

## A versatile liquid activity model for SRK, PR and a new cubic equation-of-state TST

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### Abstract

The recent development of a new excess Gibbs function  $G^E$  by Twu, Sim and Tassone allows infinite-pressure cubic equations of state/ $A^E$  (CEOS/ $A^E$ ) mixing rules to transition smoothly to the conventional van der Waals one-fluid mixing rules. The incorporation of their proposed  $G^E$  model into a cubic equation-of-state allows an equation-of-state to describe both van der Waals fluids and highly non-ideal mixtures over a broad range of temperatures and pressures in a consistent and unified framework. We continue our work to develop a versatile excess Gibbs free energy function for zero-pressure CEOS/ $A^E$  mixing rules, in addition to the infinite-pressure CEOS/ $A^E$  mixing rules.

An optimal two-parameter cubic equation-of-state TST (Twu–Sim–Tassone) has been found to allow better prediction of liquid densities for heavy hydrocarbons and polar components. The alpha function of the TST cubic equation-of-state is generalized here. The generalized alpha function is a linear function of the acentric factor at a constant reduced temperature, not a fourth-order or a sixth-order function as suggested by Soave and other researchers. The advantage of a linear function in the acentric factor is obvious in the extrapolation of the alpha function to heavy hydrocarbons, petroleum fractions, and gas condensates. The new generalized alpha function, when used with the TST, allows very accurate prediction of the vapor pressure from the triple point to the critical point of hydrocarbons. The performance of SRK, PR and TST is examined using the versatile excess Gibbs free energy function in the zero-pressure CEOS/ $A^E$  mixing rules for the prediction of high pressure and high temperature phase equilibria of highly non-ideal systems. © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Liquid  $G^E$  model; Mixing rules; Excess Gibbs free energy; Excess Helmholtz energy; Cubic equations of state; TST

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### 1. Introduction

Due to the simplicity and the accuracy of predicting  $K$ -values, cubic equations of state (CEOS) are widely used in refinery and petroleum reservoir industries for the prediction of phase behavior. Therefore, to generalize the alpha function for a cubic equation-of-state as a linear function of the acentric

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factor for estimating the vapor pressures of pure hydrocarbons, petroleum fractions and tar sands, is extremely valuable in the simulation of phase equilibrium calculations in the petroleum production and refining industries. In this paper, a generalized alpha function using our new cubic equation-of-state TST (Twu–Sim–Tassone) will be presented.

The modern development of combining cubic equations of state with excess Helmholtz or excess Gibbs free energy models has advanced the CEOS to an extent that it is now an accepted and effective method for correlating and predicting phase equilibrium behavior of highly non-ideal systems. However, it is extremely desirable that the excess Helmholtz or excess Gibbs energy mixing rules reduce to the classical mixing rules, since, it is well known that the classical mixing rules work very well for nonpolar systems. Introducing this capability into an excess energy model ensures the binary interaction parameters for the classical quadratic mixing rules available in many existing databanks for systems involving hydrocarbons and gases can be used directly in the excess energy mixing rules. In this way, the equation-of-state is able to handle non-ideal systems while still retaining the equation-of-state capability to handle non-polar systems in the accurate prediction of high pressure and high temperature phase equilibria.

A methodology is proposed to reduce excess energy zero-pressure mixing rules to the van der Waals one-fluid mixing rule. The incorporation of the new excess energy zero-pressure mixing rules into a cubic equation-of-state allows the CEOS/ $A^E$  mixing rule to transition smoothly to the conventional van der Waals one-fluid mixing rules. This can be useful for systems where only some of the binary pairs require the use of a CEOS/ $A^E$  mixing rule or an activity model, while other binary pairs can be described adequately by the van der Waals one-fluid mixing rules.

## 2. Generalized TST cubic equation-of-state

An optimal two-parameter TST cubic equation-of-state has been developed by Twu et al. [1] to allow better prediction of liquid densities for heavy hydrocarbons and polar components as well as the accurate prediction of vapor pressure. We will generalize the alpha function for the TST cubic equation-of-state as a linear function of the acentric factor for its application to systems containing undefined hydrocarbons such as petroleum fractions.

Our TST cubic equation-of-state is represented by the following equation:

$$P = \frac{RT}{v - b} - \frac{a}{v^2 + 2.5bv - 1.5b^2} \quad (1)$$

Eq. (1) can be rewritten in another form as

$$P = \frac{RT}{v - b} - \frac{a}{(v + 3b)(v - 0.5b)} \quad (2)$$

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 to zero at the critical point resulting in

$$a_c = \frac{0.470507R^2T_c^2}{P_c} \quad (3)$$

$$b_c = \frac{0.0740740RT_c}{P_c} \quad (4)$$

$$Z_c = 0.296296 \quad (5)$$

where subscript c denotes the critical point. Its worth noting that the value of  $Z_c$  from SRK and PR is both larger than 0.3 and TST is slightly below it, the closest to the real one for many substances.

The parameter  $a$  is a function of temperature. The value of  $a(T)$  at temperatures other than the critical temperature can be calculated from:

$$a(T) = \alpha(T)a_c \quad (6)$$

where the alpha function,  $\alpha(T)$ , is a function only of reduced temperature,  $T_r = T/T_c$ . We use the Twu alpha correlation [2]

$$\alpha(T) = T_r^{N(M-1)} e^{L(1-T_r^{NM})} \quad (7)$$

Eq. (7) 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. The  $L$ ,  $M$ , and  $N$  parameters used to get the correct pure component vapor pressure for all pure components used in this paper are listed in Table 1 for use with our TST equation.

Table 1  
 $L$ ,  $M$ , and  $N$  parameters of Twu  $\alpha$  function with the TST cubic equation-of-state

Component	$T_c$ (K)	$P_c$ (bar)	$L$	$M$	$N$
Methane	190.564	45.99	0.573159	0.982462	0.600000
Ethane	305.32	48.72	0.602469	0.900708	0.726375
Propane	369.83	42.48	0.856729	0.937274	0.617916
<i>n</i> -Butane	425.12	37.96	0.512768	0.846110	1.03032
<i>n</i> -Pentane	469.70	33.70	0.379003	0.817571	1.37301
<i>n</i> -Hexane	507.60	30.25	0.116525	0.861045	3.24960
<i>n</i> -Heptane	540.20	27.40	0.655021	0.829163	1.12134
<i>n</i> -Octane	568.70	24.90	0.480608	0.809353	1.51003
<i>n</i> -Nonane	594.60	22.90	0.476586	0.796538	1.59017
<i>n</i> -Decane	617.70	21.10	0.434215	0.800647	1.83141
<i>n</i> -Undecane	639.00	19.50	0.350720	0.791588	2.16104
<i>n</i> -Dodecane	658.00	18.20	0.347166	0.796276	2.32898
<i>n</i> -Tridecane	675.00	16.80	0.532094	0.784911	1.81625
<i>n</i> -Tetradecane	693.00	15.70	0.751165	0.790331	1.44854
<i>n</i> -Pentadecane	708.00	14.80	0.991001	0.837872	1.22559
<i>n</i> -Hexadecane	723.00	14.00	0.692934	0.780273	1.65416
<i>n</i> -Heptadecane	736.00	13.40	0.644891	0.787812	1.85694
<i>n</i> -Octadecane	747.00	12.70	0.672729	0.790676	1.87655
<i>n</i> -Nonadecane	758.00	12.10	0.481264	0.781396	2.45487
Eicosane	768.00	11.60	0.374821	0.799312	3.14676
Cyclohexane	553.58	40.73	0.163372	0.818375	1.94856
Benzene	562.16	48.98	0.0804681	0.861052	3.01148
Acetone	508.20	47.01	0.794606	0.925926	0.936024
Methanol	512.64	80.97	0.525320	0.873161	1.98650
Ethanol	513.92	61.48	2.74174	6.35611	0.0984540
Water	647.13	220.55	0.434175	0.871528	1.66108

The generalized alpha function being developed can be expressed as a function of two variables, reduced temperature and acentric factor

$$\alpha = \alpha(T_r, \omega) \quad (8)$$

The generalized alpha function proposed for non-library and petroleum fractions is

$$\alpha = \alpha^{(0)} + \omega(\alpha^{(1)} - \alpha^{(0)}) \quad (9)$$

where  $\alpha^{(0)}$  is for  $\omega = 0$  and  $\alpha^{(1)}$  is for  $\omega = 1$ . Each alpha is a function of reduced temperature only. The procedures to derive  $\alpha^{(0)}$  and  $\alpha^{(1)}$  are briefly described here.

The first step in generalizing the alpha function is to derive the Twu alpha as a function of temperature for each individual compound. The resulting parameters for individual components are listed in Table 1. The data of  $T_c$  and  $P_c$  in Table 1 and  $\omega$  in Table 3 are taken from DIPPR [3]. The  $\alpha$  of each compound is then computed at  $T_r$  increments of 0.02 from 0.3 to 1.0. The computed values of the  $\alpha$  at 36 different constant reduced temperatures are plotted as a function of the acentric factor. Straight lines derived from the TST equation are observed for  $\alpha$  versus  $\omega$  plots in all regions. A least-squares linear fit of  $\alpha$  versus  $\omega$  yields the intercept  $\alpha^{(0)}$  and the slope  $(\alpha^{(1)} - \alpha^{(0)})$  at each reduced temperature. A table of data of  $(T_r, \alpha^{(0)})$  and  $(T_r, \alpha^{(1)})$  are obtained for values of  $T_r$  from 0.3 to 1.0. The final step is to correlate the tabulated data of  $(T_r, \alpha^{(0)})$  and  $(T_r, \alpha^{(1)})$  using the Twu alpha function to correlate  $\alpha^{(0)}$  and  $\alpha^{(1)}$  in terms of  $T_r$  as follows:

$$\alpha^{(0)} = T_r^{N^{(0)}(M^{(0)}-1)} e^{L^{(0)}(1-T_r^{N^{(0)}M^{(0)}})} \quad (10)$$

$$\alpha^{(1)} = T_r^{N^{(1)}(M^{(1)}-1)} e^{L^{(1)}(1-T_r^{N^{(1)}M^{(1)}})} \quad (11)$$

The  $L$ ,  $M$ , and  $N$  databank for Eqs. (10) and (11) are listed in Table 2. The values of  $\alpha^{(0)}$  and  $\alpha^{(1)}$  in Eqs. (10) and (11) are consistent with the definition of acentric factor at  $\omega = 0$  and  $\omega = 1$ , respectively, i.e. these two alpha functions are forced to pass through the saturated vapor pressure at  $T_r = 0.7$  for  $\omega = 0$  and  $\omega = 1$ , respectively.

The vapor pressure data were compared with the prediction from the generalized alpha function. The results are given in Table 3. Using our generalized alpha function in TST equation-of-state gives highly accurate prediction of vapor pressures. The average absolute deviation percentage (AAD%) from the triple point to the critical point is only 1.32% for over all 1453 points of vapor pressure data.

Since the  $\alpha$  expression is derived from the vapor pressure data, using the same expression beyond the critical temperature represents extrapolation into an unknown region. We have fitted the alpha of

Table 2

The  $L$ ,  $M$ , and  $N$  databank of the generalized alpha function for Eqs. (10) and (11) with TST equation-of-state for subcritical and supercritical conditions

$\alpha$ Parameter	$T_r \leq 1$		$T_r > 1$	
	$\alpha^{(0)}$	$\alpha^{(1)}$	$\alpha^{(0)}$	$\alpha^{(1)}$
$L$	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

Table 3

AAD% of predicted vapor pressures from the triple point to the critical point from the TST equation-of-state using the generalized alpha function

Component	$\omega$	Temperature range (K)			Pressure range (bar)			AAD%
C <sub>1</sub>	0.0115	95.00	–	190.00	0.19812	–	45.124	0.26
C <sub>2</sub>	0.0995	95.00	–	300.00	3.6081E–5	–	43.519	0.43
C <sub>3</sub>	0.1523	90.00	–	365.00	9.6815E–9	–	38.741	1.32
NC4	0.2002	135.00	–	425.00	6.9258E–6	–	37.629	1.32
NC5	0.2515	145.00	–	465.00	9.4481E–7	–	31.364	0.78
NC6	0.3013	180.00	–	505.00	1.2539E–5	–	29.304	2.74
NC7	0.3495	185.00	–	540.00	2.6692E–6	–	27.119	0.94
NC8	0.3996	220.00	–	565.00	3.2395E–5	–	23.486	1.40
NC9	0.4435	220.00	–	590.00	4.5030E–6	–	21.687	0.33
NC10	0.4923	245.00	–	615.00	1.6476E–5	–	20.189	1.43
NC11	0.5303	250.00	–	635.00	5.4713E–6	–	18.505	1.41
NC12	0.5764	265.00	–	655.00	7.2280E–6	–	17.527	0.91
NC13	0.6174	270.00	–	675.00	3.2534E–6	–	16.786	0.79
NC14	0.6430	280.00	–	690.00	2.8252E–6	–	15.120	2.45
NC15	0.6863	285.00	–	705.00	1.6050E–6	–	14.211	0.87
NC16	0.7174	291.55	–	720.00	1.0666E–6	–	13.590	2.77
NC17	0.7697	300.00	–	735.00	8.1792E–7	–	13.271	0.44
NC18	0.8114	305.00	–	745.00	5.2060E–7	–	12.248	0.52
NC19	0.8522	310.00	–	755.00	2.8942E–7	–	11.625	1.41
NC20	0.9069	310.00	–	765.00	9.7590E–8	–	11.285	2.54
Total AAD%								1.32

hydrogen and methane in the supercritical region to reproduce the Henry's constants for those solutes in hydrocarbon liquids. In this work, we have modified the  $\alpha^{(0)}$  and  $\alpha^{(1)}$  constants given by Eqs. (10) and (11) to approximate these values in the supercritical regions. These constants  $L$ ,  $M$ , and  $N$  for the supercritical regions are also given in Table 2. In addition to approximating the hydrogen and methane alpha values, maintaining the continuity of the property prediction at the critical point is important. The two sets of  $L$ ,  $M$ , and  $N$  parameters given in Table 2 are matching fits at the critical point. They are smooth not only in slope (first derivative), but also in curvature (second derivative) at the critical point to make sure that the derived enthalpy departure and heat capacity properties are both smooth at the critical point. Since our TST cubic equation-of-state predicts very high accurate vapor pressures for light as well as heavy hydrocarbons, it is recommended that our TST CEOS method be used to estimate  $\omega$  for petroleum fractions. Using TST CEOS to obtain  $\omega$  will maintain internal consistency for the calculation of vapor and liquid fugacities.

We also make the comparison of the generalized alpha between TST and Soave for a very wide range of  $T_r$  from  $T_r = 0.3$  to 18 for hydrogen and methane. The values of  $T_c$ ,  $P_c$  and  $\omega$  for hydrogen and methane are taken from DIPPR databank [3]. The results as shown in Table 4 demonstrate the generalized alpha of our TST is able to describe the maximum behavior of the quantum fluid H<sub>2</sub> at the low temperature. The TST alpha function shows correct behavior, decreasing with increasing temperature at high temperatures. The Soave's alpha, however, exhibits abnormal behavior for C<sub>1</sub>, going through a minimum value of zero and then increasing with increasing temperature. We would like to point it out that if the value of the

Table 4

Comparison of the generalized alpha between TST and Soave for H<sub>2</sub> and CH<sub>4</sub>

$T/T_c$	TST		Soave	
	H <sub>2</sub>	CH <sub>4</sub>	H <sub>2</sub>	CH <sub>4</sub>
0.30	0.9387	1.3372	1.1196	1.4830
0.40	0.9711	1.2674	1.0967	1.3853
0.50	0.9896	1.2097	1.0767	1.3020
0.60	1.0003	1.1595	1.0588	1.2289
0.70	1.0056	1.1145	1.0424	1.1635
0.80	1.0069	1.0735	1.0273	1.1043
0.90	1.0049	1.0355	1.0132	1.0500
1.00	1.0000	1.0000	1.0000	1.0000
2.00	0.8498	0.7485	0.8964	0.6408
3.00	0.7140	0.6101	0.8207	0.4192
4.00	0.6190	0.5221	0.7595	0.2688
5.00	0.5500	0.4607	0.7076	0.1638
6.00	0.4974	0.4148	0.6622	0.0912
7.00	0.4559	0.3791	0.6218	0.0430
8.00	0.4221	0.3503	0.5853	0.0143
9.00	0.3941	0.3265	0.5520	0.0014
10.00	0.3703	0.3064	0.5215	0.0017
11.00	0.3499	0.2892	0.4932	0.0134
12.00	0.3321	0.2743	0.4670	0.0348
13.00	0.3165	0.2612	0.4425	0.0649
14.00	0.3026	0.2496	0.4195	0.1026
15.00	0.2901	0.2392	0.3979	0.1471
16.00	0.2789	0.2299	0.3776	0.1978
17.00	0.2687	0.2214	0.3584	0.2540
18.00	0.2595	0.2137	0.3402	0.3154

methane alpha is close to zero, it will require a very large value for the binary interaction parameter  $k_{ij}$  in order to fit the Henry's law data at that temperature.

### 3. Zero-pressure CEOS/A<sup>E</sup> mixing rules

Our TST equation will be combined with our proposed new excess energy mixing rule to evaluate its ability in the prediction of high temperature and high pressure VLE of strongly non-ideal systems. Three different approaches exist for the application of CEOS/A<sup>E</sup> mixing rules. One is the infinite-pressure approach as proposed by Huron and Vidal [4], Wong and Sandler [5], and Twu and Coon [6]. The second one is the zero-pressure approach as developed by Heidemann and Kokal [7], Michelsen [8], Dahl and Michelsen [9], Holderbaum and Gmehling [10], Twu et al. [11], and Twu et al. [12]. The third one is the no reference-pressure approach as proposed by Twu et al. [13]. There is a fundamental difference among these approaches. The infinite-pressure approach assumes excess Helmholtz energy to be independent of pressure. The zero-pressure and no reference-pressure approaches assume reduced liquid volume to be either a constant value or the same as that of van der Waals fluid.

Twu et al. [11] developed the following zero-pressure mixing rules for the cubic equation-of-state mixture  $a$  and  $b$  parameters

$$a^* = b^* \left[ \frac{a_{\text{vdw}}^*}{b_{\text{vdw}}^*} + \frac{1}{C_{v_0}} \left( \frac{A_0^E}{RT} - \frac{A_{0,\text{vdw}}^E}{RT} - \ln \left( \frac{b_{\text{vdw}}}{b} \right) \right) \right] \quad (12)$$

$$b^* = \frac{b_{\text{vdw}}^* - a_{\text{vdw}}^*}{1 - \left[ \frac{a_{\text{vdw}}^*}{b_{\text{vdw}}^*} + \frac{1}{C_{v_0}} \left( \frac{A_0^E}{RT} - \frac{A_{0,\text{vdw}}^E}{RT} - \ln \left( \frac{b_{\text{vdw}}}{b} \right) \right) \right]} \quad (13)$$

$a_{\text{vdw}}$  and  $b_{\text{vdw}}$  are the equation-of-state  $a$  and  $b$  parameters which are evaluated from the van der Waals mixing rules. The Twu mixing rule given by Eqs. (12) and (13) is volume-dependent through  $C_{v_0}$ .  $C_{v_0}$  is a function of reduced liquid volume at zero-pressure  $v_0^* = v_0/b$ :

$$C_{v_0} = -\frac{1}{w - u} \ln \left( \frac{v_0^* + w}{v_0^* + u} \right)_{\text{vdw}} \quad (14)$$

The zero-pressure liquid volume  $v_0^*$  is calculated from the cubic equation-of-state using the van der Waals mixing rule for its  $a$  and  $b$  parameters by setting pressure equal to zero and selecting the smallest root:

$$v_0^* = \frac{1}{2} \left\{ \left( \frac{a^*}{b^*} - u - w \right) - \left[ \left( u + w - \frac{a^*}{b^*} \right)^2 - 4 \left( uw + \frac{a^*}{b^*} \right) \right]^{1/2} \right\} \quad (15)$$

Eq. (15) has a root as long as

$$\frac{a^*}{b^*} \geq (2 + u + w) + 2\sqrt{(u + 1)(w + 1)} \quad (16)$$

$A_0^E$  and  $A_{0,\text{vdw}}^E$  in Eqs. (12) and (13) are the excess Helmholtz energies at zero-pressure. As mentioned, the subscript vdw in  $A_{0,\text{vdw}}^E$  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.

Useful features of the Twu mixing rule include reducing to the van der Waals mixing rule when  $A_0^E$  is equal to  $A_{0,\text{vdw}}^E$ . The mixing rule satisfies the quadratic composition dependence of the second virial coefficient boundary condition. The most important aspect is that the mixing rule is density dependent in an explicit form, which allows the mixing rule to reproduce almost exactly the incorporated  $G^E$  model. The mixing rule provides excellent agreement between the experimental data and the VLE predictions over a wide range of temperatures and pressures using only the information on the  $G^E$  model.

The mixing rule for the parameter  $b$  as given by Eq. (13) forces the mixing rule to satisfy the quadratic composition dependence of the second virial coefficient. Alternatively, the conventional linear mixing rule could be chosen for the  $b$  parameter, i.e. ignoring the second virial coefficient boundary condition.

$$b = \sum_i \sum_j x_i x_j \left[ \frac{1}{2} (b_i + b_j) \right] \quad (17)$$

Twu et al. [11] show that the mixing rule either with or without second virial coefficient condition constraint yields almost identical results. The second virial coefficient constraint has little effect on

the phase equilibrium prediction. Theoretically, it would be nice to have the mixing rule satisfying the quadratic composition dependence of the second virial coefficient boundary condition, however, practically, its simpler to use the conventional linear mixing rule for the  $b$  parameter. The same quality of phase behavior will be predicted from both cases.

As mentioned, Twu mixing rules (Eqs. (12) and (13)) are density dependent through the function  $C_{v_0}$ . Because of this density function, the mixing rule is able to reproduce almost exactly the incorporated  $G^E$  model.  $C_{v_0}$  as defined by Eq. (14) is calculated from  $v_{0,\text{vdw}}^*$  by solving it from Eq. (15). This step can cause problems when Eq. (15) has no real root, which occurs when the inequality in Eq. (16) is not satisfied. When this occurs, some sort of extrapolation for  $v_0^*$  must be made. To omit the need for the calculation of  $v_0^*$  from the equation-of-state, one can simply assume the zero-pressure liquid volume of the van der Waals fluid,  $v_{0,\text{vdw}}^*$ , to be a constant,  $r$ :

$$v_{0,\text{vdw}}^* = r \quad (18)$$

Substituting Eq. (18) into Eq. (14), it becomes

$$C_r = -\frac{1}{(w-u)} \ln \left( \frac{r+w}{r+u} \right) \quad (19)$$

The symbol  $C_r$  is used to replace  $C_{v_0}$  to signify that  $C_r$  is a constant, no longer a density dependent function. Eqs. (12) and (13) then become:

$$a^* = b^* \left[ \frac{a_{\text{vdw}}^*}{b_{\text{vdw}}^*} + \frac{1}{C_r} \left( \frac{A_0^E}{RT} - \frac{A_{0,\text{vdw}}^E}{RT} - \ln \left( \frac{b_{\text{vdw}}}{b} \right) \right) \right] \quad (20)$$

$$b^* = \frac{b_{\text{vdw}}^* - a_{\text{vdw}}^*}{1 - \left[ \frac{a_{\text{vdw}}^*}{b_{\text{vdw}}^*} + \frac{1}{C_r} \left( \frac{A_0^E}{RT} - \frac{A_{0,\text{vdw}}^E}{RT} - \ln \left( \frac{b_{\text{vdw}}}{b} \right) \right) \right]} \quad (21)$$

The simplification of the zero-pressure mixing rules avoids the calculation of liquid volume at zero-pressure and is one way to extend the usefulness and range of the method. The simplified Twu mixing rules given by Eqs. (20) and (21) is no longer a function of liquid density  $v_0^*$ , but depends only on the selected value of  $r$ . Therefore, the selection of an appropriate value of  $r$  in the mixing rule is the key factor for improving the accuracy of VLE calculations. A universal value of  $r = 1.18$  determined from the information on the incorporated  $G^E$  model for SRK has been recommended by Twu et al. [12] for use in the phase equilibrium prediction for all systems and will be used in this work.

#### 4. A versatile new liquid $G^E$ model

As we mentioned, it is desirable to have a mixing rule using the same Gibbs free energy expression that can reduce to the classical van der Waals one-fluid mixing rule. Twu et al. [14] have developed a new excess Gibbs function  $G^E$  to permit the infinite-pressure CEOS/ $A^E$  mixing rules to transition smoothly to the van der Waals mixing rules. We continue this work and propose a methodology to reduce the zero-pressure CEOS/ $A^E$  mixing rules to the van der Waals mixing rules. To do this we first examine the



term  $A_{0,\text{vdw}}^{\text{E}}$  in both Eqs. (20) and (21).  $A_{0,\text{vdw}}^{\text{E}}$  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:

$$\frac{A_{0,\text{vdw}}^{\text{E}}}{RT} = \sum_i x_i \ln \left( \frac{b_i}{b_{\text{vdw}}} \right) + C_r \left[ \frac{a_{0,\text{vdw}}^*}{b_{\text{vdw}}^*} - \sum_i x_i \frac{a_i^*}{b_i^*} \right] \quad (22)$$

$a_{\text{vdw}}$  and  $b_{\text{vdw}}$  are the equation-of-state  $a$  and  $b$  parameters which are evaluated from the conventional van der Waals mixing rules:

$$a_{\text{vdw}} = \sum_i \sum_j x_i x_j \sqrt{a_i a_j} (1 - k_{ij}) \quad (23)$$

$$b_{\text{vdw}} = \sum_i \sum_j x_i x_j \left[ \frac{1}{2} (b_i + b_j) \right] \quad (24)$$

As pointed out by Wong and Sandler [5], the excess Helmholtz energy is much less pressure-dependent than the excess Gibbs energy. Therefore, we assume that the excess Helmholtz energy of van der Waals fluid at zero-pressure can be approximated by the excess Helmholtz energy of van der Waals fluid at infinite pressure.

$$\frac{A_{0,\text{vdw}}^{\text{E}}}{RT} = \frac{A_{\infty,\text{vdw}}^{\text{E}}}{RT} = C_1 \left[ \frac{a_{\text{vdw}}^*}{b_{\text{vdw}}^*} - \sum_i x_i \frac{a_i^*}{b_i^*} \right] \quad (25)$$

The  $C_1$  in Eq. (25) is a constant and is defined as

$$C_1 = -\frac{1}{w - u} \ln \left( \frac{1 + w}{1 + u} \right) \quad (26)$$

For algebraic simplicity, we limit the following discussion to a binary mixture, we obtain the following expression for the excess Helmholtz energy of a van der Waals fluid from Eq. (25)

$$\frac{A_{0,\text{vdw}}^{\text{E}}}{RT} = \frac{x_1 x_2 b_1 b_2 \delta_{12}}{(x_1 b_1 + x_2 b_2)} \quad (27)$$

$\delta_{12}$  is a characteristic parameter of interaction between molecules 1 and 2.

$$\delta_{12} = -\frac{C_1}{RT} \left[ \left( \frac{\sqrt{a_1}}{b_1} - \frac{\sqrt{a_2}}{b_2} \right)^2 + 2k_{12} \frac{\sqrt{a_1}}{b_1} \frac{\sqrt{a_2}}{b_2} \right] \quad (28)$$

Extending these relations to a multi-component mixture, Eqs. (27) and (28) become

$$\frac{A_{0,\text{vdw}}^{\text{E}}}{RT} = \frac{1}{2} \sum_i \sum_j (b \delta_{ij}) \Phi_i \Phi_j \quad (29)$$

$$\delta_{ij} = -\frac{C_1}{RT} \left[ \left( \frac{\sqrt{a_i}}{b_i} - \frac{\sqrt{a_j}}{b_j} \right)^2 + 2k_{ij} \frac{\sqrt{a_i}}{b_i} \frac{\sqrt{a_j}}{b_j} \right] \quad (30)$$

$$\Phi_i = \frac{x_i b_i}{b} \quad (31)$$

It is worth noting that Eq. (29) is the result from Eq. (25) for a van der Waals fluid satisfying the van der Waals one-fluid mixing rules. Consequently, if we propose an expression in our mixing rule for the excess Helmholtz (or Gibbs) energy which reduces to Eq. (29), we will obtain the conventional van der Waals fluid mixing rules.

Since  $A_0^E$  in Eq. (20) is at zero-pressure, its value is identical to the excess Gibbs free energy  $G^E$  at zero-pressure. Therefore, any activity model such as the NRTL equation can be used directly for the excess Helmholtz free energy expression  $A_0^E$  in the equation. A general multi-component equation for a liquid activity model is now proposed for incorporation in the zero-pressure mixing rules as

$$\frac{G^E}{RT} = \sum_i^n x_i \frac{\sum_j^n x_j \tau_{ji} G_{ij}}{\sum_k^n x_k G_{ki}} \quad (32)$$

Eq. (29) appears to be similar to the NRTL equation, but there is a fundamental difference between them. NRTL assumes  $A_{ij}$ ,  $A_{ji}$ , and  $\alpha_{ij}$  are the parameters of the model, but our excess Gibbs energy model assumes  $\tau_{ij}$  and  $G_{ij}$  are the binary interaction parameters. More importantly, any appropriate temperature-dependent function can be applied to  $\tau_{ij}$  and  $G_{ij}$ . For example, to obtain the NRTL model,  $\tau_{ij}$  and  $G_{ij}$  are calculated as usual from the NRTL parameters  $A_{ij}$ ,  $A_{ji}$  and  $\alpha_{ij}$

$$\tau_{ji} = \frac{A_{ji}}{T} \quad (33)$$

$$G_{ij} = \exp(\alpha_{ji} \tau_{ji}) \quad (34)$$

In this way, the NRTL parameters reported in the DECHEMA Chemistry Data Series can be used directly in our mixing rules, there is no difference between NRTL and our model in the prediction of phase equilibrium calculations.

We also note Eq. (32) can recover the conventional van der Waals mixing rules when the following expressions are used for  $\tau_{ij}$  and  $G_{ij}$

$$\tau_{ji} = \frac{1}{2} \delta_{ij} b_i \quad (35)$$

$$G_{ij} = \frac{b_j}{b_i} \quad (36)$$

Eqs. (35) and (36) are expressed in terms of cubic equation-of-state parameters,  $a_i$  and  $b_i$  and the binary interaction parameter  $k_{ij}$ . Substituting Eqs. (35) and (36) into (32), Eq. (29) is thus obtained and subsequently our mixing rules, Eqs. (20) and (21), reduce to the classical van der Waals one-fluid mixing rules. The discussion above demonstrates that Eq. (32) is more generic in form than NRTL. Both the NRTL and van der Waals fluid parameters are special cases of our excess Gibbs free energy function.

We have assumed the constant (pressure-independent) excess Helmholtz free energy of the van der Waals fluid at zero-pressure to permit to develop our versatile liquid  $G^E$  model for use in our zero-pressure mixing rule. To correct the approximation that the excess Helmholtz energy of van der Waals fluid at zero-pressure equal the excess Helmholtz energy of van der Waals fluid at infinite pressure, the binary interaction parameter,  $l_{ij}$  is introduced to the equation-of-state parameter  $b$

$$b = \sum_i \sum_j x_i x_j \left[ \frac{1}{2} (b_i + b_j) \right] (1 - l_{ij}) \quad (37)$$

We label Eqs. (20), (25) (32) and (37) as versatile TST zero-pressure mixing rules. The parameter  $l_{ij}$  will be derived from reported parameters of the activity coefficient model instead of additional data or a correlation. Since  $l_{ij}$  in Eq. (37) requires no additional data or regression, our versatile TST mixing rule essentially has the same number of parameters as the incorporated liquid activity model. We will test our versatile TST zero-pressure mixing rules against our non-versatile mixing rules Eq. (20) using Eqs. (17) and (22) in the phase equilibrium calculations.

It is important to emphasize that both van der Waals fluids and highly non-ideal mixtures can now be described by using the same Gibbs excess energy model in our versatile zero-pressure mixing rules proposed here. More significantly, multi-component mixtures containing both types of binaries can be described in a unified framework. We can choose the appropriate expressions for  $\tau_{ij}$  and  $G_{ij}$  from Eqs. (35) and (36) for binary pairs which are best described by the vdW one-fluid mixing rules, while Eqs. (33) and (34) can be used for pairs which behave non-ideally. Therefore the activity model is able to describe systems ranging from mixtures of simple hydrocarbons to highly non-ideal mixtures of organic chemicals and water over a broad range of temperatures and pressures in a consistent and unified framework.

## 5. Results

We have chosen here the Twu alpha function for the SRK, PR and TST cubic equations of state and our activity model Eq. (32) for use in our non-versatile and versatile mixing rules for illustration purposes. As mentioned previously, since  $A_0^E$  in Eq. (20) is at zero-pressure, its value is identical to the excess Gibbs free energy  $G^E$  at zero-pressure. Therefore, any activity model such as the NRTL equation can be used directly for the excess Helmholtz free energy expression  $A_0^E$  in the equation. The NRTL parameters,  $A_{ij}$ ,  $A_{ji}$  and  $\alpha_{ij}$  obtained from the lowest temperature of each binary reported in the DECHEMA Chemistry Data Series, are used directly in the mixing rule models. These values of  $A_{ij}$ ,  $A_{ji}$ , and  $\alpha_{ij}$  are then used in the mixing rules at all temperatures, where temperature  $T$  is in Kelvin. The values of the NRTL binary interaction parameters for the binaries used in this study are given in Tables 5 and 6.

We have considered two cases for highly non-ideal binary mixtures, which are traditionally described by liquid activity models. They are listed in Tables 5 and 6. Since our new versatile mixing rule exactly reduces to the vdW one-fluid mixing rule, none of our tests are for mixtures of hydrocarbons that are known to be adequately described by that model. The first case is to examine the VLE prediction from the SRK, PR and TST equations of state using the non-versatile zero-pressure mixing rules; Eq. (20) for  $a$ , (17) for  $b$  and (22) for  $A_{0,\text{vdw}}^E$ . The second case is the same as the first case except using the versatile zero-pressure mixing rules; Eq. (20) for  $a$ , (37) for  $b$  and (25) for  $A_{0,\text{vdw}}^E$ . Tables 5 and 6 are the results for the case 1 and case 2, respectively. The binary interaction parameter,  $l_{ij}$ , in Eq. (37) is derived from information obtained from the NRTL model itself and is given in Table 6. When the parameters are derived from the excess free energy model, the mixing rules can be considered containing the same number of parameters as the incorporated liquid activity coefficient model.

The accuracy of reproducing the activity coefficients of component  $i$ ,  $\gamma_i$ , in terms of AAD%, from the incorporated  $G^E$  model using these two different mixing rules in the SRK, PR and TST equations is given in Tables 5 and 6. Similarly, the accuracy of the VLE prediction from the two different mixing

Table 5

Non-versatile mixing rules using NRTL interaction parameters and results of the prediction in terms of AAD% in activity coefficients, bubble point pressure and  $K$ -values

CEOS	$\gamma_1$ (%)	$\gamma_2$ (%)	$P$ (%)	$K_1$ (%)	$K_2$ (%)
Ethanol(1)/ <i>n</i> -heptane(2) from 30.12 to 70.02 C; I/2e/377, 379; I/2c/457, 458 <sup>a</sup> ( $A_{12} = 521.746$ , $A_{21} = 727.003$ , $\alpha_{12} = 0.4598$ at 30.12 C)					
SRK	0.69	0.52	0.94	1.08	2.53
PR	0.50	0.95	0.79	1.20	2.52
TST	1.01	1.40	0.96	1.28	2.54
Methanol(1)/cyclohexane(2) from 25 to 55 C; I/2a/242; I/2c/208, 209 <sup>a</sup> ( $A_{12} = 644.886$ , $A_{21} = 784.966$ , $\alpha_{12} = 0.4231$ at 25 C)					
SRK	1.13	0.64	1.84	1.91	2.89
PR	0.25	0.81	1.26	1.90	2.89
TST	0.62	1.12	1.14	1.89	2.87
Acetone(1)/methanol(2) from 45 to 55 C; I/2a/75, 80, 81 <sup>a</sup> ( $A_{12} = 31.5237$ , $A_{21} = 180.554$ , $\alpha_{12} = 0.3004$ at 45 C)					
SRK	0.30	0.51	0.88	1.04	1.23
PR	0.19	0.29	0.62	1.04	1.08
TST	0.24	0.22	0.57	1.01	1.02
Ethanol(1)/benzene(2) from 25 to 55 C; I/2a/398, 407, 415, 417, 418, 421, 422 <sup>a</sup> ( $A_{12} = 115.954$ , $A_{21} = 584.473$ , $\alpha_{12} = 0.2904$ at 25 C)					
SRK	0.29	0.47	1.54	3.45	2.68
PR	0.69	0.95	1.20	3.33	2.52
TST	1.04	1.25	1.14	3.32	2.51
Methanol(1)/water(2) from 24.99 to 100 C; I/1b/29; I/1/41, 49, 72, 73 <sup>a</sup> ( $A_{12} = -23.1150$ , $A_{21} = 188.147$ , $\alpha_{12} = 0.3022$ at 24.99 C)					
SRK	2.14	1.80	2.43	4.03	3.99
PR	2.47	2.08	2.29	3.89	3.86
TST	2.63	2.21	2.30	3.84	3.81
Methanol(1)/ <i>n</i> -hexane(2) from 25 to 45 C; I/2c/219; I/2a/252 <sup>a</sup> ( $A_{12} = 823.172$ , $A_{21} = 848.519$ , $\alpha_{12} = 0.4388$ at 25 C)					
SRK	2.14	1.05	1.27	2.69	2.52
PR	1.21	1.38	0.90	2.06	1.96
TST	0.85	1.67	0.97	1.81	1.71

<sup>a</sup> Data taken from DECHEMA chemistry data series by Gmehling, Onken, and Arlt; numbers corresponding to volume/part/page.

rules, expressed in terms of AAD% in bubble point pressure and  $K$ -values of component 1 and 2, is also presented in these two tables for these three equations of state.

Examining the accuracy of reproducing the activity coefficients, as given in Tables 5 and 6, the TST, PR and SRK equations of state produce fairly accurate and almost identical results for both mixing rules. Tables 5 and 6 also compare the VLE predictions from these two mixing rules. For the VLE predictions, both mixing rules give excellent agreement between the experimental data and the predictions over a wide range of temperatures and pressures using only the information in the  $G^E$  model. Although, the results indicate that the assumption of the excess Helmholtz energy of van der Waals fluid at zero-pressure equal the excess Helmholtz energy of van der Waals fluid at infinite pressure sacrifices slightly the accuracy of the VLE predictions, nevertheless, there is major benefit from this approximation. It allows equations

Table 6

Versatile mixing rules using NRTL interaction parameters and results of the prediction in terms of AAD% in activity coefficients, bubble point pressure and  $K$ -values

CEOS	$l_{12}$	$\gamma_1$ (%)	$\gamma_2$ (%)	$P$ (%)	$K_1$ (%)	$K_2$ (%)
Ethanol(1)/ <i>n</i> -heptane(2) from 30.12 to 70.02 C; I/2e/377, 379; I/2c/457, 458 <sup>a</sup> ( $A_{12} = 521.746$ , $A_{21} = 727.003$ , $\alpha_{12} = 0.4598$ at 30.12 C)						
SRK	0.1271	2.46	1.93	1.21	1.17	2.53
PR	0.1208	2.07	1.69	1.28	1.22	2.63
TST	0.1184	1.90	1.59	1.13	1.24	2.66
Methanol(1)/cyclohexane(2) from 25 to 55 C; I/2a/242; I/2c/208, 209 <sup>a</sup> ( $A_{12} = 644.886$ , $A_{21} = 784.966$ , $\alpha_{12} = 0.4231$ at 25 C)						
SRK	0.1057	2.09	1.71	1.85	2.05	3.04
PR	0.0993	1.75	1.50	1.64	2.20	2.99
TST	0.0965	1.59	1.41	1.58	1.97	2.94
Acetone(1)/methanol(2) from 45 to 55 C; I/2a/75, 80, 81 <sup>a</sup> ( $A_{12} = 31.5237$ , $A_{21} = 180.554$ , $\alpha_{12} = 0.3004$ at 45 C)						
SRK	0.0615	0.73	0.87	0.85	1.12	1.40
PR	0.0595	0.71	0.85	0.67	1.17	1.38
TST	0.0586	0.70	0.84	0.64	1.17	1.37
Ethanol(1)/benzene(2) from 25 to 55 C; I/2a/398, 407, 415, 417, 418, 421, 422 <sup>a</sup> ( $A_{12} = 115.954$ , $A_{21} = 584.473$ , $\alpha_{12} = 0.2904$ at 25 C)						
SRK	0.0210	0.51	0.47	1.58	3.48	2.69
PR	0.0173	0.31	1.31	1.44	3.42	2.68
TST	0.0156	0.21	0.23	1.37	3.46	2.76
Methanol(1)/water(2) from 24.99 to 100 C; I/1b/29; I/1/41, 49, 72, 73 <sup>a</sup> ( $A_{12} = -23.1150$ , $A_{21} = 188.147$ , $\alpha_{12} = 0.3022$ at 24.99 C)						
SRK	0.1131	1.53	1.97	3.44	4.95	5.90
PR	0.1118	1.56	2.01	3.30	4.96	5.88
TST	0.1112	1.57	2.03	3.27	4.96	5.91
Methanol(1)/ <i>n</i> -hexane(2) from 25 to 45 C; I/2c/219; I/2a/252 <sup>a</sup> ( $A_{12} = 823.172$ , $A_{21} = 848.519$ , $\alpha_{12} = 0.4388$ at 25 C)						
SRK	0.1672	4.70	3.28	2.19	3.67	3.27
PR	0.1609	4.36	3.16	2.16	3.69	3.35
TST	0.1580	4.20	3.11	2.06	3.65	3.33

<sup>a</sup> Data taken from DECHEMA chemistry data series by Gmehling, Onken, and Arlt; numbers corresponding to volume/part/page.

of state to describe both van der Waals fluids and highly non-ideal mixtures over a broad range of temperatures and pressures in a consistent and unified framework.

The comparisons show that there is little difference in the accuracy of the predictions with these three equation-of-state methods. Based on these results, it seems to indicate that these three equations of state are equivalent to each other and neither one has an advantage over others in phase equilibrium calculations as long as the same alpha function and mixing rules are used. Although the results demonstrate that the SRK, PR and TST cubic equations of state predict similar accuracy of  $K$ -values, their significant difference is the precision of predicting liquid density and hence the enthalpy. SRK represents methane PVT behavior closely. PR predicts better liquid density for  $C_6$  hydrocarbons. TST improves the prediction of liquid density for heavy hydrocarbons and polar systems. Therefore, the SRK, PR and TST cubic equations of state, taken together, cover the entire range of hydrocarbons and polar systems.

## 6. Conclusions

A new cubic equation-of-state TST is generalized as a linear function of acentric factor to allow the extension of its use to lower reduced temperatures and heavy hydrocarbons. The generalized TST equation-of-state accurately represents the vapor pressure over the entire range of temperature for light as well as heavy hydrocarbons. Comparing with SRK and PR, the new TST equation-of-state predicts similar accuracy in the vapor–liquid equilibria of highly non-ideal systems over a wide range of temperature and pressure.

To make any cubic equation-of-state useful for practical application, it is extremely desirable to have a mixing rule that incorporates an excess Gibbs energy expression which transitions smoothly to the conventional van der Waals one-fluid mixing rules. This is important because the same mixing rule can be applied to all binaries, whether components are polar, nonpolar, inorganic gases, or any combination of these. A versatile excess Gibbs free energy function and a new zero-pressure mixing rule are proposed in this work for this purpose. The incorporation of the proposed new excess Gibbs free energy function and the new CEOS/A<sup>E</sup> zero-pressure mixing rule into a cubic equation-of-state allows the smooth transition to the classical vdW one-fluid mixing rules. We demonstrated that the SRK, PR and TST cubic equations of state with the proposed excess Helmholtz energy mixing rules can be applied with high accuracy to the prediction of phase equilibria using available parameters for the liquid activity coefficient model.

### List of symbols

$a, b$	cubic equation-of-state parameters
$A$	Helmholtz energy
$A_{ij}, A_{ji}$	NRTL binary interaction parameters (K)
$C_1$	constant at infinite pressure as defined in Eq. (26)
$C_r$	constant at zero-pressure as defined in Eq. (19)
$C_{v0}$	zero-pressure function defined in Eq. (14)
$G$	Gibbs energy
$G_{ij}$	binary interaction parameters of TST liquid activity model
$K_i$	$K$ -value of component $i$ defined as $y_i/x_i$
$k_{ij}$	binary interaction parameter
$L, M, N$	parameters in the Twu's $\alpha$ function
$P$	pressure
$R$	gas constant
$r$	constant, equal to 1.18
$v$	molar volume
$v_0^*$	reduced zero-pressure liquid volume
$x_i$	liquid mole fraction of component $i$
$y_i$	vapor mole fraction of component $i$
$Z$	compressibility factor

### Greek letters

$\alpha$	cubic equation-of-state alpha function
$\alpha_{ij}$	NRTL binary interaction parameters
$\delta_{ij}$	characteristic of the interaction between molecules $i$ and $j$ .

$\tau_{ij}$	binary interaction parameters of TST liquid activity model
$\Phi_i$	volume fraction of component $i$ as defined in Eq. (31)
$\gamma_i$	activity coefficient of component $i$
$\infty$	infinite pressure

*Subscripts*

0	zero-pressure
c	critical property
$i, j$	property of component $i, j$
$ij$	interaction property between components $i$ and $j$
vdw	van der Waals

*Superscripts*

*	reduced property
E	excess property

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