New Solid Equation of State Combining Excess Energy Mixing Rule for Solid–Liquid Equilibria

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Crude oil is a mixture of light and heavy hydrocarbon components. The light components in crude oil keep the heavy components soluble in solution. However, the cooling of crude oil below its solidification point leads to the formation of a solid-wax phase. A number of thermodynamically based models have been proposed in the literature for the prediction of wax formation in both crude oils and fuels. Some of these models assume ideal liquid solution behavior. Others are a modification of the regular solution theory or the Flory-Huggins model for activity coefficients, with varying degrees of success. The absence of a proper model in the petroleum industry to describe the liquid-phase nonideality for mixtures of hydrocarbons with large differences in size is still one of the major problems in solid–liquid equilibrium calculations. A simple methodology is proposed to develop a cubic equation of state (CEOS) for the solid phase to allow the accurate calculation of solid–liquid equilibria. The methodology is successfully applied to the Twu-Sim-Tassone (TST) cubic equation of state. The solid TST equation of state is then combined with the TST excess Helmholtz energy mixing rule to handle highly nonideal systems for the accurate prediction of solid–liquid phase equilibria.

Introduction

Our recent efforts toward the development of a unified excess Helmholtz energy (A^E) mixing rule and a new cubic equation of state Twu-Sim-Tassone (TST) for highly nonideal systems in predicting vapor–liquid equilibria (VLE) have been highly successful. However, in spite of these advances in the prediction of vapor–liquid equilibria, a reliable thermodynamic model for solid–liquid equilibria (SLE) from an equation of state still needs to be developed. Therefore, we turn our attention to our TST cubic equation of state and extend it to solid–liquid equilibria for the prediction of solid solubility in the liquid phase.

The prediction of solid solubility is of interest to the petroleum industry. Crude oils are a mixture of light and heavy hydrocarbon components. When these oils are cooled during transportation, the solubility of the heavy components decreases because solubility depends very strongly on temperature. If the temperature of the oil is below the solidification temperature of the mixture, the solubility of the heavy hydrocarbons is significantly decreased, causing these heavy components to precipitate and form solid wax. Wax deposits may lead to capacity reduction, blockage, and other operation and transportation problems.

To prevent these problems, numerous methods have been proposed for the prediction of wax formation in both crude oils and fuels. In addition to empirical correlations, liquid activity-coefficient models are generally used for the calculation of solid–liquid equilibria with some degrees of success. Because the activity-coefficient model cannot be used to predict other thermodynamic properties of the solid and liquid phases, such as density and enthalpy, it is desired to have an

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equation-of-state method for SLE. Wenzel and Schmidt (1980) extended the Redlich-Kwong (RK) equation of state to the solid phase by adding an additional term with a six power in volume. This additional term predicts a second S-shaped isotherm in the region of the solid–liquid transition to give a solid-like volume at low molar volumes. This is similar to the S-shaped isotherm in the vapor-liquid region that yields the transition to the liquid phase. Since the Wenzel-Schmidt equation is not cubic in volume and the critical constraints are not satisfied either, the wonderful features of having a cubic equation of state for predicting vapor–liquid equlibria vanish.

Many authors have proposed their own models for handling solids, but their approaches often require the fitting of many different kinds of data such as solid-density, sublimation-pressure, and melting-pressure data. These data are often not available. Salim and Trebble (1994) refit the constants of their four-parameter cubic equation of state at the triple-point temperature to allow the calculation of equilibria involving the solid phase. Since there are four parameters in their equation of state, they have to impose four constraints to find these parameters. These four constraints are not all necessary, however. They depend upon the number of parameters in the equation of state used. After the parameters are calculated at the triple point, the two temperature-dependent parameters have yet to be found from the sublimation pressure data of the solid, which are difficult to obtain. It is well known that any cubic equation of state with three or four parameters results in more accurate predictions of density than two-parameter cubic equations of state. The three- or four-parameter cubic equations of state require density data in advance to find the extra parameters of the equation of state for each component in the system before they can start any phase-equilibrium calculations. This requirement, unfortunately, not only is inconvenient in the application of such multiparameter equations of state, but also creates inconsistencies in the regressed parameters such as Z_c from the density data for the components. Furthermore, their K-value predictions are no better than those of the two-parameter cubic equations of state. As a result of these drawbacks, the three- or four-parameter cubic equations of state have never found widespread use in industrial applications. Therefore, any cubic equation of state with more than two parameters is not considered in this work.

In view of the success of the two-parameter cubic equations of state in VLE calculations and of the need for improved methods of predicting SLE, including solid solutions, a simple methodology is proposed to extend the TST cubic equation of state to the solid phase. The solid TST equation of state is then combined with the TST A^E mixing rule to handle highly nonideal systems for the accurate prediction of solid–liquid phase equilibria.

Thermodynamic Framework

We need fugacities for the prediction of solid–liquid equilibria. There is little difficulty in calculating the liquid fugacity from any cubic equation of state, but predicting the fugacity for solid components accurately from the equation of state is difficult. The fugacity is a thermodynamic property, and thus depends on temperature, pressure, and composition. Van Ness and Abbott (1982) give a general expression for the fugacity as follows

$$d\ln f = -\frac{\Delta H}{RT^2}dT + \frac{v}{RT}dP \tag{1}$$

where ΔH is the enthalpy departure from ideal gas and v is the molar volume. Since Eq. 1 is a general expression, it can be applied to any phase. Applying Eq. 1 to the solid solution, it becomes

$$d\ln f^S = -\frac{\Delta H^S}{RT^2}dT + \frac{v^S}{RT}dP \tag{2}$$

and applying it to a liquid solution

$$d\ln f^L = -\frac{\Delta H^L}{RT^2}dT + \frac{v^L}{RT}dP \tag{3}$$

Subtracting Eq. 3 from Eq. 2 gives

$$d\ln\frac{f^S}{f^L} = \frac{\Delta H^f}{RT^2}dT - \frac{\Delta v}{RT}dP \tag{4}$$

where $\Delta H^f = \Delta H^L - \Delta H^S$ is the latent heat of fusion at the fusion temperature T_f and $\Delta v = v^L - v^S$ is the molar volume difference between the liquid and solid phases. Integrating Eq. 4 from the triple-point temperature T_t to T and from the triple-point pressure (close to zero and negligible relative to system pressure P) to P, we obtain

$$\ln\frac{f^S}{f^L} = -\frac{\Delta H^f}{RT}\left(1-\frac{T}{T_t}\right) - \frac{\Delta v P}{RT} \tag{5}$$

In the integration of Eq. 4, ΔH^f and Δv are assumed to be temperature and pressure independent, respectively. At the zero pressure limit, Eq. 5 becomes

$$\ln\frac{f^S}{f^L} = -\frac{\Delta H^f}{RT}\left(1-\frac{T}{T_t}\right) \tag{6}$$

Equation 6 is our fundamental equation for the development of an equation of state to handle solid solutions. It is worth mentioning that Prausnitz (1969) gave a similar equation, describing the solid fugacity as

$$\ln\frac{f^s}{f^L} = -\frac{\Delta H^f}{RT}\left(1-\frac{T}{T_t}\right) + \frac{\Delta C_p}{R}\left[\frac{T_t}{T} - 1 - \ln\left(\frac{T_t}{T}\right)\right] \tag{7}$$

where $\Delta C_p = C_{p(\text{liquid})}\text{-}C_{p(\text{solid})}$. The logarithmic function in the last term of Eq. 7 can be expanded in series as

$$\ln\left(\frac{T_t}{T}\right) = \left(\frac{T_t}{T}-1\right) - \frac{1}{2}\left(\frac{T_t}{T}-1\right)^2 + \cdots \tag{8}$$

The higher powers of $(T_t/T - 1)$ in Eq. 8 can be neglected at temperatures not too far from the triple point. Substituting Eq. 8 into Eq. 7, it is apparent that the last term in Eq. 7 cancels out to reduce to Eq. 6. Therefore, Prausnitz suggests that it is sufficient in many cases to consider only the term that includes ΔH^f and to neglect the term ΔC_p. Our derivation has shown that Eq. 6 is valid at zero pressure without neglecting any terms.

A methodology is proposed to extend the TST cubic equation of state to the solid phase based on Eq. 6. The TST cubic equation of state was developed by Twu et al. (2002a) to allow better prediction of liquid densities for heavy hydrocarbons and polar components as well as the accurate prediction of vapor pressure of all components in databanks. The TST cubic equation of state is represented by the following equation

$$P = \frac{RT}{v-b} - \frac{a}{(v+3b)(v-0.5b)} \tag{9}$$

The values of a and b at the critical temperature are found by setting the first and second derivatives of pressure with respect to volume equal to zero at the critical point, resulting in

$$a_c = 0.470507 R^2 T_c^2 / P_c \tag{10}$$

$$b_c = 0.0740740 RT_c / P_c \tag{11}$$

$$Z_c = 0.296296 \tag{12}$$

where subscript c denotes the critical point. It's worth noting that the values of Z_c from the SRK and PR equations are both larger than 0.3, whereas that from the TST equation is slightly below it and is closer to the true value.

Equation 9 can be rewritten in general form as

$$P = \frac{RT}{v-b} - \frac{a}{(v+ub)(v+wb)} \tag{13}$$

where the constants u and w, which are equation-of-state-dependent, are $u = 3$ and $w = -0.5$ for the TST equation.

Equation 6 requires knowledge of the fugacity at zero pressure. The fugacity of a pure component at zero pressure can be derived from Eq. 13 as

$$\ln(f) = -1 - \ln\left(\frac{b}{RT}\right) - \ln(v^* - 1) - \frac{1}{(w-u)}\frac{1}{RT}\frac{a}{b}\ln\left(\frac{v^*+w}{v^*+u}\right) \tag{14a}$$

Equation 14a can be rewritten in a reduced form by including the system pressure P to get the expression of the fugacity coefficient as

$$\ln\left(\frac{f}{P}\right) = -1 - \ln b^* - \ln(v^* - 1) - \frac{1}{(w-u)}\frac{a^*}{b^*}\ln\left(\frac{v^*+w}{v^*+u}\right) \tag{14b}$$

The parameters a^* and b^* in Eq. 14 are defined as

$$a^* = Pa/R^2T^2 \tag{15}$$

$$b^* = Pb/RT \tag{16}$$

The term $v^* = v/b$ in Eq. 14 is the reduced volume at zero pressure. If Eq. 14 is applied to the liquid phase, v^* is the reduced liquid volume at zero pressure. If the volume is the solid-phase volume, v^* is the reduced solid volume at zero pressure. The reduced volume is solved from Eq. 13 by setting the pressure equal to zero and selecting the smallest root. The approach used here eliminates the need for finding the equilibrium pressure for the system to solve for the solid or liquid volume. The solution for the reduced volume at zero pressure from Eq. 13 is

$$v^* = \frac{1}{2}\left\{\left(\frac{a^*}{b^*} - u - w\right) - \left[\left(u + w - \frac{a^*}{b^*}\right)^2 - 4\left(uw + \frac{a^*}{b^*}\right)\right]^{1/2}\right\} \tag{17}$$

An Equation-of-State Method for the Liquid Fugacity

Applying Eq. 14 to the liquid phase, the fugacity coefficient of a pure liquid f^L/P at zero pressure is obtained by

$$\ln\left(\frac{f^L}{P}\right) = -1 - \ln b^* - \ln(v^{*L} - 1) - \frac{1}{(w-u)}\frac{a^{*L}}{b^*}\ln\left(\frac{v^{*L}+w}{v^{*L}+u}\right) \tag{18}$$

Note that the equation-of-state parameter b is the pure-component constant. The superscript L denotes that the properties are for the liquid phase. The reduce liquid volume v^{*L} at zero pressure is directly obtained from Eq. 17

$$v^{*L} = \frac{1}{2}\left\{\left(\frac{a^{*L}}{b^*} - u - w\right) - \left[\left(u + w - \frac{a^{*L}}{b^*}\right)^2 - 4\left(uw + \frac{a^{*L}}{b^*}\right)\right]^{1/2}\right\} \tag{19}$$

The equation-of-state parameter a for liquid, a^L, is a function of temperature. Its liquid value at any temperature can be calculated from

$$a^L = \alpha^L a_c \tag{20}$$

where a_c is given by Eq. 10 and α^L is the alpha function, a function only of the reduced temperature, $T_r = T/T_c$. Here we use the Twu alpha function (Twu et al., 1991)

$$\alpha^L = T_r^{n(m-1)} e^{\ell(1 - T_r^{nm})} \tag{21}$$

Table 1. The ℓ, m, and n Databank of the Generalized Liquid Alpha Function α^L for Eqs. 23 and 24 with TST Equation of State for Subcritical and Supercritical Conditions

	$T_r \le 1$		$T_r > 1$	
α Parameter	$\alpha^{(0)}$	$\alpha^{(1)}$	$\alpha^{(0)}$	$\alpha^{(1)}$
ℓ	0.196545	0.704001	0.358826	0.0206444
m	0.906437	0.790407	4.23478	1.22942
n	1.26251	2.13086	−0.200000	−8.000000

Equation 21 has three parameters ℓ, m, and n. These parameters are unique to each component and are determined from the regression of pure-component vapor-pressure data. However, for hydrocarbon systems, the alpha function α^L can be generalized as a linear function of the acentric factor. The generalized alpha function is especially useful for application to systems containing defined heavy hydrocarbons and undefined hydrocarbons such as petroleum fractions, where vapor pressures are unavailable.

The generalized alpha function α^L is expressed as a function of two variables, the reduced temperature T_r and the acentric factor ω as

$$\alpha^L = \alpha^L(T_r, \omega) = \alpha^{(0)} + \omega\left(\alpha^{(1)} - \alpha^{(0)}\right) \tag{22}$$

Each alpha is a function of the reduced temperature only, and Eq. 21 is used for $\alpha^{(0)}$ and $\alpha^{(1)}$

$$\alpha^{(0)} = T_r^{n^{(0)}(m^{(0)}-1)} e^{\ell^{(0)}\left(1 - T_r^{n^{(0)}m^{(0)}}\right)} \tag{23}$$

$$\alpha^{(1)} = T_r^{n^{(1)}(m^{(1)}-1)} e^{\ell^{(1)}\left(1 - T_r^{n^{(1)}m^{(1)}}\right)} \tag{24}$$

The superscripts (0) and (1) in Eqs. 22, 23, and 24 are consistent with the definition of the acentric factor at $\omega = 0$ and $\omega = 1$, respectively. Twu et al. (2002b) developed the generalized ℓ, m, and n parameters for use in Eqs. 23 and 24 with the TST cubic equation of state. These values are listed in Table 1. By knowing the acentric factor and the reduced temperature, the alpha function of a component in the liquid phase can be computed from Eqs. 22–24. The equation-of-state parameter a for the liquid, a^L, is then calculated from Eqs. 10 and 22 using Eq. 20. Subsequently, the liquid volume and the liquid fugacity coefficient are obtained from Eqs. 19 and 18, respectively. All the necessary properties of the liquid phase required in SLE can therefore be predicted from the TST cubic equation of state.

Next is the calculation of the solid fugacity for the prediction of solid solubilities in the liquid phase. We propose a simple methodology to extend our TST equation of state for application to the solid phase.

An Equation-of-State Method for the Solid Fugacity

We assume that the density of the solid is greater than the density of the liquid due to greater attractive forces between molecules in the solid phase. This means the value of the alpha function for the solid, α^S, is larger than that for the liquid α^L. The liquid alpha function α^L has been generalized using vapor pressure data and can be calculated from Eq. 22, but α^S is still unknown at this point. Our methodology proposes that the alpha function of the solid α^S or the equation-of-state parameter a of the solid a^S be derived from Eq. 6 to maintain the internal consistency between the solid and the liquid fugacities and other predicted thermodynamic properties, such as densities and alpha functions. This approach avoids the use of the sublimation pressure of the solid at the system temperature, which can be difficult to obtain, to derive a^S.

Similar to Eqs. 18 and 19, the fugacity coefficient and the reduced volume v^{*S} of a pure solid at zero pressure f^S/P are

$$\ln\left(\frac{f^S}{P}\right) = -1 - \ln b^* - \ln\left(v^{*S} - 1\right) - \frac{1}{(w-u)}\frac{a^{*S}}{b^*}\ln\left(\frac{v^{*S}+w}{v^{*S}+u}\right) \tag{25}$$

$$v^{*S} = \frac{1}{2}\left\{\left(\frac{a^{*S}}{b^*} - u - w\right) - \left[\left(u + w - \frac{a^{*S}}{b^*}\right)^2 - 4\left(uw + \frac{a^{*S}}{b^*}\right)\right]^{1/2}\right\} \tag{26}$$

Examining these two equations just given for the solid, we found that the only unknown is the equation-of-state parameter a for the solid a^{*S}. If the value of the solid a^{*S} is found, the solid volume and its fugacity coefficient, v^{*S} and f^S/P, can then be calculated from the preceding two equations. Here is our methodology to develop the equation-of-state parameter a for the solid, a^{*S}. Substituting Eqs. 18 and 25 into Eq. 6 results in

$$-1 - \ln b^* - \ln\left(v^{*S} - 1\right) - \frac{1}{(w-u)}\frac{a^{*S}}{b^*}\ln\left(\frac{v^{*S}+w}{v^{*S}+u}\right) = \ln\left(\frac{f^L}{P}\right) - \frac{\Delta H^f}{RT}\left(1 - \frac{T}{T_t}\right) \tag{27}$$

For a pure component, the latent heat of fusion ΔH^f and the triple-point temperature, T_t, are available from any pure-component databank, such as DIPPR. The liquid fugacity coefficient f^L/P at zero pressure is calculated by Eq. 18. The value of the righthand side in Eq. 27 therefore is known at a given temperature. Using Eq. 26 for v^{*S} in Eq. 27, the only unknown remaining in Eq. 27 is a^{*S}. Consequently, the unknown, a^{*S} can be solved from Eq. 27. The following steps are used to derive the solid equation-of-state parameter a^{*S}, and, hence, the solid alpha function, α^S:

(1) Calculate the generalized alpha function of liquid α^L from Eq. 22 at a given temperature by giving the critical temperature, critical pressure, and acentric factor of the component.

(2) Calculate the equation-of-state parameter of liquid a^L from Eqs. 10 and 22 using Eq. 20.

(3) Compute the reduced liquid volume at zero pressure from Eq. 19.

(4) Compute the liquid fugacity coefficient f^L/P at zero pressure from Eq. 18 using the calculated reduced liquid volume from Eq. 19.

(5) Solve Eq. 27 for the solid equation-of-state parameter a^{*S} by substituting Eq. 26 into Eq. 27.

(6) Calculate the solid alpha function, α^S, from $\alpha^S = a^S/a_c$ by using Eq. 10 for a_c.

(7) Repeat these steps for other temperatures.

The selected range of temperatures in the preceding procedures is wide enough to cover the entire range of temperature for SLE. Since the shape of the solid alpha function as a function of temperature is different from that of the liquid, we have developed a new alpha function for the solid to correlate the solid alpha function α^S as a function of the reduced temperature

$$\alpha^S(T) = 1 + \ell_s(1 - T_r^{0.5}) + m_s(1 - T_r)^{n_s}(0.7 - T_r) \quad (28)$$

The new solid alpha function, α^S, gives extremely high accuracy in the correlation of the data of the derived solid alpha function over a wide range of temperatures for any cubic equation of state. There are three parameters ℓ_S, m_S, and n_S in Eq. 28. These parameters are unique to each component and are determined from the procedures proposed earlier. We have developed the ℓ_S, m_S, and n_S parameters for use in Eq. 28 with the TST cubic equation of state. Some of these values are listed in Table 2.

Using the developed solid alpha function given by Eq. 28 in Eq. 9, we have successfully extended the TST cubic equation of state to the solid phase for predicting the solid fugacity coefficient at any temperature and pressure. Even though the methodology developed for the solid alpha function is at zero pressure, it can be used in the TST equation of state to predict the solid fugacity at elevated pressures, because the solid alpha function is temperature-dependent only, not pressure-dependent. The TST equation of state developed from this methodology predicts thermodynamic properties such as fugacity coefficients, volumes, and alpha functions for both solid and liquid phases in a totally consistent way.

The new methodology gives a predictive ability to the TST equation of state for SLE like that of the van't Hoff equation. However, unlike the van't Hoff equation, which is unable to handle solid solutions and unable to predict other properties, the equation-of-state method developed here is applicable to equilibria with formation of solid solutions. We will incorporate our A^E mixing rules in the TST equation of state to handle highly nonideal solid–liquid equilibrium systems.

Solid–Liquid Equilibria

At solid–liquid equilibrium, the respective fugacities of the components in both phases are equal

$$f_i^S = f_i^L \quad (29)$$

In terms of the fugacity coefficient, Eq. 29 becomes

$$\phi_i^S x_i^S = \phi_i^L x_i^L \quad (30)$$

We only consider the pure solid in this work. The application of our equation-of-state method to solid solutions will be presented in a separate article. If the solid is a pure component i, that is, $x_i^S = 1$. Equation 30 becomes

$$\phi_i^{oS} = \phi_i^L x_i^L \quad (31)$$

where ϕ_i^{oS} is the fugacity coefficient of the pure solid component i. The solubility of solid i in liquid, x_i^L, is then

$$x_i^L = \frac{\phi_i^{oS}}{\phi_i^L} \quad (32)$$

Equation 32 requires the calculation of the fugacity coefficients for both the solid and liquid phases. The general expression for the fugacity coefficient of component i in mixture can be derived from Eq. 13

$$\ln\left(\frac{f_i}{x_i P}\right) = (Z-1)\left[\frac{1}{b}\left(\frac{\partial nb}{\partial n_i}\right)\right] - \ln(Z - b^*) + \frac{1}{(w-u)}\frac{a^*}{b^*}\left\{\left[\frac{1}{b}\left(\frac{\partial nb}{\partial n_i}\right)\right] - \left[\frac{1}{na}\left(\frac{\partial n^2 a}{\partial n_i}\right)\right]\right\}\ln\left(\frac{Z + wb^*}{Z + ub^*}\right) \quad (33)$$

In this work, the TST cubic equation of state is applied to both the solid and liquid phases. The solid phase takes over

Table 2. ℓ_s, m_s, and n_s Parameters of Solid Alpha Function, α^S, with the TST Cubic Equation of State

Comp.	T_c (K)	P_c (bar)	T_f (K)	H_f (J/kg-mol)	ω	ℓ_s	m_s	n_s
CH	553.80	40.80	279.60	2,740,000	0.208054	1.40116	0.929097	0.753477
NC6	507.60	30.25	177.83	13,080,000	0.301261	−0.345243	5.17464	1.23093
2MP	497.70	30.40	119.55	6,268,000	0.279149	1.70022	3.49187	5.71100
NC7	540.20	27.40	182.57	14,050,000	0.349469	−0.0471049	5.37875	1.46981
NC16	723.00	14.00	291.308	53,358,000	0.717404	−4.48506	14.3126	0.636420
NC18	747.00	12.70	301.31	61,706,000	0.811359	−5.08971	16.0139	0.635623
NC22	787.00	10.60	317.15	48,953,000	0.972190	−1.64851	12.5644	0.849707
NC28	832.00	8.50	334.35	64,643,000	1.23752	−2.19647	15.7724	0.866198

Abbreviations: CH = cyclohexane C_6H_{12}; NC6 = *n*-hexane, C_6H_{14}; 2MP = 2-methylpentane, C_6H_{14}; NC7 = *n*-heptane, C_7H_{16}; NC16 = *n*-hexadecane, $C_{16}H_{34}$; NC18 = *n*-octadecane $C_{18}H_{38}$; NC22 = docosane $C_{22}H_{46}$; NC28 = octacosane $C_{28}H_{58}$.

the role of the liquid phase in vapor–liquid equilibrium calculations by replacing the liquid alpha function with the solid alpha function derived in the previous section. Although the equation-of-state parameter a for the solid is different from the liquid, the equation-of-state parameter b is the same for both phases. More specifically, the solid fugacity coefficient at system temperature and pressure is calculated from the TST cubic equation of state using the solid alpha function in Eq. 28 and the liquid fugacity coefficient is calculated from the same TST equation of state but using the generalized liquid alpha function given by Eq. 22 in the solid–liquid equilibrium calculations.

Equation 33 requires the mixing rule for the equation of state parameters a and b. The excess Helmholtz-energy zero-pressure mixing rules of TST are used for the a and b parameters

$$a^* = b^* \left[\frac{a^*_{vdw}}{b^*_{vdw}} + \frac{1}{C_r} \left(\frac{A_0^E}{RT} - \frac{A^E_{0vdw}}{RT} - \ln\left(\frac{b_{vdw}}{b} \right) \right) \right] \tag{34}$$

$$b^* = \frac{b^*_{vdw} - a^*_{vdw}}{1 - \left[\frac{a^*_{vdw}}{b^*_{vdw}} + \frac{1}{C_r} \left(\frac{A_0^E}{RT} - \frac{A^E_{0vdw}}{RT} - \ln\left(\frac{b_{vdw}}{b} \right) \right) \right]} \tag{35}$$

The C_r in the preceding equations is a constant, and is defined as

$$C_r = -\frac{1}{(w-u)} \ln\left(\frac{r+w}{r+u} \right) \tag{36}$$

A universal value of the reduced liquid volume $r = 1.18$ is assigned in this work (Twu et al. 1998). In Eqs. 34 and 35 A_0^E and A^E_{0vdw} are the excess Helmholtz energies at zero pressure. The subscript vdw in A^E_{0vdw} denotes that the properties are evaluated from the cubic equation of state using the van der Waals mixing rule for its a and b parameters. The expression for A^E_{0vdw} can be derived from the equation of state by assuming a fixed reduced liquid volume r for a van der Waals fluid at zero pressure

$$\frac{A^E_{0vdw}}{RT} = \sum_i x_i \ln\left(\frac{b_i}{b_{vdw}} \right) + C_r \left[\frac{a^*_{vdw}}{b^*_{vdw}} - \sum_i x_i \frac{a_i^*}{b_i^*} \right] \tag{37}$$

Here a_{vdw} and b_{vdw} are the equation of state a and b parameters, which are evaluated from the conventional van der Waals one-fluid mixing rules without using any binary interaction parameters

$$a_{vdw} = \sum_i \sum_j x_i x_j \sqrt{a_i a_j} \tag{38}$$

$$b_{vdw} = \sum_i \sum_j x_i x_j \left[\frac{1}{2} (b_i + b_j) \right] \tag{39}$$

The mixing rule for the parameter b as given by Eq. 35 forces the mixing rule to satisfy the quadratic composition dependence of the second virial coefficient. Alternatively, the conventional van der Waals mixing rule could be chosen for the b parameter, that is, ignoring the second virial coefficient boundary condition. We have chosen $b = b_{vdw}$ in this work. Equations 34 and 35 are then simplified to

$$a^* = a^*_{vdw} + \frac{b^*_{vdw}}{C_r} \left(\frac{A_0^E}{RT} - \frac{A^E_{0vdw}}{RT} \right) \tag{40}$$

$$b = \sum_i \sum_j x_i x_j \left[\frac{1}{2} (b_i + b_j) \right] \tag{41}$$

Since A_0^E in Eq. 40 is at zero pressure, its value is identical to the excess Gibbs free energy G^E at zero pressure. Therefore, any activity model can be used directly for the excess Helmholtz energy expression A_0^E in the equation. Twu et al. (2001) have presented a general multicomponent equation for a liquid activity model for incorporation in the A^E mixing rules as

$$\frac{G^E}{RT} = \sum_i^n x_i \frac{\sum_j^n x_j \tau_{ji} G_{ji}}{\sum_k^n x_k G_{ki}} \tag{42}$$

Equation 42 appears to be similar to the NRTL equation, but there is a fundamental difference between them. NRTL assumes A_{ij}, A_{ji}, and α_{ij} are the parameters of the model, but our excess Gibbs energy model assumes τ_{ij} and G_{ij} are the binary interaction parameters. More importantly, any appropriate temperature-dependent function can be applied to τ_{ij} and G_{ij}. For example, to obtain the NRTL model, τ_{ij} and G_{ij} are calculated as usual from the NRTL parameters A_{ij}, A_{ji}, and α_{ij}

$$\tau_{ji} = \frac{A_{ji}}{T} \tag{43}$$

$$G_{ji} = \exp(-\alpha_{ji} \tau_{ji}) \tag{44}$$

We also note Eq .42 can recover the conventional van der Waals mixing rules when the following expressions are used for τ_{ij} and G_{ij}

$$\tau_{ji} = \frac{1}{2} \delta_{ij} b_i \tag{45}$$

$$G_{ji} = \frac{b_j}{b_i} \tag{46}$$

where

$$\delta_{ij} = -\frac{C_1}{RT} \left[\left(\frac{\sqrt{a_i}}{b_i} - \frac{\sqrt{a_j}}{b_j} \right)^2 + 2k_{ij} \frac{\sqrt{a_i}}{b_i} \frac{\sqrt{a_j}}{b_j} \right] \tag{47}$$

$$C_1 = -\frac{1}{(w-u)} \ln\left(\frac{1+w}{1+u} \right) \tag{48}$$

Equations 45–48 are expressed in terms of the cubic equation-of-state parameters, a_i and b_i, and the binary interaction parameter, k_{ij}. The preceding discussion demonstrates that Eq. 42 is more generic in form than NRTL. Both the NRTL and van der Waals fluid parameters are special cases of our excess Gibbs energy function.

Results

The systems considered here are highly nonideal mixtures due to the large differences in the size of the molecules. In this work, we apply two tests for the prediction and correlation of SLE data using our equation-of-state method. The tests are designed for two cases. Case 1 is to test the ability of predicting solid–liquid equilibrium data without use of binary interaction parameters. Case 2 is to test the ability of correlating solid–liquid equilibrium data by using Eqs. 42–44 for G^E in our A^E mixing rules, Eqs. 40 and 41.

Case 1. The ability to predict SLE from our equation of state is tested. The predictions will be checked against actual solid–liquid equilibrium data. The results will be compared with those predicted from the van't Hoff equation. The van't Hoff equation is the only one widely used in the prediction of SLE for performing preliminary design calculations. According to the best of our knowledge, our equation of state is probably the only equation-of-state method possessing the same accuracy in the predictive capability as the van't Hoff equation.

To demonstrate, we have chosen here the excess Gibbs energy model G^E given by Eqs. 42–44 for use in our A^E mixing rules of Eqs. 40 and 41. As mentioned previously, because A_0^E in Eq. 40 is at zero pressure, its value is identical to the excess Gibbs energy, G^E, at zero pressure. Since Eqs. 42–44 are the same as the NRTL equation, the NRTL parameters, A_{ij}, A_{ji} and α_{ij}, if available from a database, can be used directly in the mixing rule for the prediction of solid solubilities in liquid from vapor–liquid equilibrium data. However, it is well known that the NRTL binary interaction parameters (BIPs) are a strong function of temperature. The BIPs regressed from VLE data at one temperature are not accurate for the prediction of VLE at the other temperatures. Furthermore, the vapor–liquid data at low temperatures where the solid is in equilibrium with liquid are often unavailable. To test the true ability of predicting solid–liquid equilibria from our equation of state, we therefore decided not to use binary interaction parameters in this case.

Two systems are considered in detail: *n*-hexadecane ($C_{16}H_{34}$)/*n*-hexane (C_6H_{14}) and docosane ($C_{22}H_{46}$)/2-methylpentane (C_6H_{14}). The predicted solid solubilities are shown in Tables 3 and 4. In Tables 3 and 4, we label x_1, van't Hoff, and TST CEOS as the experimental solid solubility in the liquid phase, predicted from the van't Hoff equation and our equation-of-state method, respectively. The predicted solid solubility in the liquid phase for *n*-hexadecane ($C_{16}H_{34}$)/*n*-hexane (C_6H_{14}) is very accurate, with an AAD% of 2.87% and 2.83% from the van't Hoff equation and our equation-of-state method, respectively, despite the assumption of using zero values for the NRTL BIPs. However, both the van't Hoff equation and our equation-of-state method underpredict solid solubilities for the system docosane ($C_{22}H_{46}$)/2-methylpentane (C_6H_{14}) by 29%. Although the prediction is not accurate enough, the model predicts reasonable and consistent values. Because of this, solubility data can be correlated with a high accuracy by our equation of state using the A^E mixing rules. The accurate results are given in Table 5, and the BIPs are given in Table 6. The AAD% of the regression for this system is 3.00%. This AAD% is principally due to two points at 316.00 K and 315.25 K that deviate by 17.77% and 12.86%.

Table 3. Comparison of Experimental and Predicted Solid Solubilities of Hexadecane ($C_{16}H_{34}$), Designated as Component 1, in the Binary Liquid System Hexadecane ($C_{16}H_{34}$) and Hexane (C_6H_{14}) from the van't Hoff Equation and TST Cubic Equation of State Without Use of Binary Interaction Parameters

No.	T (K)	x_1	van't Hoff	Devi%	TST CEOS	Devi%
1	277.35	0.3273	0.3300	0.81	0.3313	1.23
2	280.00	0.4087	0.4107	0.50	0.4123	0.87
3	281.90	0.4602	0.4794	4.16	0.4808	4.48
4	283.35	0.5157	0.5386	4.44	0.5399	4.69
5	284.35	0.5630	0.5833	3.60	0.5843	3.78
6	285.25	0.6069	0.6263	3.20	0.6270	3.32
7	286.35	0.6576	0.6829	3.84	0.6831	3.87
8	287.15	0.6993	0.7269	3.94	0.7266	3.90
9	288.10	0.7470	0.7824	4.75	0.7815	4.62
10	288.70	0.7949	0.8195	3.10	0.8180	2.91
11	289.35	0.8355	0.8615	3.11	0.8593	2.85
12	289.90	0.8729	0.8985	2.93	0.8957	2.61
13	290.55	0.9254	0.9441	2.03	0.9404	1.63
14	290.95	0.9577	0.9733	1.62	0.9690	1.18
15	291.45	1.0000	1.0000	0.00	1.0000	0.00
AAD%				2.87		2.83

Table 4. Comparison of Experimental and Predicted Solid Solubilities of Docosane ($C_{22}H_{46}$), Designated as Component 2, in the Binary Liquid System 2-Methylpentane (C_6H_{14}) and Docosane ($C_{22}H_{46}$) from the van't Hoff Equation and TST Cubic Equation of State Without Use of Binary Interaction Parameters.

No.	T (K)	x_1	van't Hoff	Devi%	TST CEOS	Devi%
1	317.05	0.0000	0.0000	0.00	0.0000	0.00
2	316.50	0.0543	0.0374	−31.10	0.0407	−25.01
3	316.00	0.0795	0.0653	−17.82	0.0681	−14.36
4	315.85	0.1043	0.0736	−29.46	0.0762	−26.98
5	315.40	0.1654	0.0979	−40.82	0.1000	−39.53
6	315.35	0.1666	0.1006	−39.64	0.1026	−38.39
7	315.25	0.1985	0.1059	−46.67	0.1079	−45.66
8	314.40	0.2589	0.1499	−42.10	0.1512	−41.62
9	313.50	0.3209	0.1944	−39.42	0.1950	−39.23
10	313.35	0.3395	0.2016	−40.62	0.2021	−40.47
11	312.40	0.3915	0.2460	−37.18	0.2459	−37.19
12	311.35	0.4473	0.2924	−34.63	0.2919	−34.75
13	310.35	0.5019	0.3342	−33.41	0.3334	−33.58
14	309.65	0.5241	0.3622	−30.90	0.3611	−31.10
15	309.35	0.5352	0.3738	−30.15	0.3727	−30.36
16	308.70	0.5751	0.3984	−30.72	0.3972	−30.94
17	307.40	0.6294	0.4451	−29.29	0.4436	−29.52
18	305.75	0.6794	0.4996	−26.47	0.4980	−26.70
19	304.05	0.7268	0.5506	−24.24	0.5491	−24.45
20	302.35	0.7631	0.5970	−21.77	−0.5956	−21.95
21	300.95	0.7905	0.6319	−20.06	0.6306	−20.23
22	298.50	0.8331	0.6865	−17.60	0.6855	−17.72
23	295.75	0.8704	0.7391	−15.09	0.7383	−15.17
24	293.50	0.8957	0.7760	−13.37	−0.7755	−13.42
AAD%				28.85		28.26

Table 5. Comparison of Experimental and Predicted Solid Solubilities of Docosane ($C_{22}H_{46}$), Designated as Component 2, in the Binary Liquid System 2-Methylpentane (C_6H_{14}) and Docosane ($C_{22}H_{46}$) from TST Cubic Equation of State Using the CEOS/A^E Zero Pressure-Mixing Rules

No.	T (K)	x_1	TST CEOS	Diff.	Devi%
1	317.05	0.0000	0.0000	0.0000	0.00
2	316.50	0.0543	0.0490	−0.0053	−9.73
3	316.00	0.0795	0.0936	0.0141	17.77
4	315.85	0.1043	0.1087	0.0044	4.24
5	315.40	0.1654	0.1567	−0.0087	−5.23
6	315.35	0.1666	0.1621	−0.0045	−2.67
7	315.25	0.1985	0.1730	−0.0255	−12.86
8	314.40	0.2589	0.2576	−0.0013	−0.49
9	313.50	0.3209	0.3299	0.0090	2.81
10	313.35	0.3395	0.3405	0.0010	0.30
11	312.40	0.3915	0.4008	0.0093	2.37
12	311.35	0.4473	0.4571	0.0098	2.18
13	310.35	0.5019	0.5038	0.0019	0.38
14	309.65	0.5241	0.5336	0.0095	1.80
15	309.35	0.5352	0.5457	0.0105	1.96
16	308.70	0.5751	0.5708	−0.0043	−0.74
17	307.40	0.6294	0.6171	−0.0123	−1.96
18	305.75	0.6794	0.6692	−0.0102	−1.50
19	304.05	0.7268	0.7164	−0.0104	−1.43
20	302.35	0.7631	0.7577	−0.0054	−0.71
21	300.95	0.7905	0.7876	−0.0029	−0.37
22	298.50	0.8331	0.8315	−0.0016	−0.19
23	295.75	0.8704	0.8699	−0.0005	−0.06
24	293.50	0.8957	0.8942	−0.0015	−0.17
AAD/AAD%				0.0073	3.00

Neglecting these two points in the analysis results in an AAD% of less than 2%. This case demonstrates that our methodology is very successful in developing a cubic equation of state for the prediction of solid–liquid equilibria to have the same accuracy of predicted solubilities as the van't Hoff equation.

Case 2. The ability of correlating solid–liquid equilibrium data over the entire liquidus line is tested. We have considered five highly nonideal binary mixtures, which may be described by the solid fugacity equation given by Prausnitz (1969) combined with any liquid activity model for the liquid phase. The nonideal systems selected for testing the cubic equation-of-state method for SLE are listed in Table 6. Since the NRTL binary interaction parameters are not available for these systems at low temperatures, we have to regress the SLE data to derive the binary interaction parameters. The binary interaction parameters of our A^E mixing rules used in the TST equation of state are A_{ij} and A_{ji} with the value of α_{ij} set equal to 0.2. Table 6 gives the values of binary interaction parameters for each system. The accuracy of the correlation, which is in the terms of average absolute deviation percentage (AAD%) in the solid solubility in the liquid phase, is also given in Table 6. There are two results for comparison, one is by prediction and the other is by correlation. The AAD% of the prediction from the TST equation of state is obtained by setting the binary interaction parameters, equal to zero. The AAD% of the correlation is obtained by the regression of the SLE data into the two binary interaction parameters, A_{ij} and A_{ji}, for each binary while fixing the third parameter of α_{ij} to a constant value of 0.2. The results of the prediction are quite accurate for all systems, except for the system docosane ($C_{22}H_{46}$)/2-methylpentane (C_6H_{14}), as just discussed. The predicted results can be improved significantly by using the binary interaction parameters, as given in Table 6. The equations-of-state method accurately correlates data covering the entire liquidus curve with a typical error of 1 to 5% deviation in solid solubility in the liquid phase for highly nonideal systems.

The results of the NRTL binary interaction parameters obtained from solid–liquid equilibria are the values at the lowest temperature limit for the phase equilibria. Since the binary interaction parameters are a function of temperature, the binary interaction parameters derived from SLE data are very valuable for extending the application of a cubic equation of state and the NRTL model to vapor–liquid equilibria at very low temperatures.

Conclusions

A thermodynamic framework for predicting solid–liquid equilibria from an equation-of-state method combined with an excess Helmholtz-energy mixing rule is developed. The developed TST equation of state is able to predict solid–liquid equilibria with the same accuracy as the van't Hoff equation. The data of solid–liquid equilibria can be correlated accurately by our equation-of-state method using A^E mixing rules. The binary interaction parameters of the activity coefficient model used in the A^E mixing rule obtained from SLE extend the application of a cubic equation of state and activity coefficient model to the lowest temperature limit for the prediction of vapor–liquid equilibria. Our approach developed here will be applied to solid–liquid equilibria of solid solutions in our next work.

Table 6. Average Absolute Deviation Percent (AAD%) for the Predicted and Correlated Solid Solubilities of Component 1 in Binary Liquid System from TST Cubic Equation of State Using the CEOS/A^E Zero-Pressure Mixing Rules ($\alpha_{ij} = 0.2$)*

	Predicted			Correlated		
Binary	A_{12}	A_{21}	AAD%	A_{12}	A_{21}	AAD%
NC16 (1)/NC6 (2)	0.0	0.0	2.83	936.963	−606.385	0.79
CH (1)/NC16 (2)	0.0	0.0	7.99	−748.160	1,325.78	5.42
2MP (1)/NC22 (2)	0.0	0.0	28.26	−583.952	1,136.67	3.00
NC28 (1)/NC7 (2)	0.0	0.0	5.71	2,588.26	−1,243.95	0.95
CH (1)/NC18 (2)	0.0	0.0	6.07	−760.282	1,350.08	2.84

* Data taken from International DATA Series, Selected Data on Mixtures: Ser. A.

Abbreviations: CH = Cyclohexane, C_6H_{12}; NC6 = *n*-hexane, C_6H_{14}; 2MP = 2-methylpentane, C_6H_{14}; NC7 = *n*-heptane, C_7H_{16}; NC16 = *n*-hexadecane, $C_{16}H_{34}$; NC18 = *n*-octadecane $C_{18}H_{38}$; NC22 = docosane, $C_{22}H_{46}$; NC28 = octacosane, $C_{28}H_{58}$.

Notation

a, b = cubic equation-of-state parameters
a^*, b^* = defined as Pa/R^2T^2 and Pb/RT, respectively
A = Helmholtz energy
C_1 = constant as defined in Eq. 48
C_r = constant as defined in Eq. 36
C_p = heat capacity
G = Gibbs energy
k_{ij} = binary interaction parameter
ℓ, m, n = parameters in the Twu's α function
P = pressure
R = gas constant
T = temperature
u, w = cubic equation-of-state constants
v = volume
x_i = mole fraction of component i
Z_c = critical compressibility factor

Greek letters

α = cubic equation-of-state alpha function
δ_{ij} = characteristic of the interaction between molecules i and j as defined by Eq. 47

Subscripts and superscripts

i, j = property of components i, j
ij = interaction property between components i and j
o = zero pressure
vdw = van der Waals
* = reduced property
E = excess property
L = liquid properties
S = solid properties

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Manuscript received Feb. 25, 2002, revision received Nov. 26, 2002, and final revision received May 19, 2003.