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Vapor–Liquid Equilibrium and Volumetric Properties Calculations for Solutions in the Supercritical Carbon Dioxide[1]

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The calculations of gas solubilities in supercritical solvents require equations of state remaining accurate in the critical range, which are difficult to obtain with classical models. In this work, the Helmholtz energy of a mixture is considered as the sum of the Helmholtz energies of pure components taken at a constant packing fraction and of a residual term which may have the form of a Redlich–Kister, Van Laar, NRTL, UNIQUAC, or UNIFAC function. Thus it is possible to assign to a given component an equation of state whose form is different from that of the others. This model has been applied to binary systems containing supercritical carbon dioxide. The results are improved with respect to those obtained with the classical model for vapor–liquid equilibria and for volumetric properties.

KEY WORDS: carbon dioxide; critical phenomena; equations of state; high pressure; phase equilibria; solutions.

1. INTRODUCTION

Vapor–liquid equilibria for fluid mixtures containing supercritical carbon dioxide are difficult to represent by cubic equations of state using classical mixing rules. Vidal [1] and Huron and Vidal [2] modified these mixing rules in simple equations of state by introducing an infinite-pressure excess free energy term expressed by a NRTL-like model.

In this work, we propose a method, EOSRF (equation of state–residual function), which allows the simultaneous use of excess

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functions and equations of state suited to each component. In fact, it is possible to use in the same calculation any type of equation of state developed specifically for each pure component.

2. DESCRIPTION OF THE MODEL

The Helmholtz energy of a mixture may be written as follows:[3]

$$A(T, b/v, n_k) = \sum_{i=1}^{p} n_i A_i(T, b_i/v_i) - RT \sum_{i=1}^{p} n_i \ln x_i + nA_{\text{res}}(T, b/v, n_k) + \sum_{i=1}^{p} x_i \ln(b_i/b) \qquad (1)$$

where n_i is the number of moles of component i in the system, x_i is the mole fraction of component i, n is the total number of moles of p components of the system, A_i is the molar Helmholtz energy of pure component i, and A_{res} is a residual energy which depends on the temperature, composition, and packing fraction. The latter is denoted by v^0/v, where v^0 is the close-packed volume. We consider v^0 proportional to the covolume b and we measure the packing fraction by the ratio $\eta = b/v$. We choose the same packing fraction for the pure components as for the mixture, which means

$$\eta = b/v = b_i/v_i \qquad (i = 1, \ldots, p) \qquad (2)$$

If we represent the properties of a pure compound by an equation of state of the form

$$P = RT/(v - b) - (1/bv)\,\psi(\eta) \qquad (3)$$

in which $\psi(\eta)$ is dependent on the chosen equation of state, Eq. (1) can be written as

$$A = A^* - nRT \ln(1 - \eta) - \sum_{i=1}^{p} (n_i/b_i)\,\Psi_i(\eta) + nA_{\text{res}} \qquad (4)$$

where A^* is the ideal Helmholtz energy of the mixture and $\Psi(\eta)$ is the integral of $\psi(\eta)/\eta$ whose lower limit is zero if $\eta \to 0$.

The fugacity coefficient ϕ_i of component i in the mixture is evaluated from

$$RT \ln \phi_i = [\partial(A - A^*)/\partial n_i]_{T,V,n_j} \qquad (j \neq i) \qquad (5)$$

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[3] For an explanation of symbols, see Nomenclature

By assuming linear mixing rules for the covolume

$$b=\sum_{i=1}^{p} x_i b_i \tag{6}$$

we obtain

$$\ln \phi_i=(b_i/b)(Pv/RT-1)-\ln[P(v-b)/RT] - (1/b_i RT)\,\Psi_i(\eta)+A_i'(T,x,\eta) \tag{7}$$

with

$$A_i'=[\partial(nA_{\text{res}})/\partial n_i]_{T,V,n_j} \tag{8}$$

The mixture equation of state is calculable from the expression

$$n(Pv-RT)=\eta[\partial(A-A^*)/\partial\eta]_{T,n_j} \tag{9}$$

Differentiating Eq. (5), we obtain

$$P=RT/(v-b)-\sum_{i=1}^{p} (x_i/b_i v)\,\psi_i(\eta)+A'(T,x,\eta)/v \tag{10}$$

with

$$A'=\eta[\partial A_{\text{res}}/\partial\eta]_{T,n_j} \tag{11}$$

3. CHOICE OF RESIDUAL TERM

We assume that the residual function may be separated into two parts:

$$A'(T,x,\eta)=E(T,x)\,F(\eta) \tag{12}$$

$E(T,x)$ may have any classical form as a Redlich–Kister, Van Laar, NRTL, UNIQUAC, or UNIFAC function. Here we take the Van Laar equation:

$$E=(\tfrac{1}{2})\sum_{i=1}^{p}\sum_{j=1}^{p} (q_i q_j/q)\,x_i x_j E_{ij} \tag{13}$$

with

$$q=\sum_{i=1}^{p} x_i q_i \tag{14}$$

where x_i denotes the mole fraction of component i, q_i is a parameter which has been fixed for carbon dioxide $q_{CO_2}=b_{CO_2}=32\ \text{cm}^3\cdot\text{mol}^{-1}$, and E_{ij} is the binary interaction parameter.

After several trials we found that the function $F(\eta)$ can be expressed by

$$F(\eta)=\eta/(1+\gamma\eta) \tag{15}$$

The calculations were performed with $\gamma=20$.

4. CHOICE OF EQUATIONS OF STATE

Equation (10) shows that it is possible to assign to a given component an equation of state with a form different from that assigned to the others.

We take for carbon dioxide the IUPAC equation [3]:

$$P=RT/v\left[1+(\rho/\rho_1)\sum_{i=0}^{9}\sum_{j=0}^{6}c_{ij}(T_1/T-1)^j(\rho/\rho_1-1)^i\right] \tag{16}$$

where $\rho_1=0.01063\ \text{mol}\cdot\text{cm}^{-3}$ and $T_1=304.2$ K. The coefficients c_{ij} have the values given in IUPAC tables [3]. The function $\psi(\eta)$ defined by Eq. (3) can be written as follows:

$$\psi(\eta)=(RTb\eta)\left[1/(1-\eta)-(1/\eta_1)\sum_{i=0}^{9}\sum_{j=0}^{6}c_{ij}(T/T_1-1)^j(\eta/\eta_1-1)^i\right] \tag{17}$$

where $\eta_1=b\rho_1$. The parameter b may be chosen as any likely value. We take $b_{CO_2}=32\ \text{cm}^3\cdot\text{mol}^{-1}$.

The Peng–Robinson equation of state [4] is used for the other components:

$$P=RT/(v-b)-a/[v(v+b)+b(v-b)] \tag{18}$$

in which

$$b=\Omega_b RT_c/P_c \tag{19}$$

$$a=\Omega_a\{1+(m_0+m_1\omega+m_2\omega^2)[1-(T/T_c)^{1/2}]\}^2\,R^2T_c^2/P_c \tag{20}$$

For the five parameters Ω_a, Ω_b, m_0, m_1, and m_2, we used in this work the values given by Peng and Robinson [4]. Molar volumes v calculated using this equation of state are corrected by a translation of the form

$$v_{\text{cor}}=v-c(T) \tag{21}$$

with

$$c=v_s(T)-v_{sRA}(T) \tag{22}$$

where $v_s(T)$ is the saturated liquid volume calculated by the equation of state at temperature T, and v_{sRA} is the Rackett volume at the same temperature according to Spencer and Danner [5].

The mixture molar volumes v are thus corrected, carbon dioxide being component number 1:

$$v_{\mathrm{cor}} = v - \sum_{i=2}^{p} x_i c_i \tag{23}$$

This correction leaves the predicted equilibrium conditions unchanged, as shown in a previous paper [6].

5. REMARKS

If we take the same equation of state for all the components and if we postulate that $\psi_i(\eta)/a_i = F(\eta)$, Eq. (10) becomes

$$P = RT/(v-b) - \sum_{i=1}^{p} [(x_i a_i/b_i) + E]\, F(\eta)/v \tag{24}$$

We give the Van Laar form to E [Eq. (13)], with $q_i = b_i$ and we write the binary interaction parameters E_{ij} in the form

$$E_{ij} = a_i/b_i^2 + a_j/b_j^2 - 2a_{ij}/b_i b_j \tag{25}$$

Then Eq. (24) reduces to the following expression:

$$P = RT/(v-b) - (a/bv)\, F(\eta) \tag{26}$$

with

$$a = \sum_{i=1}^{p} \sum_{j=1}^{p} x_i x_j a_{ij} \tag{27}$$

In this case the proposed model is equivalent to the classical mixing rules but expressed in a different form. Expression (25) shows the relation between the two binary interaction parameters E_{ij} and k_{ij} as

$$a_{ij} = (a_i a_j)^{1/2}(1 - k_{ij}) \tag{28}$$

which leads to

$$E_{ij} = (\delta_i - \delta_j)^2 + 2k_{ij}\delta_i\delta_j, \qquad \text{where} \quad \delta_i = \sqrt{a_i}/b_i \tag{29}$$

6. RESULTS

In order to improve the proposed method, we have studied the binary systems containing carbon dioxide–n-paraffins and we have compared our results with these given by the classical Peng–Robinson method [4].

Table I. Values of Parameters k_{12}, E_{12}, and q_2/q_1 and Mean Relative Deviations $\overline{\delta_r(P)}$ Between Experimental and Predicted Pressures

	T (K)	N	k_{12}	E_{12} (J)	q_2/q_1	$\overline{\delta_r(P)}$ PR (%)	$\overline{\delta_r(P)}$ EOSRF (%)
C3	277.59	12	0.1231	421.0	1.243	1.35	0.62
	294.26	17	0.1256	395.1	1.414	0.74	0.38
	310.93	16	0.1327	381.1	1.535	0.21	0.19
	327.59	14	0.1386	385.2	1.581	0.32	0.13
	344.26	11	0.1497	351.6	8.907	0.96	0.81
C4	283.15	10	0.1326	470.5	1.428	3.26	1.05
	310.93	20	0.1344	422.3	1.605	1.25	0.43
	344.26	18	0.1355	407.6	1.625	0.54	0.17
	377.59	13	0.1490	414.3	1.558	0.33	0.45
	410.93	8	0.1581	581.5	0.584	1.43	0.46
iC4	310.93	9	0.1198	373.2	1.578	1.14	0.68
	344.26	7	0.1336	368.8	1.711	0.46	0.31
C5	277.65	11	0.1356	511.5	1.451	4.68	1.34
	311.04	14	0.1182	419.1	1.875	2.96	1.96
	344.15	14	0.1255	398.4	1.933	2.47	1.86
	377.59	9	0.1345	411.5	1.762	2.15	2.25
iC5	277.65	12	0.1180	440.6	1.767	2.50	0.54
	310.95	11	0.1115	385.9	1.879	1.92	1.35
	344.32	12	0.1270	393.3	1.837	1.64	0.79
	377.65	11	0.1376	432.9	1.457	1.42	1.26
C7	310.65	21	0.1093	431.3	2.448	2.15	1.21
	352.59	16	0.1018	354.3	2.730	0.70	0.54
	394.26	16	0.0880	279.2	3.131	2.67	1.78
C10	277.59	12	0.1298	609.0	2.788	4.66	0.83
	310.93	11	0.1185	543.1	2.818	4.64	1.18
	344.26	8	0.1117	472.5	3.036	3.94	0.61
	377.59	11	0.1060	417.4	3.166	1.83	0.74
	410.93	13	0.1050	383.5	3.115	1.25	1.05
	444.26	12	0.1092	356.9	3.215	0.89	0.88
	477.59	12	0.1207	362.5	2.854	1.16	1.29
	510.93	10	0.1496	385.9	2.746	1.80	1.91

The data used for our comparison are as follows:

carbon dioxide–propane (C3) system [7],

carbon dioxide–*n*-butane (C4) system at 283.15 K [8] and at other temperatures [9],

carbon dioxide–isobutane (iC4) system [10],

carbon dioxide–*n*-pentane (C5) system [11],

carbon dioxide–isopentane (iC5) system [12],

carbon dioxide–*n*-heptane (C7) system [13], and

carbon dioxide–*n*-decane (C10) system [14].

Critical constants and acentric factors were taken from data compiled by Reid *et al.* [15] for *n*-paraffins and by IUPAC for carbon dioxide. The binary interaction parameters E_{12} $(1 = CO_2)$, the parameters q_2/q_1 [Eq. (13)] used with the method EOSRF, and the interaction parameters k_{12} [Eq. (28)] used with the Peng–Robinson method were adjusted at each temperature for each system by the method of Nelder and Mead [16] from experimental data by minimizing the objective function:

$$\overline{\delta_r(P)} = (100/N) \sum_{i=1}^{N} |P_{\text{obs},i} - P_{\text{cal},i}|/P_{\text{obs},i} \tag{30}$$

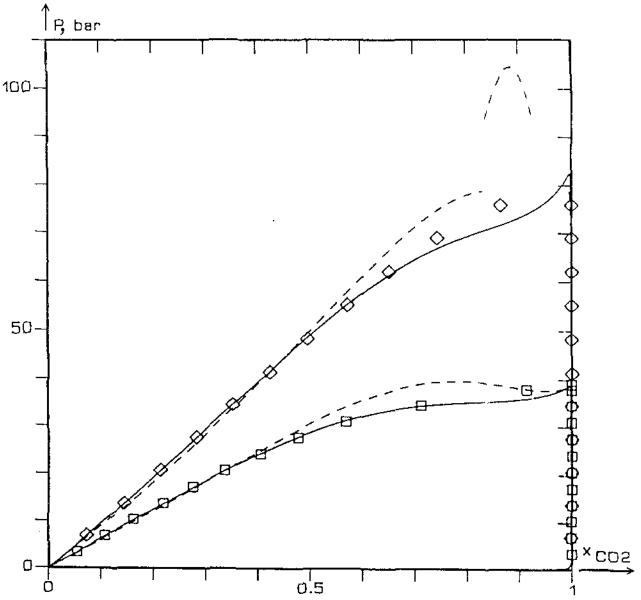

Fig. 1. Comparison between experimental and calculated vapor–liquid equilibria for the CO_2–*n*-$C_{10}H_{22}$ system. Dashed lines, Peng–Robinson method; solid lines, EOSRF method. Experimental points: (□) at 277.59 K; (◇) at 310.93 K.

Table II. Mean Deviations $\overline{\delta(y)}$ Between Experimental and Predicted Vapor Mole Fractions and Mean Relative Deviations $\overline{\delta_r(v_l)}$ and $\overline{\delta_r(v_g)}$ Between Experimental and Predicted Saturated Liquid and Vapor Volumes

		$\overline{\delta(y)}$		$\overline{\delta_r(v_l)}$		$\overline{\delta_r(v_g)}$	
	T (K)	PR	EOSRF	PR (%)	EOSRF (%)	PR (%)	EOSRF (%)
C3	277.59	0.0060	0.0029	3.55	0.34	2.27	1.28
	294.26	0.0045	0.0031	5.29	1.09	3.21	1.77
	310.93	0.0101	0.0047	5.34	3.13	1.37	2.01
	327.59	0.0117	0.0070	5.36	3.52	0.86	1.68
	344.26	0.0128	0.0129	7.77	3.40	1.65	2.96
C4	283.15	0.0048	0.0048	3.46	1.05	1.29	1.72
	310.93	0.0053	0.0059	5.80	0.17	1.16	0.81
	344.26	0.0056	0.0054	2.92	0.74	0.99	0.52
	377.59	0.0056	0.0050	3.75	1.28	1.16	0.60
	410.93	0.0146	0.0069	9.55	0.76	1.42	1.45
iC4	310.93	0.0077	0.0099	5.33	1.11	4.45	2.13
	344.26	0.0130	0.0076	4.04	2.29	1.66	1.44
C5	277.65	0.0029	0.0035	2.60	0.53	2.57	2.11
	311.04	0.0078	0.0032	6.27	0.44	2.21	3.38
	344.15	0.0179	0.0109	2.25	0.97	3.80	4.73
	377.59	0.0242	0.0172	2.70	0.74	3.88	4.23
iC5	277.59	0.0031	0.0028	3.39	0.73	3.37	3.48
	310.93	0.0055	0.0043	5.61	0.83	2.12	3.75
	344.32	0.0131	0.0083	4.04	0.80	3.92	4.58
	377.65	0.0224	0.0115	2.90	1.03	4.71	5.10
C7	310.65	0.0020	0.0018	6.68	1.73	5.49	4.24
	352.59	0.0037	0.0054	4.70	1.94	3.28	2.61
	394.26	0.0139	0.0050	6.59	3.57	2.76	2.52
C10	277.59	0.0000	0.0000	8.10	0.72	0.48	1.01
	310.93	0.0009	0.0003	7.74	0.77	13.00	12.43
	344.26	0.0050	0.0014	7.30	1.13	1.37	2.59
	377.59	0.0033	0.0014	7.08	0.90	1.13	1.42
	410.93	0.0042	0.0017	6.62	1.58	1.06	1.69
	444.26	0.0053	0.0032	7.21	1.39	1.19	0.60
	477.59	0.0079	0.0057	7.45	1.37	2.20	1.32
	510.93	0.0078	0.0124	8.66	1.66	1.82	0.56

Their values are listed in Table I. We have also reported the temperature and the number of determinations N for each isotherm and the mean relative deviations between experimental and calculated pressures defined above.

As shown in Fig. 1 for the carbon dioxide–n-decane system, the new method leads to good results, especially in the vicinity of the carbon dioxide critical point, whereas the Peng–Robinson method predicts liquid–liquid and triphasic equilibria which do not exist at this temperature.

The values of mean deviations between experimental and predicted vapor mole fractions given by

$$\overline{\delta(y)} = (1/N) \sum_{i=1}^{N} |y_{\mathrm{obs},i} - y_{\mathrm{cal},i}| \tag{31}$$

are reported in Table II.

We are also interested in the volumes of saturated liquid and vapor phases. The comparisons were made without vapor–liquid equilibrium estimations: volumes were calculated using experimental values for temperature, pressure, and liquid and vapor compositions but with adjusted values from liquid–vapor equilibrium for the parameters E_{12}, q_2/q_1, and k_{12}.

The values of mean relative deviations between experimental and predicted saturated liquid and vapor volumes defined by

$$\overline{\delta_r(v)} = (100/N) \sum_{i=1}^{N} |v_{\mathrm{obs},i} - v_{\mathrm{cal},i}|/v_{\mathrm{obs},i} \tag{32}$$

are given in Table II.

Table III. Mean Relative Deviations $\overline{\delta_r(P)}$ Between Experimental and Predicted Pressures, Mean Deviations $\overline{\delta(y)}$ Between Experimental and Predicted Vapor Mole Fractions, and Mean Relative Deviations $\overline{\delta_r(v_l)}$ and $\overline{\delta_r(v_g)}$ Between Experimental and Predicted Saturated Liquid and Vapor Volumes for Each System

		$\overline{\delta_r(P)}$		$\overline{\delta(y)}$		$\overline{\delta_r(v_l)}$		$\overline{\delta_r(v_g)}$	
	N	PR (%)	EOSRF (%)	PR	EOSRF	PR (%)	EOSRF (%)	PR (%)	EOSRF (%)
C3	70	0.67	0.39	0.0088	0.0058	5.41	2.28	1.91	1.91
C4	69	1.20	0.46	0.0064	0.0055	4.76	0.75	1.16	0.90
iC4	16	0.85	0.52	0.0100	0.0089	4.77	1.63	3.23	1.83
C5	48	3.06	1.84	0.0127	0.0081	3.58	0.67	3.07	3.64
iC5	46	1.88	0.97	0.0109	0.0067	3.97	0.84	3.53	4.22
C7	53	1.87	1.18	0.0061	0.0038	6.06	2.35	4.00	3.23
C10	89	2.44	1.06	0.0042	0.0032	7.50	1.19	2.86	2.82

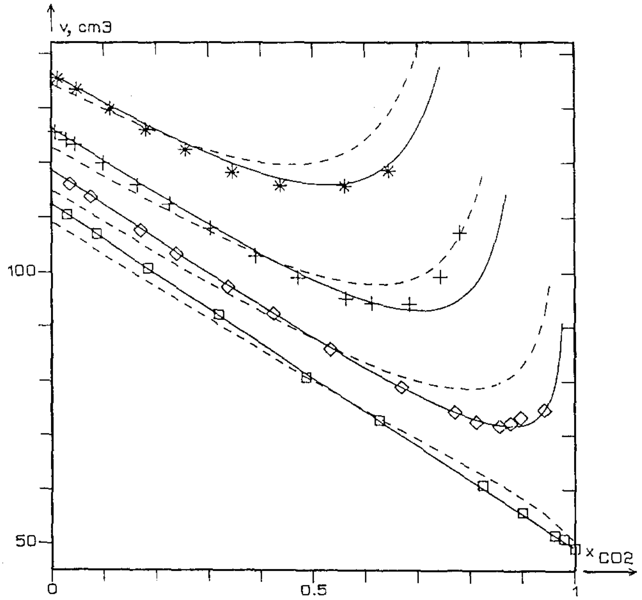

Fig. 2. Comparison between experimental and calculated saturated liquid molar volumes equilibria for the CO_2-*n*-C_5H_{12} system. Dashed lines, Peng–Robinson method; solid lines, EOSRF method. Experimental points: (□) at 277.65 K; (◇) at 311.04 K; (+) at 344.32 K; (∗) at 377.59 K.

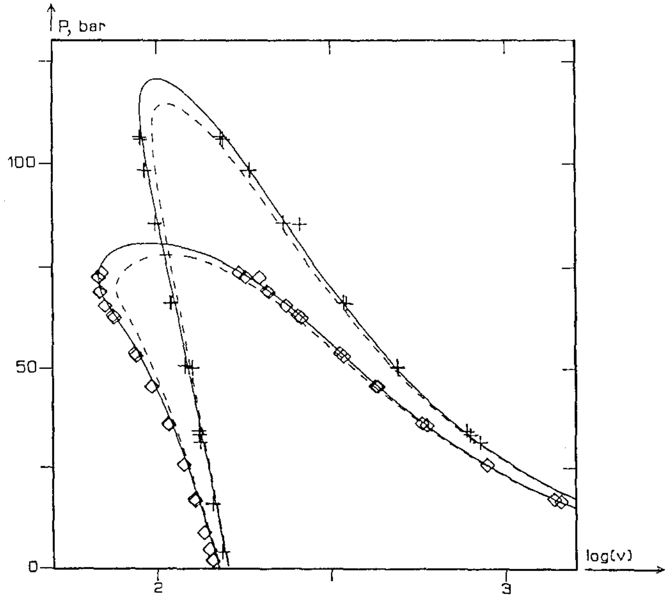

Fig. 3. Comparison between experimental and calculated saturated liquid and vapor molar volumes equilibria for the CO_2-*n*-C_7H_{14} system. Dashed lines, Peng–Robinson method; solid lines, EOSRF method. Experimental points: (◇) at 310.65 K; (+) at 352.59 K.

Table III gives for each system the number of determinations used, the mean relative deviations for the pressure, the liquid and vapor volumes, and the mean deviations for vapor composition. As can be seen, the method EOSRF leads to a great improvement over the Peng–Robinson results for the saturated liquid volumes. Figure 2 shows full agreement with the measured values, especially in the critical range of carbon dioxide.

In Fig. 3 the bubble pressures are plotted as a function of the logarithm of volume for the carbon dioxide–*n*-heptane system; the results obtained are good for liquid volumes and for vapor volumes, although these are not greatly improved by our method.

7. CONCLUSION

The proposed method leads to good phase-behavior prediction, especially in the neighborhood of the carbon dioxide critical point, but it also gives good estimates of the volumetric properties. It is a very general method which can be used with different equations of state and other excess functions for improving systems difficult to represent by simple methods.

NOMENCLATURE

A	Helmholtz energy of a system
A'	Residual term
A_i	Molar Helmholtz energy of pure component i
A_{res}	Residual energy
a	Parameter of equations of state
b	Covolume
c_{ij}	Parameters of IUPAC equation of state
E_{ij}	Binary interaction parameter
k_{ij}	Binary interaction coefficient
m	Constant in Eq. (20)
N	Number of determinations
n	Total number of moles
n_i	Number of moles of component i
P	Pressure
p	Number of components
q_i	Parameter of residual term
R	Gas constant
T	Temperature (K)

V	Volume
v	Molar volume
v_{cor}	Corrected molar volume
v^0	Close-packed volume
v_{RA}	Rackett volume
x_i	Mole fraction of component i
δ	Deviation
η	Reduced density ($\eta = b/v$)
ρ	Molar density in IUPAC equation of state
ϕ_i	Fugacity coefficient of component i
Ω_a, Ω_b	Factor in Eqs. (19), (20)
ω	Acentric factor

Subscripts

c	Critical
r	Relative

Superscript

*	Ideal state

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