

Correlation of vapor-liquid equilibria for binary mixtures with free energy-based equation of state mixing rules: Carbon dioxide with alcohols, hydrocarbons, and several other compounds

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Abstract—The correlation of vapor-liquid equilibrium data for high-pressure carbon dioxide systems is of interest in a number of industrial applications, including supercritical extraction. Here, we consider the correlation of data for 12 binary systems of carbon dioxide separately with alcohols, with hydrocarbons, and with acetone, benzene, and water. The Wong-Sandler (W-S) and modified Huron - Vidal first order (MHV1) free energy-based equation of state mixing rules (the W-S and MHV1 models) were used in the calculations. Both combined equation of state+free energy models generally resulted in good correlations of the experimental data over wide ranges of temperature and pressure with temperature - independent parameters. However, for the carbon dioxide+water system, the W-S model produced an 11% average absolute deviation in pressure, while no parameter that resulted in an AAD in pressure of less than 20% could be found for the MHV1 model.

Key words: Vapor-Liquid Equilibrium, High Pressure, Carbon Dioxide, W-S Mixing Rule

INTRODUCTION

The vapor-liquid equilibrium (VLE) of gas containing systems at high pressure with equations of state (EOS) is interesting because of the industrial importance of these mixtures and their asymmetric behavior [Shim et al., 2006; Mulero et al., 2006]. The correlation of the VLE of such systems using equations of state and the classic one-fluid mixing rules has not been good at high pressures and temperatures, especially as the critical point of the mixture is approached.

The VLE of binary mixtures containing carbon dioxide is of importance to industrial applications, in particular to the analysis of supercritical extraction using carbon dioxide. There have been several studies of mixtures with carbon dioxide. Recently, Berro et al. [1996] used an excess free energy-equation of state model to predict the solubility of carbon dioxide in high molecular weight solvents. Shyu et al. [1997] presented a new procedure to obtain the parameters of Wong-Sandler [1992] mixing rule (W-S MR) to correlate phase equilibria of the carbon dioxide+water system. Cassel et al. [1997] presented an excess function formalism to represent the VLE of binary systems of carbon dioxide and polar or non-polar components.

The representation of VLE in the vicinity of the critical temperature and pressure depends on the choice of equations of state and their mixing rules. Many alternative mixing rules have been proposed. In this work, there is a two parameters version of van der Waals one-fluid mixing rule [Adachi and Sugie, 1988], the Wong-Sandler mixing rule [Wong and Sandler, 1992] and other excess free energy - EOS models, of which the linear combination of Vidal and Michelsen methods [LCVM, Boukouvalas et al., 1994], the

modified Huron - Vidal second order [MHV2, Dahl and Michelsen, 1990] and the modified Huron-Vida first order [MHV1, Michelsen, 1990b] methods are examples. Based on the previous literature, here we correlate the VLE of binary mixtures containing carbon dioxide with the MHV1 and Wong - Sandler mixing rules.

PHASE EQUILIBRIUM DATA

There exist numerous phase equilibrium data for binary systems containing carbon dioxide. From among these systems, we chose 12 representative systems: carbon dioxide+alcohols (methanol, ethanol, 1-butanol, and 2-propanol); carbon dioxide+hydrocarbons (n-pentane, cyclohexane, n-hexane, n-heptane, and n-decane); and carbon dioxide separately with acetone, benzene, and water. The list of systems with data references, the number of isotherms, and number of experimental data points considered are listed in Table 1. We chose only systems for which several sets of isothermal data were available.

EQUATION OF STATE

There are a large number of equations of state available in the literature. In this work we used the Peng-Robinson [1976] equation of state (PR-EOS):

$$P = \frac{RT}{\underline{V} - b} - \frac{a(T)}{\underline{V}(\underline{V} + b) + b(\underline{V} - b)} \quad (1)$$

where P is the pressure, T is the temperature, \underline{V} is the molar volume, R is the gas constant, b is the co-volume parameter and a is the energy parameter. In the PR-EOS, the parameters a and b are

$$a = 0.457235 \alpha(T) R^2 T_c^2 / P_c \quad (2)$$

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Table 1. The list of systems with references, the number of isotherms, and number of experimental data used in this work

Second component	# of isotherms	Temperature range (K)	# of data	References
Methanol	4	323-477	40	Leu et al. [1991]
	4	298-313	30	Knapp et al. [1982]
	6	230-330	64	Hong and Kobayashi [1988]
	1	298	13	Katayama et al. [1975]
	1	313	8	Suzuki and Sue [1990]
	2	298-313	17	Ohgaki and Katayama [1976]
	4	323-398	67	Semenova et al. [1979]
Ethanol	1	308	20	Tanaka and Kato [1995]
	5	291-313	68	Day et al. [1996]
	2	304	19	Takishima et al. [1986]
2-Propanol	4	316-394	21	Radosz [1986]
	1	313	11	Yaginuma et al. [1997]
1-Butanol	3	314-337	28	Jenning et al. [1991]
	1	313	7	Ishihara et al. [1996]
n-Pentane	4	277-377	53	Besserer and Robinson [1973]
	10	252-458	108	Cheng et al. [1989]
Cyclohexane	2	366-410	20	Shibata and Sandler [1989]
	7	473-573	28	Knapp et al. [1982]
n-Hexane	2	298-313	20	Ohgaki and Katayama [1976]
	3	313-393	39	Li et al. [1981]
	3	303-323	26	Wagner and Wichterle [1987]
	4	273-303	24	Kaminishi et al. [1987]
n-Heptane	4	310-477	63	Kalra et al. [1978]
	3	394-502	23	Inomata et al. [1986]
n-Decane	2	344-377	47	Nagarajan et al. [1986]
	2	344-377	8	Chou et al. [1990]
	8	277-510	97	Knapp et al. [1982]
	4	342-594	24	Inomata et al. [1986]
	4	462-583	20	Sebastian et al. [1980]
Acetone	5	291-313	76	Day et al. [1996]
	2	298-313	25	Katayama et al. [1975]
	1	298	4	Kato et al. [1991]
	3	308-333	5	Truab et al. [1990]
Benzene	2	298-313	17	Ohgaki et al. [1988]
	4	313-393	45	Gupta et al. [1982]
Water	7	373-473	49	Muller et al. [1988]
	10	383-623	109	Takenouchi et al. [1964]

$$b = 0.077796RT_c/P_c \quad (3)$$

These relations ensure that the pure component critical point at the correct temperature and pressure is obtained from the equation of state (EOS). The term $\alpha(T)$ in Eq. (2) is dependent on temperature, and has unity at the critical temperature, so it has been chosen to ensure that the vapor pressure calculated from the EOS at other temperatures is acceptably accurate. One such representation is

$$\alpha(T) = [1 + k(1 - (T/T_c))]^2 \quad (4)$$

which is applicable to hydrocarbons and organic gases with the following generalized form:

$$k = 0.37464 + 1.5422\omega - 0.26992\omega^2 \quad (5)$$

where ω is the acentric factor. In this form the equation is completely predictive once the critical temperature, critical pressure and acentric factor are given.

This generalized form of $\alpha(T)$ function does not give accurate vapor pressures for nonhydrocarbon fluids. Other expressions have to be used for dependence of $\alpha(T)$ on temperature for nonhydrocarbons, usually with one or more parameters that are specific to the fluid of interest, rather than completely generalized in terms of only the critical properties and the acentric factor. Several investigators [Mathias and Copeman, 1983; Stryjet and Vera, 1986] have introduced additional, species-specific constants to provide accurate vapor pressure correlations. Here we use the temperature dependence of the $\alpha(T)$ term proposed by Stryjet and Vera [1986] in which Eq. (5) is replaced by the relation

Table 2. Pure component parameters for the PRSV equation of state

Compound	T _c , K	P _c , bar	ω	k ₁
Methanol	512.58	80.96	0.56533	-0.16816
Ethanol	513.92	61.48	0.64439	-0.03374
2-Propanol	508.40	47.64	0.66372	0.23264
1-Butanol	562.98	44.13	0.59022	0.33431
n-Pentane	469.70	33.69	0.25143	0.03946
Cyclohexane	553.64	40.75	0.20877	0.07023
n-Hexane	507.30	30.12	0.30075	0.05104
n-Heptane	540.10	27.36	0.35022	0.04648
n-Decane	617.50	21.03	0.49052	0.04510
Acetone	508.10	46.96	0.30667	-0.00888
Benzene	562.16	48.98	0.20929	0.07919
Water	647.29	220.90	0.34380	-0.06635

$$k = k_0 + k_1(1 + T_r^{0.5})(0.7 - T_r) \quad (6)$$

with

$$k_0 = 0.378893 + 1.4897153\omega - 0.1713184\omega^2 + 0.0196554\omega^3 \quad (7)$$

The constant k_1 is specific for each pure compound and used to accurately fit vapor pressures (P^{vp}) as a function of temperature. This version of the Peng-Robinson EOS is referred to as the PRSV equation. The pure component constants of the PRSV equation for the substances considered here are given in Table 2. The Stryjet - Vera modification of $\alpha(T)$ takes care of the inaccuracies in the correlation of vapor pressures at low temperatures. However, since the $\alpha(T)$ term is based on vapor pressure, it is not well defined at temperatures above the critical temperature of a component.

MIXING RULES

1. MHV1 Model

Equating the mixture excess free energies from an equation of state and from an excess free energy (activity coefficient) model leads to a functional relation between the a and b parameter of the EOS in the form

$$\alpha = a/bRT = I(a_i, b_i, x_i, G_i^{ex} \text{ or } A_i^{ex}) \quad (8)$$

where a_i and b_i are the pure component EOS parameters, x_i is mole fraction, and G_i^{ex} and A_i^{ex} are molar excess Gibbs and Helmholtz free energies, respectively, obtained from a liquid activity coefficient model such as UNIQUAC, NRTL etc. The function I depends on whether the Helmholtz free energy or the Gibbs free energy is used, whether the excess free energy terms are equated in the limit of zero pressure or infinite pressure, and the EOS used.

For the model being considered here, the mixing rule for the b parameter of the EOS is taken to be

$$b = \sum x_i b_i \quad (9)$$

The combination of Eqs. (8) and (9) completely defines the EOS mixing rule. Huron and Vidal [1979] first proposed this class of mixing rules. They equated the excess Gibbs free energy from an EOS to the excess Gibbs free energy of a free energy model at infinite

pressure.

The modified Huron-Vidal mixing rule of Michelsen [1990] is one of the most used of this class. The relation is

$$a = bRT \left\{ \sum_i Z_i \frac{a_i}{b_i RT} + \frac{1}{q_1} \left[\frac{G_i^{ex}(T, Z_i)}{RT} + \sum_i Z_i \ln \left(\frac{b_i}{b} \right) \right] \right\} \quad (10)$$

where q_1 is an empirical parameter obtained by fitting pure component information. Here the value of -0.53 is used. This relation, combined with Eq. (9), is known as the MHV1 model and will be referred to as such in this work. In this model with the PRSV EOS the fugacity coefficient of species i mixture is

$$\ln \phi_i = \frac{b_i}{b} (Z - 1) - \ln(Z - B) - \frac{1}{2\sqrt{2}} \left[\frac{a_i}{b_i RT} + \frac{\ln \gamma_i}{q_1} + \frac{1}{q_1} \ln \left(\frac{b_i}{b} \right) + \frac{1}{q_1} \left(\frac{b_i}{b} - 1 \right) \right] \ln \left\{ \frac{Z + (1 + \sqrt{2})B}{Z + (1 - \sqrt{2})B} \right\} \quad (11)$$

where $Z = pv/RT$ is compressibility factor, q_1 an empirical parameter of Eq. (10) and $B = bp/RT$ a reduced equation of state constant.

2. W-S Model

Wong and Sandler [1992] have developed a mixing rule that combines an EOS with a free energy model, but it produces the desired EOS behavior at low and high densities without being density dependent, uses existing table of G_i^{ex} parameters, and allows extrapolation over wide ranges of temperature and pressure.

Using the composition dependence of the second virial coefficient from an expansion of the EOS and from statistical mechanics, they obtained

$$B(x, T) = \sum_i \sum_j x_i x_j B_{ij}(T) = \sum_i \sum_j x_i x_j \left(b_{ij} - \frac{a_{ij}}{RT} \right) = b - \frac{a}{RT} \quad (12)$$

Wong and Sandler used this last equality as one of the restrictions on the EOS parameters, together with the combining rule

$$b_{ij} - \frac{a_{ij}}{RT} = \frac{1}{2} \left[\left(b_i - \frac{a_i}{RT} \right) + \left(b_j - \frac{a_j}{RT} \right) \right] (1 - k_{ij}) \quad (13)$$

which introduces the binary interaction parameter k_{ij} . Note that Eq. (12) does not provide relations for the parameters a and b separately, but only does for the sum $(b - a/RT)$, so that an additional equation is needed. By using Eq. (12) as one of the relations to determine the EOS parameters, the proper composition dependence of the second virial coefficient is assured, regardless of which additional is used.

The second equation in their mixing rule is based on the observation that the excess Helmholtz free energy of mixing calculated from a cubic EOS is much less sensitive to pressure than the Gibbs free energy. Consequently, to an excellent approximation

$$G_i^{ex}(T, P=1 \text{ bar}, x) = A_i^{ex}(T, P=1 \text{ bar}, x) = G_i^{ex}(T, \text{high pressure}, x) \quad (14)$$

The first of these equalities follows from the fact that $G^{ex} = A^{ex} + PV^{ex}$ and PV^{ex} the term are very small at low pressures, and the second from the relative insensitivity of the excess Helmholtz free energy to pressure at liquid densities. The second equation for the a and b parameters in the equation of the state for the mixture then from Eq. (14) in the form of

$$A_{EOX}^{ex}(T, P=\infty, x) = A_i^{ex}(T, P=\text{low } P, x) = G_i^{ex}(T, P=\text{low } P, x) \quad (15)$$

Combining Eqs. (12)–(15) gives the following mixing rules

$$b - \frac{a}{RT} = \sum_i \sum_j \left(b - \frac{a}{RT} \right)_{ij} \quad (16)$$

and

$$\frac{G^{\text{ex}}}{C^* RT} = \frac{a}{bRT} - \sum_i x_i \frac{a_i}{b_i RT} \quad (17)$$

where C^* is a constant specific to each EOS, here $C^* = -0.6232$ for the Peng-Robinson EOS and the cross term in Eq. (16) is obtained from Eq. (13); any excess Gibbs free energy parameters of Eq. (17). Details on the use of this mixing rule are given in Wong and Sandler [1992].

EXCESS FREE ENERGY (ACTIVITY COEFFICIENT) MODELS

Numerous successful excess Gibbs free or activity coefficient models have been proposed and for being used in the mixing rules discussed above. The Wilson [1964] model, the UNIQUAC model of Abrams and Prausnitz [1975], and the NRTL model of Renon and Prausnitz [1986] are most notable among these models. These local composition models usually represent the properties of the non-ideal mixtures better than the models based on the overall composition with the same number of adjustable parameters. We chose the Non-Random-Two-Liquid (NRTL) model for use here. In the NRTL model, the molar excess Gibbs free energy for a binary mixture is

$$\frac{G^{\text{ex}}}{RT} = x_1 x_2 \left(\frac{\tau_{21} G_{21}}{x_1 + x_2 G_{21}} + \frac{\tau_{12} G_{12}}{x_2 + x_1 G_{12}} \right) \quad (18)$$

with $\ln G_{ij} = -\sigma \tau_{ij}$. The adjustable parameters in this model are σ , τ_{ij} and τ_{ji} . The activity coefficient expression from this model is

$$\ln \gamma_1 = x_2^2 \left(\tau_{21} \left(\frac{G_{21}}{x_1 + x_2 G_{21}} \right)^2 + \frac{\tau_{12} G_{12}}{(x_2 + x_1 G_{12})^2} \right) \quad (19)$$

and $\ln \gamma_2$ obtained by the interchange of indices 1 and 2.

RESULTS AND DISCUSSION

The VLE calculations here were done by using an isothermal bubble point program optimizing the model parameters to minimize the objective function

$$F = \sum [P_{i, \text{exp}} - P_{i, \text{cd}}] \quad (20)$$

by using a simplex formalism.

A summary of the results for the 12 binary systems studied is given in Table 3. The average absolute percent deviation (AAD%) in the calculated pressure of each model is given in Table 3. The interaction parameter k_{12} of the W-S model and the different adjustable parameters τ_{12} and τ_{21} of W-S and MHV1 models, respectively, are given in Table 4. With both models mentioned above, the parameters τ_{12} and τ_{21} were taken to be independent of temperature. The third parameter of the NRTL model, σ , was fixed at 0.3. While the results in the table are reasonably good, even better fits would be obtained if the parameters were allowed to vary with temperature.

Especially, we obtained good results for the systems of CO₂-meth-

Table 3. AAD% in bubble pressure

System	# of isotherm	Temp. range (K)	# of data points	AAD%	
				W-S model	MHV1 model
CO ₂ /Methanol	22	230-477	239	5.0	5.7
CO ₂ /Ethanol	8	291-313	107	10.0	9.2
CO ₂ /2-Propanol	5	313-394	32	7.5	8.3
CO ₂ /1-Butanol	4	314-337	35	2.2	3.3
CO ₂ /n-Pentane	12	277-423	161	6.2	8.1
CO ₂ /Cyclohexane	9	366-503	48	4.0	5.8
CO ₂ /n-Hexane	12	298-393	109	4.5	7.6
CO ₂ /n-Heptane	6	310-477	86	6.0	7.1
CO ₂ /n-Decane	18	277-542	196	9.4	9.6
CO ₂ /Acetone	11	291-333	110	4.2	4.0
CO ₂ /Benzene	6	298-393	62	2.8	3.6
CO ₂ /Water	15	373-573	158	11.0	a

a: No parameters that resulted in a reasonable AAD% (<20%) could be found.

Table 4. NRTL interaction parameters for each model

System	Parameters				
	W-S model			MHV1 model	
	k_{12}	τ_{12}	τ_{21}	τ_{12}	τ_{21}
CO ₂ -Methanol	0.3239	1.2384	-0.0129	1.4042	-0.1958
CO ₂ -Ethanol	0.3546	3.3343	-1.0603	1.9492	-0.7031
CO ₂ -2-Propanol	0.3398	3.3596	-0.3323	0.3330	0.0126
CO ₂ -1-Butanol	0.5220	1.6988	-0.0597	0.4200	0.0619
CO ₂ -n-Pentane	0.4303	9.4331	0.2782	-0.0072	0.1000
CO ₂ -Cyclohexane	0.5274	2.3435	-0.6184	-0.2438	0.0943
CO ₂ -n-Hexane	0.5701	2.2336	-0.1392	0.1934	0.0533
CO ₂ -n-Heptane	0.5230	7.9685	0.0090	-0.4139	0.1202
CO ₂ -n-Decane	0.6395	7.9837	0.1614	1.3560	-1.6455
CO ₂ -Acetone	0.3630	0.0646	-0.1848	-0.5100	0.0749
CO ₂ -Benzene	0.4591	1.2840	-0.0763	0.1535	0.1012
CO ₂ -Water	0.0535	2.4509	2.6335	a	a

a: No parameters that resulted in an AAD of less 20% could be found.

anol and CO₂-n-pentane which have 239 and 148 data points that are more abundant than other systems. AAD% values are the average values of individual AAD% for the several isotherms. We typically plotted two different figures. Fig. 1 shows the calculated result for the CO₂-methanol system at 348 K and Fig. 2 for the CO₂-n-pentane system at 344.15 K. In the two figures the W-S model correlated the data better than the MHV1 model. In the system of CO₂-methanol, the AAD% was 5.0 for the W-S model and 5.7% for the MHV1 model. In the system of CO₂-pentane, the AAD% was 6.2% for the W-S model and 8.1% for the MHV1 model.

Because the systems of CO₂-alcohols form a hydrogen bond due to association of OH groups, the correlation of vapor-liquid equilibria does not show good results for the system with usual mixing rules. But in this study we have good correlations for the systems with the W-S mixing rule. As expected, good results for the CO₂-

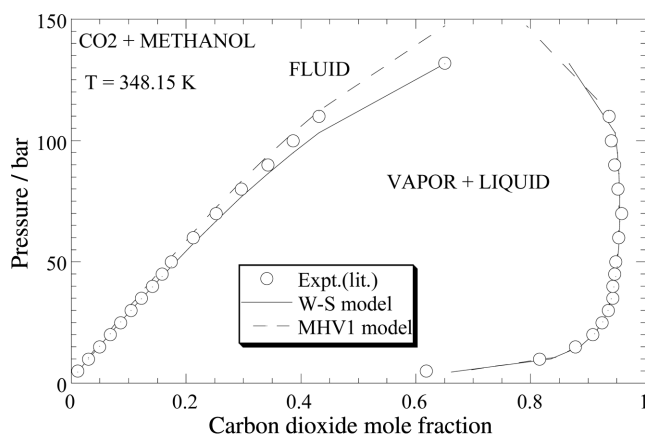


Fig. 1. A Comparison of the literature data (symbols) for the carbon dioxide-methanol system with calculations obtained with W-S model (solid lines) and MHV1 model (dotted lines) at 348.15 K.

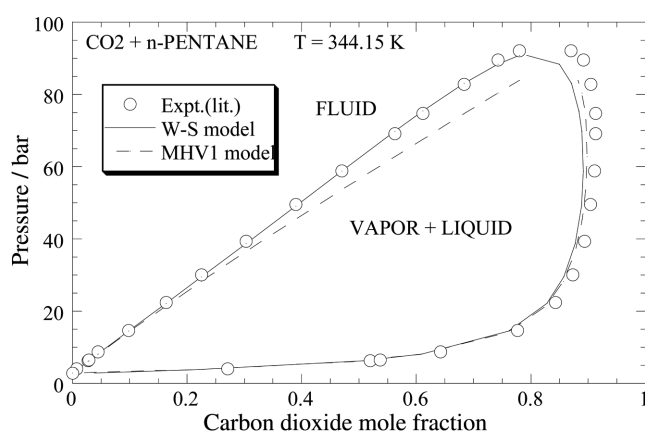


Fig. 2. A Comparison of the literature data (symbols) for the carbon dioxide-n-pentane system with calculations obtained with W-S model (solid lines) and MHV1 model (dotted lines) at 344.15 K.

alkane systems were obtained because of symmetry. For the system of CO₂-alcohols, the AAD% ranged from 2.2 to 10.0% for the W-S model and from 3.3 to 9.2% for the MHV1 model. For the systems of CO₂-alkane (C₃, C₆, C₇, C₁₀), the AAD% ranged from 4.5 to 9.4% for the W-S model and from 7.1 to 9.6% for the MHV1 model. For the 12 systems, the W-S model showed correlation of the data slightly better than the MHV1 model except for the carbon dioxide+methanol and carbon dioxide+acetone systems as seen in Table 3. With the W-S model the AAD% in pressure for 11 binary systems, excluding carbon dioxide+water, was 6.1% and ranged from 2.2 to 10.0 AAD%. For the MHV1 model, the AAD% was 6.9% for the same 11 binary systems and ranged from 3.3 to 9.6 AAD%. For the system carbon dioxide and water, W-S model produced an AAD of 11.0%, while for the MHV1 model no parameter set that resulted in an AAD of less than 20% could be found.

CONCLUSIONS

Correlations of vapor-liquid equilibrium data were made in 12 binary systems containing carbon+alcohols (methanol, ethanol, 1-

butanol, and 2-propanol); carbon dioxide+hydrocarbons (n-pentane, cyclohexane, n-hexane, n-heptane, and n-decane); and carbon dioxide separately with acetone, benzene, and water. Two free energy based-equation of state mixing rules (the W-S and MHV1 models) were used for the high pressure vapor-liquid equilibrium calculations. Both combined equation of state+free energy models resulted in generally good correlations of the experimental data of bubble pressures over wide ranges of temperature and pressure with temperature-independent parameters. With the W-S model, AAD in pressure for 11 binary systems other than carbon dioxide+water was 6.1% and ranged from 2.2 to 10.0 AAD%. With the MHV1 model, the AAD% was 6.9% for the same 11 binary systems and ranged from 3.3 to 9.6 AAD%. However, for the carbon dioxide+water systems, W-S model produced an 11.0% average absolute deviation in pressure, while no parameter that resulted in an AAD in pressure of less than 20% could be found for the MHV1 model.

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NOMENCLATURE

- a : equation of state constant
- a_i : equation of state constant for pure component
- a_{ij} : interaction parameters for mixture (Eq. (12), Eq. (13))
- \underline{A}^{ex} : molar excess Helmholtz free energy
- \underline{A}_{EOS}^{ex} : molar excess Helmholtz free energy from an equation of state
- $\underline{A}_\gamma^{ex}$: molar excess Helmholtz free energy from an activity coefficient model
- b : equation of state constant
- b_i : equation of state constant for pure component
- b_{ij} : interaction parameters for mixture (Eq. (12), Eq. (13))
- B : second virial coefficient
- B_{ij} : interaction parameters for mixture (Eq. (12))
- C^* : constant of Eq. (17)
- F : objective function (Eq. (17))
- G^{ex} : molar excess Gibbs free energy of mixture
- G_γ^{ex} : molar excess Gibbs free energy of mixture from a liquid activity coefficient model
- G_{12} : NRTL liquid activity model parameter (Eq. (18))
- G_{21} : NRTL liquid activity model parameter (Eq. (18))
- G_{ij} : NRTL liquid activity model parameter
- k_{ij} : binary interaction parameter
- P : pressure
- P_c : critical pressure
- $P_{i,cal}$: calculated pressure at point I
- $P_{i,exp}$: experimental pressure at point I
- P^{vap} : pure component saturation pressure
- q_i : parameter in Eq. (10)
- R : gas constant
- T : absolute temperature
- T_c : critical temperature
- \underline{V} : molar volume of mixture (or of pure component)
- \underline{V}^{ex} : excess volume of a mixture
- x : mole fraction of species i (in liquid)

Z : compressibility factor, PV/RT
 z_i : mole fraction of species i (generic)

Greek Letters

Γ : a function depended on molar excess Gibbs or Helmholtz free energy (Eq. (8))
 α : temperature dependent equation of state parameter (Eq. (4))
 ϕ_i : fugacity coefficient of species i in a mixture
 γ_i : activity coefficient of species i in a mixture
 γ_1 : activity coefficient of species 1 in a mixture
 γ_2 : activity coefficient of species 2 in a mixture
 k : PRSV equation parameter (Eq. (6))
 k_0 : PRSV equation parameter (Eq. (6))
 k_1 : PRSV equation parameter (Eq. (6))
 σ : NRSV model parameter (Eq. (18))
 τ_{12} : binary interaction parameter in NRTL model (Eq. (18))
 τ_{21} : binary interaction parameter in NRTL model (Eq. (18))
 τ_{ij} : binary interaction parameter in NRTL model (Eq. (18))

Subscripts

1 : component 1
 2 : component 2
 i : component i
 j : component j
 EOS : equation of state
 γ : activity coefficient
 c : critical property

Superscripts

ex : excess property
 vap : vapor

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