

**Prediction of Vapor-Liquid Equilibria for Polar Mixtures at High Pressures
using Infinite-Dilution Activity Coefficients¹**

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ABSTRACT

The infinite-dilution activity coefficients are important data in process separation calculations. Interpolation from infinite dilution toward the middle of the composition field generally yields acceptable values for the activity coefficients. The present study investigates the use of infinite-dilution activity coefficients in cubic equation of state mixing rules for the prediction of high pressure phase behavior for strongly non-ideal systems. A modified procedure of coupling the Huron-Vidal mixing rule with infinite dilution activity coefficients at low pressures and low temperatures (called HVID model) was used for predicting vapor-liquid equilibria (VLE) over the whole composition range for strongly non-ideal polar mixtures at high pressures and temperatures. Since attractive forces are related only to the residual part of the UNIQUAC model-called the UNIQUAC-R model – the procedure is based on the UNIQUAC-R model, suitable for infinite-pressure conditions, coupled to cubic equations of state. Three variants of the original Soave-Redlich-Kwong (SRK) equation incorporating different functional forms for the temperature dependence of the cohesive energy parameter a , and the Peng-Robinson-Stryjek-Vera (PRSV) equation were used. Infinite-pressure activity coefficients at infinite dilution were obtained from low-pressure activity coefficients at infinite dilution at several temperatures, using excess Gibbs energy (G^E) model (UNIQUAC) parameters reported in DECHEMA Chemistry Data Series. The parameters of the UNIQUAC-R model at infinite pressure were calculated at each temperature and fitted to a temperature – dependent function. The consideration of model parameters to be temperature dependent was found to be useful for extrapolation to higher temperatures and led to accurate VLE predictions for six binary polar mixtures at high pressures and temperatures.

KEY WORDS: cubic equations of state; high pressure; Huron-Vidal mixing rule; infinite-dilution activity coefficients; polar mixtures; UNIQUAC-R model; vapor-liquid equilibria.

1. INTRODUCTION

The accurate design and operation of separation process units requires reliable knowledge of phase equilibrium behavior. Cubic equations of state (EOS) are widely used for phase equilibrium calculations [1]. Much effort in recent years has been devoted toward developing multiparameter mixing rules, especially those that incorporate the excess free energy (G^E or A^E) to extend the cubic EOS for the phase equilibrium calculations of asymmetric and strongly non-ideal mixtures [2-3]. Huron and Vidal [4] pioneered linking the EOS parameter a to the excess Gibbs energy (G^E) at infinite pressure. However, their mixing rule has not become widely used because the available G^E parameters at low pressures cannot be used in their mixing rules.

Because of that, several authors have proposed different approaches to use directly the existing G^E model parameters in cubic EOS through the mixing rules. Among them, two EOS- G^E models have been quite successful. One is a zero-pressure model [5-9] and the other is an infinite-pressure model [10,11]. Both models can directly use available activity coefficient model parameters from low-pressure data in their mixing rules for predicting phase equilibria at high temperatures and pressures quite successfully. However, neither the zero-pressure model nor the infinite-pressure model can reproduce accurately the G^E model with which it is combined [12,13].

Recently, Soave et al.[14] applied the Huron-Vidal (H-V) mixing rule at infinite-dilution conditions, where the Michelsen approach [5,6] cannot be used, and at zero pressure. Infinite pressure activity coefficients used for high pressure VLE calculations over the whole composition range were predicted using group contributions of a UNIFAC-type model regressed from experimental infinite-dilution activity coefficients. Feroiu and Geana[15], following the approach of Soave et al.[14], suggested the coupling of the H-V mixing rule with infinite-dilution activity coefficients (called the HVID model) based on the reduced UNIQUAC model, suitable for infinite-pressure conditions, coupled to SRK equation of state [16]. Geana and Feroiu[17] proposed a similar procedure using UNIFAC'93[18] activity coefficients at infinite-dilution. Twu et al.[19] developed a zero-pressure cubic EOS mixing rule for predicting high pressure phase equilibria for strongly non-ideal systems using infinite-dilution activity coefficients at low temperature.

In this work, following the approach of Feroiu and Geana [15], a modified procedure of coupling the H-V mixing rule with infinite-dilution activity coefficients at low pressure (HVID model) was used for predicting VLE over the whole composition range for strongly non-ideal polar mixtures at high pressures and temperatures. Since attractive forces are related only to the residual part of the UNIQUAC model [20]-called the UNIQUAC-R model-, the procedure is based on the UNIQUAC-R model, suitable for infinite-pressure conditions, coupled to cubic equations of state. Three variants of the original SRK equation incorporating different functional forms for the temperature dependence of the parameter a i.e. SRK-I [21], SRK-II [22], and SRK-III [23], and the Peng-Robinson-Stryjek-Vera, PRSV, equation [24] were used. Infinite-pressure activity coefficients at infinite dilution were obtained from low-pressure activity coefficients at infinite dilution at several temperatures, using G^E model (UNIQUAC) parameters reported in the DECHEMA

Chemistry Data Series. The parameters of the UNIQUAC-R model at infinite pressure were calculated at each temperature and fitted to a temperature-dependent function. The consideration of model parameters to be temperature dependent led to accurate VLE predictions for six binary polar mixtures at high pressures and temperatures.

2. THE HVID – UNIQUAC-R MODEL

The cubic equations of state used in this study are three variants of the SRK equation, and the PRSV equation given by

$$P = \frac{RT}{v-b} - \frac{a[T]}{(v+c_1b)(v+c_2b)} \quad (1)$$

where P, T, v, and R are pressure (Pa), temperature (K), molar volume ($\text{m}^3 \text{mol}^{-1}$), and universal gas constant ($\text{J mol}^{-1} \text{K}^{-1}$), respectively.

$$a [T] = a_c \alpha [T_r] \quad (2)$$

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

$$b = \Omega_b \frac{RT_c}{P_c} \quad (4)$$

Here T_c (K) and P_c (Pa) are the critical temperature and pressure, respectively and T_r is the reduced temperature, T/T_c .

For the SRK equation: $c_1 = 0$, $c_2 = 1$, $\Omega_a = 0.42748$, $\Omega_b = 0.08664$

For the PRSV equation: $c_1 = 1 - \sqrt{2}$, $c_2 = 1 + \sqrt{2}$, $\Omega_a = 0.457235$, $\Omega_b = 0.077796$

The three variants of the SRK equation, namely SRK-I, SRK-II and SRK-III, used the $\alpha [T_r]$ functions proposed by Mathias and Copeman [21], Twu et al. [22], and Soave [23], respectively. The function $\alpha [T_r]$ used in the PRSV equation is a function of acentric factor ω also, and was proposed by Stryjek and Vera [24].

The fugacity coefficient for the pure component i, ϕ_i^o , is given by

$$\ln \phi_i^o = (z_i - 1) - \ln \left(z_i - \frac{b_i P}{RT} \right) - \frac{1}{(c_2 - c_1)} \left(\frac{a_i}{b_i RT} \right) \ln \left(\frac{v_i + c_2 b_i}{v_i + c_1 b_i} \right) \quad (5)$$

where z_i is the pure component compressibility factor.

For mixtures, the Huron-Vidal mixing rule was used:

$$\frac{a}{bRT} = \sum_i x_i \left(\frac{a_i}{b_i RT} - \frac{\ln \gamma_i(P \rightarrow \infty)}{C} \right) \quad (6)$$

where, x_i is the mole fraction of component i , $C = \frac{1}{(c_2 - c_1)} \ln \left(\frac{1 + c_2}{1 + c_1} \right)$ and $\gamma_i (P \rightarrow \infty)$ is the activity coefficient of component i in the mixture at infinite pressure.

$$b = \sum x_i b_i \quad (7)$$

The fugacity coefficient of component i in the mixture is given by

$$\ln \phi_i = \frac{b_i}{b} (z - 1) - \ln \left(z - \frac{bP}{RT} \right) - \frac{1}{(c_2 - c_1)} \left(\frac{a_i}{b_i RT} - \frac{\ln \gamma_i (P \rightarrow \infty)}{C} \right) \ln \left(\frac{v + c_2 b}{v + c_1 b} \right) \quad (8)$$

where z is the mixture compressibility factor.

The fugacity coefficient of component i in a binary mixture at infinite-dilution conditions ($x_i \rightarrow 0$; $x_j \rightarrow 1$) is

$$\ln \phi_{i(j)}^\infty = \frac{b_i}{b_j} (z_j - 1) - \ln \left(z_j - \frac{b_j P}{RT} \right) - \frac{1}{(c_2 - c_1)} \left(\frac{a_i}{b_i RT} - \frac{\ln \gamma_{i(j)}^\infty (P \rightarrow \infty)}{C} \right) \ln \left(\frac{v_j + c_2 b_j}{v_j + c_1 b_j} \right) \quad (9)$$

where the properties of the mixture are the corresponding ones for the pure solvent j .

The activity coefficient is given through the general thermodynamic relationship

$$\gamma_i = \frac{\phi_i}{\phi_i^o} \quad (10)$$

and the corresponding expression for the infinite-dilution activity coefficient is

$$\ln \gamma_{i(j)}^\infty = \frac{b_i}{b_j} (z_j - 1) - (z_j - 1) - \ln \left(\frac{v_j - b_j}{v_i - b_i} \right) - \frac{1}{(c_2 - c_1)} \left(\frac{a_i}{b_i RT} \right) \cdot \ln \left(\frac{(v_i + c_1 b_i)(v_j + c_2 b_j)}{(v_i + c_2 b_i)(v_j + c_1 b_j)} \right) + \frac{1}{(c_2 - c_1)} \left(\frac{\ln \gamma_{i(j)}^\infty (P \rightarrow \infty)}{C} \right) \ln \left(\frac{v_j + c_2 b_j}{v_j + c_1 b_j} \right) \quad (11)$$

Eq.(11) relates the infinite-dilution activity coefficient at infinite pressure $\gamma_{i(j)}^\infty (P \rightarrow \infty)$ to its value $\gamma_{i(j)}^\infty$ at pressure P . If Eq.(11) is applied under the limiting condition ($P \rightarrow 0$), the following equation is obtained:

$$\ln \gamma_{i(j)}^{\infty}(P \rightarrow \infty) = \frac{C}{\frac{1}{(c_2 - c_1)} \ln \left(\frac{v_j + c_2 b_j}{v_j + c_1 b_j} \right)} \cdot \left[\gamma_{i(j)}^{\infty}(P \rightarrow 0) - \left(1 - \frac{b_i}{b_j} + \ln \frac{b_i}{b_j} \right) + \ln \left(\frac{v_j / b_j - 1}{v_i / b_i - 1} \right) + \frac{1}{(c_2 - c_1)} \left(\frac{a_i}{b_i RT} \right) \ln \left(\frac{(v_i + c_1 b_i)(v_j + c_2 b_j)}{(v_i + c_2 b_i)(v_j + c_1 b_j)} \right) \right] \quad (12)$$

where the molar volumes (v_i , v_j) are the solutions of Eq.(1) at $P \rightarrow 0$:

$$v = \frac{b}{2} \left[\frac{a}{bRT} - (c_1 + c_2) \pm \left(\left(\frac{a}{bRT} \right)^2 - 2(c_1 + c_2 + 2) \frac{a}{bRT} + (c_1 - c_2)^2 \right)^{1/2} \right] \quad (13)$$

Since the liquid molar volume is needed, the smallest root in Eq.(13) is used.

The UNIQUAC model reduced to its residual part only (UNIQUAC-R) suitable for infinite pressure conditions is used. It is given by

$$\ln \gamma_i(P \rightarrow \infty) = q_i \left[1 - \ln \left(\sum_j \theta_j \tau_{ji} \right) - \sum_j \frac{\theta_j \tau_{ij}}{\sum_k \theta_k \tau_{kj}} \right] \quad (14)$$

$$\theta_i = \frac{q_i x_i}{\sum_j q_j x_j}; \tau_{ij} = \exp \left(-\frac{\psi_{ij}}{T} \right) \quad (15)$$

where θ_i is the area fraction of component i , and τ_{ij} is the i - j interaction parameter.

Neglecting the combinatorial part, only component surface areas, q_i , are used for the calculation of activity coefficients.

For a binary system, the interaction parameters are related to the infinite-dilution activity coefficients at infinite pressure $\gamma_{i(j)}^{\infty}(P \rightarrow \infty)$, calculated from its value at zero pressure $\gamma_{i(j)}^{\infty}(P \rightarrow 0)$ using Eq.(12).

$$\tau_{12} = \exp(k_2 - \tau_{21}); \tau_{21} = \exp(k_1 - \tau_{12}) \quad (16)$$

$$\text{where } k_1 = 1 - \frac{1}{q_1} \ln \gamma_{1(2)}^{\infty}(P \rightarrow \infty); \quad k_2 = 1 - \frac{1}{q_2} \ln \gamma_{2(1)}^{\infty}(P \rightarrow \infty) \quad (17)$$

The interaction parameters are considered temperature –dependent:

$$\psi_{12} = \psi_{12}^o + \psi_{12}^1 \left(\frac{1}{T} \right); \psi_{21} = \psi_{21}^o + \psi_{21}^1 \left(\frac{1}{T} \right) \quad (18)$$

3. RESULTS AND DISCUSSION

For each component in the mixture, T_c , P_c and ω were taken from Ref.[24] and q from Ref.[25]. The literature source of the substance-specific parameters of the various $\alpha[T_r]$ functions of the cubic EOS is as follows: SRK-I [9,26] SRK-II[22], SRK-III[27], and PRSV [24]. The low-pressure infinite-dilution activity coefficients, $\gamma_{1(2)}^\infty(P \rightarrow 0)$ and $\gamma_{2(1)}^\infty(P \rightarrow 0)$, for each system at several temperatures were obtained from the UNIQUAC model parameters reported in DECHEMA Chemistry Data Series [25]. The infinite-dilution activity coefficients at infinite pressure, $\gamma_{1(2)}^\infty(P \rightarrow \infty)$ and $\gamma_{2(1)}^\infty(P \rightarrow \infty)$, at these temperatures were calculated for each system from the corresponding low-pressure values, $\gamma_{1(2)}^\infty(P \rightarrow 0)$ and $\gamma_{2(1)}^\infty(P \rightarrow 0)$, using Eq.(12), and the UNIQUAC-R interaction parameters (ψ_{12} and ψ_{21}) were obtained using Eqs.(14) through (17). These temperature-dependent parameters were fitted to a linear function in $1/T$ given by Eq.(18) and the set of constants ($\psi_{12}^0, \psi_{12}^1, \psi_{21}^0, \psi_{21}^1$) in the temperature function for the six systems studied were obtained for use with each of the three variants of the SRK equation and the PRSV equation of state.

Table I gives the literature source of high-pressure isothermal VLE data at several temperatures for six binary polar systems studied. High-pressure VLE predictions were made using the HVID mixing rules with the UNIQUAC-R model. Table II gives the results of VLE predictions with each of the three variants of the SRK equation and the PRSV equation of state. The results are expressed as percent absolute average deviations in bubble pressure [$\overline{\Delta P/P(\%)}$] and vapor phase composition [$\overline{\Delta y(\%)}$] at each temperature, where

$$\overline{\Delta P/P(\%)} = \frac{1}{N} \sum_{i=1}^N \frac{|P_{\text{exp}} - P_{\text{cal}}|}{P_{\text{exp}}} \times 100 \quad (19)$$

$$\overline{\Delta y(\%)} = \frac{1}{N} \sum_{i=1}^N |y_{\text{exp}} - y_{\text{cal}}| \times 100 \quad (20)$$

and N is the number of data points.

The results obtained with the three variants of the SRK equation and the PRSV equation are generally good, with SRK-III version being slightly superior. The HVID mixing rules coupled with the UNIQUAC-R model allow the use of low-pressure activity coefficients at infinite dilution for accurate VLE predictions at high pressures and temperatures.

Table I. Literature Source for High-Pressure VLE Data

System	T(K)	N	P range (bar)	References
Methanol (1)-Water (2)	373.15	16	1.04-3.37	[28]
	423.15	14	5.05-13.73	[28]
	443.15	35	6.77-20.99	[29]
	473.15	32	15.49-39.43	[28, 29]
	508.15	18	30.60-70.61	[29]
	523.15	12	46.95-85.08	[28]
Ethanol(1)-Water (2)	423.15	25	5.58-9.86	[30,31]
	473.15	24	17.93-29.51	[30,31]
	523.15	24	40.82-71.71	[30,31]
	548.15	13	61.36-98.59	[30]
	573.15	9	88.46-128.93	[30]
	598.15	7	123.97-157.06	[30]
623.15	4	170.64-189.74	[30]	
Acetone(1)-Water (2)	373.15	22	1.11-3.69	[28]
	423.15	17	5.00-11.56	[28]
	473.15	25	16.00-27.92	[28]
	523.15	17	40.40-66.53	[28]
2-Propanol(1)-Water(2)	423.15	20	5.17-8.74	[30]
	473.15	19	18.48-26.86	[30]
	523.15	16	43.09-64.88	[30]
	548.15	18	69.02-92.94	[30]
	573.15	6	88.94-123.48	[30]
Methanol(1)-Benzene(2)	373.15	10	3.12-3.95	[32]
	393.15	10	4.87-6.87	[32]
	413.15	10	6.74-11.55	[32]
	433.15	10	9.62-17.96	[32]
	453.15	10	13.18-27.34	[32]
	473.15	10	17.03-40.58	[32]
	493.15	10	22.61-57.57	[32]
Acetone(1)-Methanol(2)	372.80	24	3.65-3.82	[33,34]
	373.15	14	3.52-3.68	[28]
	397.70	21	6.67-7.56	[33,34]
	422.60	12	11.21-13.67	[33]
	423.15	15	11.65-14.13	[28]
	473.15	10	29.51-39.85	[28]

Table II. VLE Results for HVID Mixing Rules with UNIQUAC-R Model

T(K)	SRK-I		SRK-II		SRK-III		PRSV	
	$\frac{\Delta P}{P}$ (%)	Δy (%)						
Methanol (1) – Water (2) System								
373.15	3.10	1.09	3.44	1.18	3.55	1.16	3.22	1.12
423.15	1.94	1.88	2.05	1.92	1.97	1.90	2.27	1.88
443.15	3.47	3.97	3.35	4.12	3.46	4.07	3.80	3.84
473.15	3.50	1.82	3.61	1.88	3.69	1.88	3.64	1.75
508.15	2.26	1.88	2.24	1.90	1.92	2.00	1.76	1.81
523.15	2.08	0.85	2.05	0.86	2.21	0.91	2.23	0.87
Ethanol (1) – Water (2) System								
423.15	1.80	0.98	2.03	1.22	1.87	1.20	2.31	1.36
473.15	2.08	1.30	1.80	1.37	1.80	1.37	1.88	1.40
523.15	1.66	1.53	1.61	1.51	1.35	1.43	1.39	1.50
548.15	1.46	1.62	1.45	1.58	1.22	1.48	1.31	1.54
573.15	1.61	1.26	1.75	1.25	1.52	1.21	1.66	1.23
598.15	1.82	0.84	3.07	1.40	3.61	1.49	1.92	0.89
623.15	0.66	0.22	1.74	0.67	0.76	0.66	1.67	0.67
Acetone (1) – Water (2) System								
373.15	3.63	1.24	3.53	1.21	3.19	1.29	3.45	1.32
423.15	2.48	1.40	2.43	1.41	2.02	1.40	2.31	1.44
473.15	2.15	1.24	2.21	1.24	2.12	1.23	2.23	1.30
523.15	3.07	1.36	3.10	1.35	3.42	1.29	3.44	1.39
2-Propanol(1)-Water(2) System								
423.15	4.55	0.94	4.52	0.88	3.80	1.00	4.46	0.85
473.15	4.80	1.08	4.59	1.05	3.74	1.13	4.44	1.00
523.15	5.98	1.27	5.94	1.26	5.80	1.24	5.76	1.25
548.15	3.98	2.99	3.75	2.93	4.11	2.84	3.74	3.00
573.15	1.50	4.63	1.50	4.65	1.47	4.50	1.62	4.66
Methanol (1) – Benzene (2) System								
373.15	1.06	0.82	1.14	0.72	1.07	0.71	1.34	0.81
393.15	1.20	0.90	1.28	0.73	1.57	0.70	0.95	0.96
413.15	0.67	0.95	0.78	0.81	0.84	0.83	0.74	1.15
433.15	1.20	1.46	1.39	1.35	1.29	1.39	1.04	1.73
453.15	1.40	2.00	1.57	1.88	1.34	1.96	0.99	2.35
473.15	1.41	2.82	1.58	2.74	1.35	2.80	1.05	3.12
493.15	7.64	3.75	5.90	6.34	6.09	4.56	6.40	4.45
Acetone (1) – Methanol (2) System								
372.80	0.63	0.89	0.48	0.79	0.25	0.65	0.59	0.81
373.15	2.15	1.26	1.98	1.14	2.11	0.91	1.74	1.17
397.70	0.71	3.33	0.54	3.35	0.24	3.39	0.67	3.33
422.60	1.23	0.37	1.30	0.36	0.82	0.37	0.92	0.37
423.15	0.52	1.83	0.59	1.75	0.78	1.64	0.86	1.86
473.15	2.62	3.19	2.78	3.16	2.56	3.13	2.31	3.26

4. CONCLUSIONS

High-pressure VLE predictions for polar systems were made using the HVID mixing rule model and the infinite-dilution activity coefficients. The procedure is based on the UNIQUAC-R model, suitable for infinite-pressure conditions, coupled to cubic equations of state.

Infinite-pressure activity coefficients at infinite dilution were obtained from available low-pressure activity coefficients at infinite dilution at several temperatures. The parameters of the UNIQUAC-R model at infinite pressure were calculated at each temperature. A temperature-dependent function of the parameters was determined and extrapolated at higher temperatures.

The method was applied to predict high-pressure VLE for six binary polar systems for which data are available over a large temperature and pressure range, and the results obtained using the HVID model were generally good. The consideration of the UNIQUAC-R model parameters to be temperature dependent was found to be useful for extrapolation to higher temperatures and led to accurate VLE predictions.

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