volume integration of the compressibility factor as [14]:

$$\frac{\Delta G^{\text{*sol}}}{RT} = (z - 1) + \int_{V=\infty}^V \frac{1 - z}{V} dV \quad (4)$$

For a fluid following Peng–Robinson EOS [17] the compressibility is

$$z = \frac{PV}{RT} = \frac{V}{V - b} - \frac{aV/RT}{V^2 + 2bV - b^2} = \frac{u}{u - 1} - \frac{\alpha u}{u(u + 1) + (u - 1)} \quad (5)$$

where  $a$  and  $b$  are the size and energy interaction parameters of the mixture. Note that in the last identity the compressibility is expressed in terms of two dimensionless quantities  $\alpha = a/(bRT)$  and  $u = V/b$ . Thus, the solvation free energy of a PR fluid becomes:

$$\begin{aligned} \frac{\Delta G^{\text{*sol}}}{RT} &= \left( \ln \frac{V}{V - b} + \frac{b}{V - b} \right) \\ &+ \frac{a}{bRT} \left[ \frac{1}{2\sqrt{2}} \ln \frac{V + b(1 - \sqrt{2})}{V + b(1 + \sqrt{2})} - \frac{bV}{V^2 + 2bV - b^2} \right] \\ &= \ln \frac{u}{u - 1} + \frac{1}{u - 1} \\ &+ \alpha \left[ \frac{1}{2\sqrt{2}} \ln \frac{u + (1 - \sqrt{2})}{u + (1 + \sqrt{2})} - \frac{u}{u(u + 1) + (u - 1)} \right] \quad (6) \end{aligned}$$

in which the cavity contribution is (i.e., by setting the energy interaction parameter  $a$  to zero):

$$\frac{\Delta G^{\text{*cav}}}{RT} = \ln \frac{V}{V - b} + \frac{b}{V - b} = \ln \frac{u}{u - 1} + \frac{1}{u - 1} \quad (7)$$

and the charging contribution:

$$\frac{\Delta G^{\text{*chg}}}{RT} = \alpha \left[ \frac{1}{2\sqrt{2}} \ln \frac{u + (1 - \sqrt{2})}{u + (1 + \sqrt{2})} - \frac{u}{u(u + 1) + (u - 1)} \right] \quad (8)$$

It should be noted here that the decomposition of the solvation free energy used here is slightly different from the formal definition for the cavity formation and charging processes [16], in which only the solute molecule (and not the solvent) is being charged from the state of a hard particle. Here the cavity formation free energy corresponds to the insertion of a hard particle in to a fluid of hard particles [18–22]; and the charging free energy corresponds to that of charging the solute and solvent molecules simultaneously.

### 3. The MHV1 mixing rule

Using the relations presented in Section 2, we can examine the MHV1 mixing rule for the PR EOS in terms of solvation. For MHV1 mixing rule, the excess Gibbs free energy from an EOS at zero pressure is set to that from an activity coefficient model, i.e.,

$$G_{\text{EOS}}^{\text{ex}}(T, P \rightarrow 0, x) = G_{\text{LM}}^{\text{ex}}(T, x) \quad (9)$$

The excess Gibbs free energy from the PR EOS is obtained from Eqs. (1), (3), (7) and (8):

$$\begin{aligned} \frac{\Delta G_{\text{PREOS}}^{\text{ex}}}{RT} &= \left( \frac{\Delta G^{\text{*chg}}}{RT} - \sum x_i \frac{\Delta G_i^{\text{*chg}}}{RT} \right) + \ln \frac{u}{u - 1} + \frac{1}{u - 1} \\ &- \sum x_i \left( \ln \frac{u_i}{u_i - 1} + \frac{1}{u_i - 1} \right) + \sum x_i \ln \frac{u_i b_i}{u b} \quad (10) \end{aligned}$$

An implicit assumption in MHV1 is that  $u = u_i = \text{constant}$  for the liquid phase at zero pressure (we will elaborate on this point later). As a consequence:

$$\frac{\Delta G_{\text{PREOS}}^{\text{ex}}(P \rightarrow 0)}{RT} = \left( \frac{\Delta G^{\text{*chg}}}{RT} - \sum x_i \frac{\Delta G_i^{\text{*chg}}}{RT} \right) + \sum x_i \ln \frac{b_i}{b} \quad (11)$$

Therefore, we can see that physical origin of the last term in Eq. (11) is the difference in the liberation free energy in different fluids (cf. Eq. (2)). More importantly, the cavity terms are cancelled as a result of the assumption of constant and equal value of  $u$  for the mixture and its components. Therefore, the charging term in the PR EOS has to include the complete solvation free energy when matching the excess Gibbs free energy to a liquid model (Eq. (9)).

Such mismatching of energy contributions impairs the original idea of forcing the VLE description from EOS to behave like that from LM at a given temperature and composition. To illustrate this, we compare the value of  $G^{\text{ex}}$  for a binary mixture calculated from the Margules model [23] ( $G^{\text{ex}} = -1000x_1x_2$  J/mol) and from the PR EOS with MHV1 mixing rule with the same Margules model for  $G^{\text{ex}}$ . The pure component parameters  $a$  for both components are set to be the same ( $a_1 = a_2 = 2.67$  J m<sup>3</sup>/mol) but with different ratios of parameter  $b$  ( $b_1 = 7.4 \times 10^{-5}$  m<sup>3</sup>/mol). As the vapor phase is close to ideal, one can expect that the same VLE description can be retained only when the calculated liquid phase  $G^{\text{ex}}$  from PR EOS is identical to that from the Margules model. However, it can be seen in Fig. 1a that only when  $b_1 = b_2$  will PR + MHV1 + Margules behave the same as the original Margules model. As  $b_1/b_2$  deviates from unity (0.5 and 1.4 case in Fig. 1a) PR + MHV1 + Margules will predict a higher value of  $G^{\text{ex}}$ , and in some instances even the sign of  $G^{\text{ex}}$  is reversed. Since the volume parameter  $b$  dominates the cavity contribution (see Eq. (7)), lacking of cavity contributions in MHV1 could lead to poor VLE predictions even at the temperatures where VLE predictions from the liquid model are accurate.

In Fig. 2a the Margules model is replaced with a more flexible Wilson model [23] ( $G^{\text{ex}}/RT = -x_1 \ln(x_1 + x_2 \Lambda_{12}) - x_2 \ln(x_2 + x_1 \Lambda_{21})$ ). The two parameters ( $\Lambda_{12} = 0.05$  and  $\Lambda_{21} = 3.0$ ) are chosen such that  $G^{\text{ex}}$  varies from positive numbers to negative numbers with varying the liquid composition (solid line in Fig. 2a). It is seen again that unless  $b_1/b_2$  equals unity, the liquid phase  $G^{\text{ex}}$  from PR + MHV1 + Wilson deviates from the Wilson model alone.

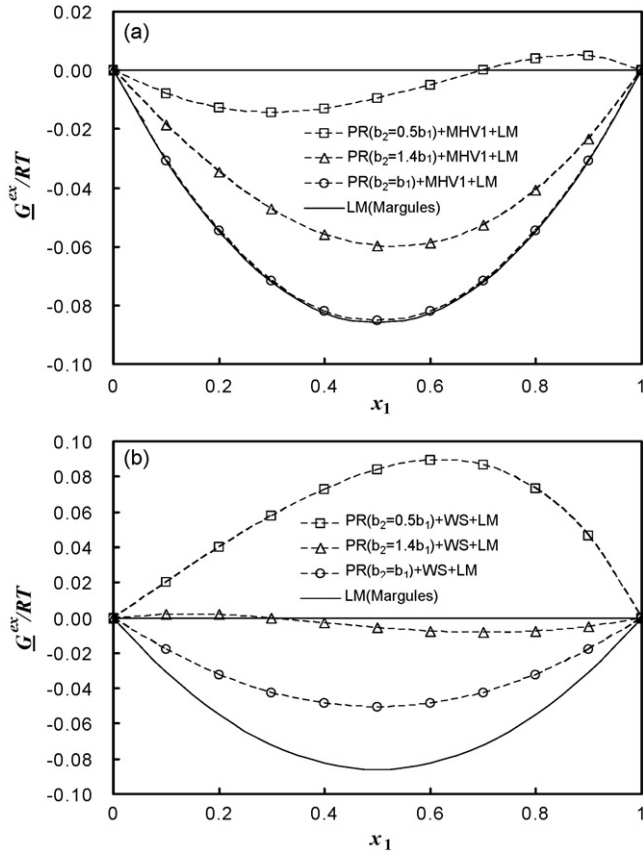
To show that Eq. (11) indeed gives the MHV1 equation, we need to express the charging free energy in terms of  $\alpha$ . At zero pressure  $u$  and  $\alpha$  are related according to the PR EOS (Eq. (5)) as

$$\frac{u}{u - 1} = \frac{\alpha u}{u(u + 1) + (u - 1)} \quad (12)$$

Thus, the charging free energy (Eq. (8)) becomes:

$$\frac{\Delta G^{\text{*chg}}(P \rightarrow 0)}{RT} = \alpha \left[ \frac{1}{2\sqrt{2}} \ln \frac{u + (1 - \sqrt{2})}{u + (1 + \sqrt{2})} \right] - \frac{u}{u - 1} \quad (13)$$

In MHV1, the dimensionless volume  $u$  was effectively a constant of value 1.2276. [Note in the original paper of Michelsen [2],  $q(\alpha) = \ln(f_0 b/RT) = \alpha q_1 + q_0$ . With the notation used here  $q(\alpha) = (\alpha/2\sqrt{2}) \ln[(u + (1 - \sqrt{2})) / (u + (1 + \sqrt{2}))] - 1 - \ln(u - 1)$ . Thus, a linearly function of  $q(\alpha)$  implies the use of a constant value



**Fig. 1.** Comparison of the value of  $G^{\text{ex}}$  from the Margules model ( $G^{\text{ex}} = -1000x_1x_2$ /mol) and from the PR EOS (dashed lines) combined with the same Margules model through the MHV1 (a) and WS (b) mixing rules at 350 K for different ratios of parameter  $b$  ( $b_1 = 7.4 \times 10^{-5}$  m<sup>3</sup>/mol):  $b_2/b_1 = 1.0$  (circle), 1.4 (triangle), and 0.5 (square). Pure component parameters  $a$  are set to be the same ( $a_1 = a_2 = 2.673$  m<sup>3</sup>/mol) for both components.

of  $u$  ( $=1.2276$ , giving  $q_1 = -0.53$  and  $q_2 = 0.48$ .) In such a case, the charging term (Eq. (13)) becomes a linear function of  $\alpha$ , i.e.,  $(\Delta G^{\text{ch}}/RT) = \alpha C_{\text{MHV1}} + \text{const}$  with  $C_{\text{MHV1}} = [(1/2\sqrt{2})\ln((u + (1 - \sqrt{2}))/(u + (1 + \sqrt{2})))] = -0.53$ .

Thus we recover the expression for MHV1 as

$$\frac{G^{\text{ex}}_{\text{PREOS}}(P \rightarrow 0)}{RT} = C_{\text{MHV1}} \left( \alpha - \sum_i x_i \alpha_i \right) + \sum_i x_i \ln \frac{b_i}{b} \quad (14)$$

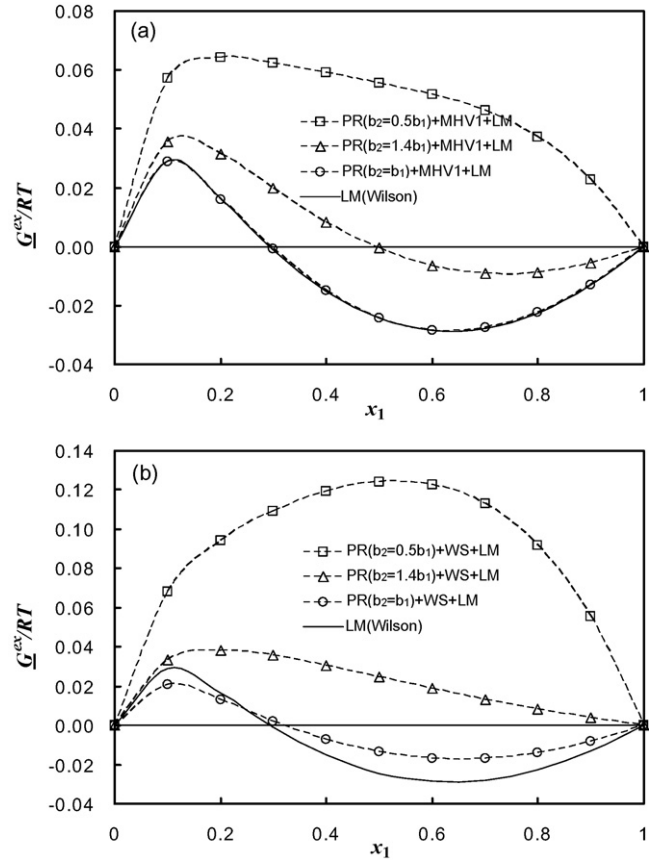
#### 4. The WS mixing rule

Here we show that the WS mixing suffers the same issues as seen previously in the MHV1 mixing rule. In the WS mixing rule, the excess Helmholtz free energy from an EOS at infinite pressure is set to the excess Gibbs free energy from an activity coefficient model:

$$A^{\text{ex}}_{\text{EOS}}(T, P \rightarrow \infty, x) \cong G^{\text{ex}}_{\text{LM}}(T, x) \quad (15)$$

Since  $G^{\text{ex}} = A^{\text{ex}} + PV^{\text{ex}}$ , Eq. (3) can be used to evaluate  $A^{\text{ex}}$  from solvation free energy as

$$\begin{aligned} \frac{A^{\text{ex}}}{RT} &= \frac{\Delta G^{\text{sol}}}{RT} - \sum_i x_i \frac{\Delta G_i^{\text{sol}}}{RT} + \sum_i x_i \ln \frac{z_i}{z} - z + \sum_i x_i z_i \\ &= \frac{\Delta G^{\text{ch}}}{RT} - \sum_i x_i \frac{\Delta G_i^{\text{ch}}}{RT} - \ln \left( 1 - \frac{\alpha(u-1)}{u(u+1)+(u-1)} \right) \end{aligned}$$



**Fig. 2.** Comparison of the value of  $G^{\text{ex}}$  from the Wilson model ( $G^{\text{ex}}/RT = -x_1 \ln(x_1 + x_2 \Lambda_{12}) - x_2 \ln(x_2 + x_1 \Lambda_{21})$ ) with  $\Lambda_{12} = 0.05$  and  $\Lambda_{21} = 3.0$ ) (solid line) and from the PR EOS (dashed lines) combined with the same Wilson model through the MHV1 (a) and WS (b) mixing rules at 350 K for different ratios of parameter  $b$ . The legends are the same as in Fig. 1.

$$\begin{aligned} &+ \sum_i x_i \ln \left( 1 - \frac{\alpha_i(u_i - 1)}{u_i(u_i + 1) + (u_i - 1)} \right) \\ &+ \left( \frac{\alpha u}{u(u+1) + (u-1)} \right) - \sum_i x_i \left( \frac{\alpha_i u_i}{u_i(u_i + 1) + (u_i - 1)} \right) \quad (16) \end{aligned}$$

In the limit of infinite pressure, WS assumed that the liquid molar volume is equal to the close packed hard-core volume, i.e.,  $u = u_i = 1$ . Therefore, the cavity terms  $\Delta G^{\text{cav}}$  are also canceled:

$$\frac{A^{\text{ex}}_{\text{PREOS}}}{RT} = \frac{\alpha}{2} + \frac{\Delta G^{\text{ch}}}{RT} - \sum_i x_i \left( \frac{\alpha_i}{2} + \frac{\Delta G_i^{\text{ch}}}{RT} \right) \quad (17)$$

Note that the difference between Eq. (11) ( $\sum_i x_i \ln(b_i/b)$ ) and (17) ( $(\alpha/2) - \sum_i x_i (\alpha_i/2)$ ) reflects the  $PV^{\text{ex}}$  term. Again, we see that the cavity contributions from PR EOS are cancelled as a result of constant  $u$ .

In addition, the charging term (Eq. (8)) becomes  $\Delta G^{\text{ch}}/RT = \alpha C$  with  $C = [(1/2\sqrt{2})\ln((2 - \sqrt{2})/(2 + \sqrt{2})) - (1/2)] = -1.1232$ . Therefore, we recover the expression in WS mixing rule:

$$\frac{A^{\text{ex}}_{\text{PREOS}}}{RT} = (C + 0.5) \left( \alpha - \sum_i x_i \alpha_i \right) = C_{\text{WS}} \left( \alpha - \sum_i x_i \alpha_i \right) \quad (18)$$

with  $C_{\text{WS}} = -0.6232$ .

Figs. 1b and 2b illustrate the performance of PR EOS combined with the Margules and Wilson model through the WS mixing rule.

The pure component  $a$  and  $b$  parameters and the liquid models are chosen to be the same as in Section 3 for examining the MHV1 mixing rule. It is seen that even in the case when  $b_1 = b_2$  PR + WS + LM deviates from the original liquid model. Because the WS is matching  $A^{\text{ex}}$  at infinite pressure (and not  $G^{\text{ex}}$  at ambient conditions) from PR to  $G^{\text{ex}}$  from a liquid model (Eq. (15)) and the  $PV^{\text{ex}}$  term is negligible at ambient conditions, the difference seen here reflects the pressure dependence of  $A^{\text{ex}}$  in the PR EOS. As  $b_1/b_2$  deviates from unity (0.5 and 1.4 case in Fig. 1b), much larger discrepancy is observed between PR + WS + LM and the original liquid models. This is, similar to those seen in the MHV1 mixing rule (Figs. 1a and 2a), a result of mismatching of free energy component in the WS mixing rule.

## 5. Conclusion

The fundamental idea of matching the excess Gibbs free energy from an equation of state and a liquid model is impaired by the assumption of constant ratio between the liquid molar volume and molecular volume in many  $G^{\text{ex}}$ -based mixing rules, such as MHV1 and WS. As a consequence, these mixing rules are indeed matching the complete solvation free energy from a liquid model to only the charging free energy from an equation of state. The calculated phase boundary for vapor–liquid equilibrium from an equation of state would be different from that from a liquid model alone, especially for mixtures containing molecules of dissimilar sizes.

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