# Maximizing Cubic EoS Potential by Fusing a Theoretically Sound Mixing Rule with an Uncharted Activity Coefficient Model

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Equations of State (EoS) are one of the most widely used tools in chemical and process engineering because of their ability to predict the thermodynamic properties of pure compounds and mixtures in any given state. It is clear, therefore, that their performance in predicting such properties must be carefully and systematically studied in order to quantify their strengths and weaknesses.

However, regardless of the sophistication of a thermodynamic model and the number of parameters in the mixing rule, you are in trouble if the properties of the pure components, and in particular the vapor pressures, are inaccurate. Indeed, such a property defines the endpoints of isothermal ( $P,x,y$) phase diagrams and is therefore of vital importance. For this reason it was decided to build a database of over 300,000 pseudo-experimental data points for pure components. These data come from a carefully selected portion of the DIPPR database and originate from 1800 different pure components representing all chemical families. Experimental data incorporated in the database include vapor pressures, liquid densities, enthalpies of vaporization, liquid heat capacities, and critical coordinates. Such a database emerges as a tool for fairly assessing the performances of equations of state applied to pure components. In this study, such a database was used:

1. to determine the optimal values of the (u,w) parameters involved in the volume function of a cubic equation of state.
2. to determine the optimal way of selecting the volume translation parameter
3. to determine the optimal mathematical shape of the a-function and to derive an entirely transparent and universal protocol for setting the compound-specific parameters involved in such an a-function.

Finally, the *tc*-PR (translated and consistent Peng-Robinson) cubic EoS was proposed. To the best of our knowledge, this is the most accurate cubic EoS ever developed. According to the 6th edition of the Properties of Gases and Liquids the *tc*-PR EoS "stands out for vapor pressure" and *"provides similar accuracy for multiple properties and broad compound coverage as the* (much more complex) *PC-SAFT and SPEADMD EoSs."*

In a second step, our goal was to extend the *tc*-PR EoS to mixtures in order to see if it could compete with SAFT-type EoS for correlating binary systems containing self-associating species. The extension to mixtures requires mixing rules (MR), and a classical choice is the so-called Van der Waals one-fluid (VdW1f) mixing rules. Other options are related to the use of the advanced EoS/$g^E$ MR. The starting point for deriving EoS/$g^E$ models is to equate the excess Gibbs energy expression obtained from an EoS [$g^{E,EoS}$] with that from an explicit activity coefficient model [$g^{E, g}$]. By construction, the latter is temperature- and composition-dependent but pressure-independent; however, $g^{E,EoS}$ is pressure, temperature and composition dependent, which explains why a reference pressure, $P_{ref}$, must be selected before the two quantities are equated. The initial equation for deriving EoS/$g^E$ models is thus: $g^{E,EoS}(T,P_{ref},\mathbf{z}) = g^{E,g}(T, \mathbf{z})$. It is believed that the consistency of such an equation can be questioned for the following two main observations:

1. In accordance with the way they were derived, the low-pressure $g^{E, g}$ models classically used to calculate activity coefficients should be better regarded as $a^{E,g}$ models;
2. In the previous equation [$g^{E,EoS}(T,P_{ref},\mathbf{z}) = g^{E,g}(T, \mathbf{z})$], the combinatorial part and the residual part of $g^E$ stemming from the EoS and from the activity coefficient model do not match. Although $g^{E,EoS} = g^{E,g}$, we do not get: $g^{E,EoS,combinatorial} = g^{E,g,combinatorial}$ and $g^{E,EoS,residual} = g^{E,g, residual}$. We can therefore expect poor

results when modelling athermal or regular solutions that only require a combinatorial or a residual contribution.

We are convinced that in order to derive theoretically sound mixing rules, special attention must be paid to the combinatorial and residual contributions separately. The advantage of treating the combinatorial and residual contributions from the EoS and the $a^{E,g}$ model separately is that it ensures that quantities containing the same information are equated. These observations led to a modification of the classical way of deriving mixing rules and resulted in a new and theoretically sound formulation of the EoS/$a^E$ mixing rules.

In particular, the efficiency of the approach is illustrated by the combination of the *tc*-PR EoS and the Wilson activity-coefficient model. It is acknowledged that such an activity coefficient model is not capable of predicting a liquid-liquid equilibrium. However, it is emphasized that its use in the proposed MR can not only reproduce liquid-liquid equilibria but can also be used to correlate very complex systems. If sufficient experimental data are available to use a 4-parameter version of the Wilson $a^E$ model, the model becomes able to simultaneously correlate VLE, LLE, and mixing properties with high accuracy even for systems containing associating compounds. A comparison with SAFT-type models will be given.