Determination of cubic equation of state parameters for pure and mixture fluids from first principle solvation calculations

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Abstract

A new method for estimating the cubic of equation of state parameters for both pure and mixture fluids without using critical properties is proposed. In this method, the solvation charging free energy and the solvation cavity are used to determine the temperature-dependent energy parameter $a(T)$ and volume parameter b. This method requires only element specific parameters (3 parameters for each element, including one atomic radius and two parameters for describing dispersion interactions), and 10 universal parameters for electrostatic and hydrogen-bonding interactions. The equation of state (EOS) parameters so determined allow for the description of the complete phase diagram, including the critical point, for pure and mixture fluids. We have examined this method using the Peng-Robinson (PR) EOS[1] for 1295 compounds and 141 binary mixture systems. For pure compounds, this model achieved an accuracy of 48% in vapor pressure at normal boiling point, 21.4% in liquid density, 4.1% in critical temperature, 10% in critical pressure, and 5.3% in critical volume. For binary mixture systems, the overall average deviation in total pressure and vapor phase composition are 28.5% and 5.5%, respectively. The errors can be reduced significantly (to 6.8% and 2.5%) if the critical properties and acentric factor of the pure components are used. This method is, in principle, applicable to any chemical species and is especially useful for those whose experimental data are not available.

Theory

The solvation free energy ΔG^{*sol} is the work needed for transferring a solute molecule from ideal gas to a solution under constant temperature T and pressure P. Considering the solution as a pseudo-pure fluid, the free energy change can be obtained from the compressibility z($=P\underline{V}/RT$) of the solution as[2]

$$\Delta \underline{G}^{*sol} = (z-1)RT + RT \int_{\underline{V}=\infty}^{\underline{V}} \frac{(1-z)}{\underline{V}} d\underline{V} \qquad (1)$$

where the underscore ($\underline{G}$ and $\underline{V}$) denotes that the properties are expressed in a molar basis. If the solution obeys the PR EOS[1]

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

(2)

The solvation free energy becomes

$$\frac{\Delta\underline{G}^{*sol}}{RT} = \left(\ln\frac{\underline{V}}{\underline{V}-b} + \frac{b}{\underline{V}-b}\right) + \frac{a}{bRT}\left[\frac{1}{2\sqrt{2}}\ln\frac{\underline{V}+b(1-\sqrt{2})}{\underline{V}+b(1+\sqrt{2})} - \frac{b\underline{V}}{\underline{V}^2+2b\underline{V}-b^2}\right]$$

(3)

As temperature approaches infinity, the solvation free energy is mainly a result of hard-core repulsions between the solute and solvent, and can be considered as creating a cavity volume with the size and shape of the solute in the solvent. Thus, it is referred to as the hard-core cavity formation free energy (*hcav*)

$$\frac{\Delta\underline{G}^{*hcav}}{RT} = \left(\ln\frac{\underline{V}}{\underline{V}-b} + \frac{b}{\underline{V}-b}\right)$$

(4)

The difference between the solvation free energy and the hard-core cavity formation free energy is referred to as the charging free energy

$$\frac{\Delta\underline{G}^{*chg}}{RT} = \frac{a}{bRT}\left[\frac{1}{2\sqrt{2}}\ln\frac{\underline{V}+b(1-\sqrt{2})}{\underline{V}+b(1+\sqrt{2})} - \frac{b\underline{V}}{\underline{V}^2+2b\underline{V}-b^2}\right]$$

(5)

Equation 5 infers that the energetic interaction parameter *a* can be obtained from the charging free energy as

$$a(T,\underline{x}) = \frac{b(\underline{x})}{C_{PR}}\Delta\underline{G}^{*chg}(T,\underline{V},\underline{x})$$

(6)

where the value of C_{PR} (the subscript *PR* denotes that this parameter depends on the EOS used), defined as the terms in the square brackets in eq. 5, its value is empirically set to -0.623 for better accuracy from the model proposed here.

The volume parameter *b* can be assumed to be the same as the volume of the solvation cavity. For a pseudo-pure fluid, it can be approximated from the mole fraction average of pure component contributions, i.e.,

$$b(\underline{x}) = \sum_i x_i b_i$$

(7)

Therefore, together with eq.7 for $b(\underline{x})$, eq. 6 provides a way to estimate $a(T,\underline{x})$ from the charging free energy. This approach is referred to as PR+COSMOSAC hereafter.

According to Lin et al.[2] the total charging free energy ($\Delta\underline{G}^{*sol}$) of a mixture solvent is the sum of contributions from all the species in the mixture,

$$\Delta\underline{G}^{*chg} = \sum_i x_i \Delta\underline{G}^{*chg}_{i/S}$$

(8)

where $\Delta\underline{G}^{*chg}_{i/S}$ is the charging free energy of solute *i* in the mixture solvent *S*. The

individual charging free energy is calculated based on the solvation model developed previously[3-4]

$$\Delta \underline{G}_{i/S}^{*chg}(T,\underline{x}) = \Delta \underline{G}_i^{*is} + \Delta \underline{G}_i^{*cc} + \Delta \underline{G}_{i/S}^{*res}(T,\underline{x}) + \Delta \underline{G}_i^{*dsp}(T) \tag{9}$$

where the superscripts *is*, *cc*, *res*, and *dsp* are the abbreviation of the ideal solvation, the charging correction, the restoring, and the dispersion contributions to the charging free energy. The evaluation of *is*, *cc*, and *res* contributions is based on the result of quantum mechanical solvation calculation (COSMO)[5] and their formulation can be found elsewhere[3-4].

The dispersion solvation free energy is assumed to be proportional to the exposed surface area of the atom comprising the molecule, that is,

$$\Delta G_i^{*dsp}(T) = \sum_k S_k (A_{dsp,k} T + B_{dsp,k}) + G_R(T) + G_{HB}(T) \tag{10}$$

where $A_{dsp,k}$ and $B_{dsp,k}$ are the dispersion parameter of atom type k, S_k is the total exposed surface area of atom type k, and G_R and G_{HB} are empirical corrections for cyclic (including aromatic) and hydrogen bonding containing molecules. The expressions of these two terms are

$$G_R(T) = N_{AR}(A_{dsp,R} T + B_{dsp,R}) \tag{11}$$

$$G_{HB}(T) = \frac{1}{N_{HBH}}\left[\frac{A_{dsp,HB}}{1 + \exp[-(T - B_{dsp,HB})/C_{dsp,HB}]} \right] \tag{12}$$

where N_{AR} and N_{HBH} are the number of atoms involved in ring-structure and hydrogen bonding acceptors. $A_{dsp,R}$, $B_{dsp,R}$, $A_{dsp,HB}$, and $B_{dsp,HB}$ are constant coefficients for ring and hydrogen-bonding corrections. All the dispersion parameters are determined by the regression to experimental vapor pressure data using selected compounds.

It is possible to increase its level of accuracy of PR+COSMOSAC in the calculation of mixture properties by incorporating experimental data of pure substances. When the critical properties (T_c and P_c) and acentric factor (ω) are available, they can be used to correct the charging free energy as follows

$$\Delta \underline{G}_{i/S}^{*chg} = \left(\Delta \underline{G}_{i/S}^{*chg} - \Delta \underline{G}_{i/i}^{*chg} \right) + \frac{a_i C_{PR}}{b_i} \tag{14}$$

where $\Delta \underline{G}_{i/i}^{*chg}$ is the charging free energy of species i in its pure fluid, $a_i(T)$ and b_i are determined as those in the original PR EOS, This approach, denoted as PR+COSMOSAC+$T_cP_c\omega$, ensures that the pure component vapor pressures will be the same as those determine from the original PR EOS.

Results and Discussion

In this work, vapor-liquid equilibrium data of 1295 pure compounds (whose experimental data and molecular information are available in DIPPR[6] and VT[7-8] database) and 114 binary mixtures (including about 3000 data points) to examine our model.

The overall average absolute errors are listed in Table 1. The overall average absolute deviation for a total 1295 pure compounds (which are only composed by atoms C, H, O, N, Cl, and F) in $\ln P^{vap}$ and liquid density at normal boiling temperature are 0.37 (or 48% in P^{vap}) and 21.4%, respectively. Except for the worst described carbon monoxide (6.77 deviation in $\ln P^{vap}$), predicting results for all the other compounds are acceptable. Besides, PR+COSMOSAC can describe the complete fluid phase diagram (Figure 1).
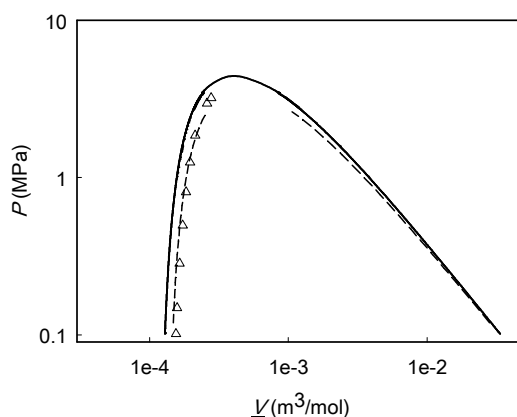

Figure 1. The P-V diagram for cyclooctane. The triangles are experimental data.[6] The solid and dashed lines are results from PR+COSMOSAC and PR EOS, respectively.

Table 1 also shows the overall average absolute errors for critical properties of compounds whose experimental critical properties are available in the DIPPR database. The critical volume is estimated from the volume of solvation cavity in COSMO calculation. The deviations in T_c are less than 120 K, except for carbon monoxide and methacrylic acid. The accuracy for predicted T_c and V_c are acceptable. The critical pressure can be obtained from $P_c = z_c R T_c / V_c$ once $\underline{V}_c$ and T_c are known. While the PR EOS has a fixed value of $z_c (=0.307)$[9] for all compounds, experimental values of z_c ranges from 0.2 to 0.3 for most chemicals.[10] Therefore, we have rescaled the calculated P_c by 0.26/0.307 for better accuracy. The poorly predicted P_c are caused either by the constant critical compressibility factor in PR EOS or the error in the predicted T_c and V_c. These results are similar to our previous work.[3]

Table 1. The accuracy of PR+COSMOSAC in predicting properties of pure components

Propertites	Number of compounds	Error
Pc	348	9.96 % [b]
Tc	433	4.13 % [b]
Vc	272	5.34 % [b]
Vapor Pressure [a]	1295	0.37 [c]
Liquid Density [a]	1289	21.40 % [b]

$a.$ at normal boiling point. $b.$ $\text{Error} = \dfrac{1}{N} \sum\limits_{i=1}^{N} \left| \dfrac{p_i^{\text{cal}} - p_i^{\text{exp}}}{p_i^{\text{exp}}} \right|$ $c.$ $\text{Error} = \ln \left| \dfrac{P_{cal}^{vap}}{101325} \right|$.

As shown in Table 2, the overall absolute average errors from the proposed PR+COSMOSAC method are 28.48% in pressure and 5.49 in vapor phase composition. The errors reduce significantly to 6.75% and 2.48% from PR+COSMOSAC+$T_c P_c \omega$. Figure 2(a) shows the *P-x-y* diagram for ethyl acetate + 1-Octene binary mixtures. In this system the pure component vapor pressures are well predicted by PR+COSMOSAC and the predicted results from all three methods are almost identical. (Note that results from PR+COSMOSAC and PR+COSMOSAC+$T_c P_c \omega$, are shown in dotted and dashed, respectively) In Figure 2(b)~(d), we can find that if the deviations in vapor pressure increases, the larger deviations are observed in the mixture VLE as well. When the needed experimental data for PR+COSMOSAC+$T_c P_c \omega$ are available, this method reliably improves the accuracy in VLE regardless the mixture is ideal (e.g., Figure 2(b)) or highly non-ideal (e.g., Figures 2(c) and (d)). Therefore, while the completely predictive PR+COSMOSAC approach provides the general shape of VLE phase diagram, its accuracy in describing mixture VLE is limited by its capability of predicting pure component vapor pressures.

Table 2. The overall absolute average errors in equilibrium pressure and the liquid phase composition from different methods

Method	AARD P [a] (%)	AARD y [b] (%)	Number of data points	Number of systems	Number of binary mixtures
PR+COSMOSAC	28.48	5.49	2953	214	114
PR+COSMOSAC+$T_c P_c \omega$	6.75	2.48	2953	214	114

$a.$ $\text{AARD } P = \dfrac{1}{M} \sum\limits_{i=1}^{M} \left| \dfrac{P_i^{\text{cal}} - P_i^{\text{exp}}}{P_i^{\text{exp}}} \right|$ $b.$ $\text{AARD } y = \dfrac{1}{M} \sum\limits_{i=1}^{M} \left| y_i^{\text{cal}} - y_i^{\text{exp}} \right|$
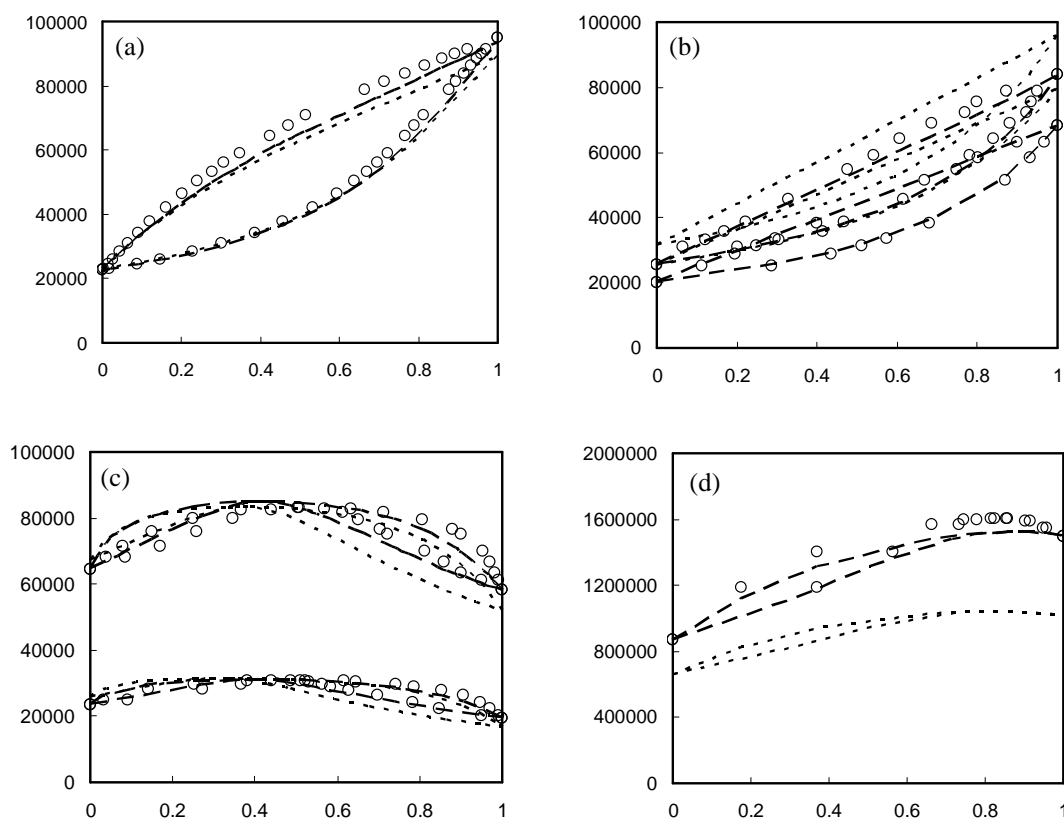
Figure 1. The *P-x-y* phase diagram of vapor-liquid equilibrium for (a) ethyl acetate + 1-Octene at 348.15 K, (b) pentane + hexane at 298.15 and 303.70 K, (c) morpholine + Octane at 353.35 and 383.35 K, and (d) 1,1-difluoroethane and isobutene at 333.20 K. The circles, dotted lines and dashed lines are the predicted results from the experimental data[11-13], PR+COSMOSAC, and PR+COSMOSAC+ $T_cP_c\omega$.

Conclusion

In this work, we show that accurate first principle predictions for vapor-liquid equilibria can be achieved though the combined use of quantum mechanical solvation calculations and a cubic EOS. The temperature and composition dependence of PR EOS parameters are determined from a solvation model based on COSMO calculations (PR+COSMOSAC). The critical properties, vapor pressures, and liquid densities for pure components can be predicted in reasonable agreement with experimental data. This approach only provides qualitative results for mixtures because of the inaccuracy in vapor pressure predictions. However, the predicted accuracy for mixtures can be improved significantly if the critical properties and acentric factor (PR+COSMOSAC+$T_cP_c\omega$) are available. Although the accuracy of PR+COSMOSAC is far from excellent, it also provide a totally predictive way to

describing pure fluids and mixtures, especially when no experimental data are available.

Acknowledgement

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