Critical Properties of Dilute Multicomponent Mixtures

Equations for the critical properties of dilute multicomponent mixtures have been derived using the Soave-Redlich-Kwong equation of state. The utility and limitations of the approach are described using data on 47 mixtures from the literature. New data on three dilute multicomponent mixtures have also been measured in this work and are compared with the predictions of our method. In general, it is possible to predict all three critical properties of dilute multicomponent systems with a satisfactory degree of accuracy. Predictions are as good as those obtained from conventional equation of state methods, which employ a rigorous solution of the Gibbs criteria for the critical point, but offer the advantage that no iterations are required in the calculations.

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Introduction

Dilute mixtures are composed almost entirely of one species, the solvent, with the remaining small fraction of the mixture, the solute or impurity, consisting of one or more other species. The thermodynamic properties of dilute mixtures are important in many applications. For example, in supercritical extraction, a knowledge of the critical point of the dilute system consisting of the supercritical solvent and the extracted material is necessary to determine the conditions at which maximum changes in solubility occur. However, the prediction of the properties of multicomponent mixtures that are common in supercritical extraction and other processes is difficult. This is because the number and complexity of equations that must be solved to obtain the phases in equilibrium increase rapidly with the number of components. The nature of dilute systems, however, can often be used to reduce the mathematical complexity of the equations that must be solved. Gualtieri et al. (1982) recently derived a general framework for the calculation of the critical properties of dilute mixtures. They used their procedure with the van der Waals (vdW) equation of state to obtain analytical expressions for the critical properties. The van der Waals equation was chosen because of the long derivation necessary to obtain the final expressions for the critical properties. More recently, Morrison and Kincaid (1984) compared their experimental measurements of the critical properties of a number of dilute mixtures with the predictions of the dilute mixture–van der Waals (dilute-vdW) theory of Gualtieri et al., and concluded that the agreement between theory and experiment was only qualitative. In the present work, we have used the general framework of Gualtieri et al. (1982) with the Soave-Redlich-Kwong (SRK) equation of state to obtain expressions for the critical properties (T_c, V_c) of dilute multicomponent mixtures. The approach of Gualtieri et al. was also extended to the calculation of P_c in this work. Although the derivation of the expressions is substantially more complex than in the case of the vdW equation, the final expressions are very easy to apply and involve no iterations. We have tested the range of applicability of these expressions using data on 47 mixtures obtained from the literature. In addition, new data on the critical properties of three dilute multicomponent mixtures were measured to better illustrate the limitations of the method.

Definition of a Dilute Multicomponent Mixture

Dilute multicomponent mixtures are composed of mostly one species, the solvent (denoted by index 1 and mole fraction x_1 in the work described below), and other components (denoted by indices 2, 3, . . . , c and mole fractions $x_2, x_3, \ldots, x_c$). These other components may be termed impurities because of their low concentrations. Thus, $\Sigma_{j=2}^{c} x_j = \epsilon$ is small. Since number densitites are a more appropriate set of variables than mole fractions in the Gualtieri et al. framework, we can also characterize a dilute mixture by the number density of each of its components: ρ_1 for the solvent and $\rho_2, \ldots, \rho_n$ for the impurities. By convention,

$$\rho_i = \frac{n_i}{V} = \frac{x_i}{\tilde{v}} \tag{1}$$

$$\eta = \sum_{j\geq 2} \rho_j \tag{2}$$

where η is small, N_i is the number of molecules of component i, V is the total volume of the system, and $\tilde{v}$ is the volume per molecule.

The Soave-Redlich-Kwong Equation of State

To be consistent with the method of Gualtieri et al., the Soave-Redlich-Kwong (SRK) equation of state must first be expressed in terms of the molecular volume $\tilde{v}$. Thus:

$$\beta P = \frac{1}{\tilde{v} - b} - \frac{\beta a(T)}{\tilde{v}(\tilde{v} + b)} \tag{3}$$

where $\beta = 1/kT$, and k is the Boltzmann constant. The pure component parameters a_{ii} and b_i are given by:

$$a_{ii} = 0.42748 \frac{k^2 T_{ci}^2}{P_{ci}} \alpha_i(T) \tag{4}$$

and

$$b_i = 0.08664 \frac{kT_{ci}}{P_{ci}} \tag{5}$$

where

$$\sqrt{\alpha_i(T)} = 1 + M_i(1 - \sqrt{T_{ri}}) \tag{6}$$

with

$$M_i = 0.480 + 1.57\omega_i - 0.176\omega_i^2 \tag{7}$$

T_{ci}, P_{ci}, and ω_i are the critical temperature, critical pressure, and acentric factor of component i, respectively, and $T_{ri} = T/\mathrm{T}_{ci}$ is the reduced temperature. The Helmholtz energy per unit volume, $\tilde{A} = NA/V$, can be obtained by integration of the expression for the pressure. This gives:

$$\beta \tilde{A}(T, \{\rho_i\}) = \sum_i \rho_i \ln \rho_i - \rho + \sum_i \rho_i \ln (\Lambda_i)^3 + \pi \tag{8}$$

where Λ_i is the thermal de Broglie wavelength. The righthand side of Eq. 8 consists of an ideal mixing term and a nonideal mixing term π, with

$$\pi = -\rho \ln(1 - \rho b) - \beta\rho \frac{a}{b} \ln(1 + \rho b) \tag{9}$$

Conventional mixing rules with a binary interaction parameter k_{ij} are used to extend the SRK equation to mixtures.

Critical Properties of Dilute Mixtures

As demonstrated by Gualtieri et al. (1982), when the critical point conditions are applied to dilute multicomponent mixtures, they lead the the following equations:

$$\left.\left(\frac{dT_c}{d\eta}\right)\right|_{\eta=0} = \left.\left(\frac{\langle \rho_1 \pi_{ij}^2 \rangle - \dfrac{\partial \rho_1 \pi_{11}}{\partial \eta}}{\dfrac{\partial \rho_1 \pi_{11}}{\partial T}}\right)\right|_{\eta=0} \tag{10}$$

and

$$\left.\left(\frac{\partial \rho_c}{\partial \eta}\right)\right|_{\eta=0} = \left\{ 3 \left\langle \rho_1 \pi_{1j} \frac{\partial \pi_{1j}}{\partial \rho_1} \right\rangle - \langle \rho_1 (\pi_{1j})^3 \rangle \right.$$
$$\left. - \rho_1 \left.\left(\frac{\partial^2 \pi_{11}}{\partial \rho \partial T} \frac{dT_c}{d\eta}\right)\right|_{\eta=0} - \rho_1 \left.\left(\frac{\partial^2 \pi_{11}}{\partial \rho_1 \partial \eta}\right)\right|_{\eta=0} \right\} \left\{ \frac{\partial^2 (\rho_1 \pi_{11})}{\partial \rho_1^2} \right\}^{-1} \tag{11}$$

where π_{ij} denotes $(\partial^2 \pi)/\partial \rho_i \partial \rho_j)$ and $\langle\ \rangle$ denotes an averaging process defined by:

$$\langle h_{ij} \rangle \equiv \frac{1}{\eta} \sum_{j=2}^{c} \rho_j h_{ij} = \frac{1}{\epsilon} \sum_{j=2}^{c} x_j h_{ij} \tag{12}$$

$$\langle g_j \rangle \equiv \frac{1}{\eta} \sum_{j=2}^{c} \rho_j g_j = \frac{1}{\epsilon} \sum_{j=2}^{c} x_j g_j \tag{13}$$

where h_{ij} and g_j are generic quantities. The derivation of Eqs. 10 and 11 can be found in Gualtieri et al. (1982). Combining the nonideal parts of the Helmholtz density function for the SRK equation, Eq. 9, with Eqs. 10 and 11 leads to the following expressions for the critical temperature and volume of a dilute multicomponent mixture:

$$T_c = T_{c1} \left\{ 1 + \frac{\epsilon}{1 + M_1} \left[0.25666 \left\langle \left(\frac{b_j}{b_1}\right)^2 \right\rangle + 2.26989 \left\langle \left(\frac{a_{1j}}{a_{11}}\right)^2 \right\rangle \right.\right.$$
$$\left.\left. - 1.52654 \left\langle \frac{a_{1j} b_j}{a_{11} b_1} \right\rangle + 0.01323 \left\langle \frac{b_j}{b_1} \right\rangle - 1.01322 \left\langle \frac{a_{1j}}{a_{11}} \right\rangle \right] \right\} \tag{14}$$

$$v_c = v_{c1} \left\{ 1 + \epsilon \left[1 - 0.14952 \left\langle \left(\frac{b_j}{b_1}\right)^3 \right\rangle + 3.93341 \left\langle \left(\frac{a_{1j}}{a_{11}}\right)^3 \right\rangle \right.\right.$$
$$+ 0.11973 \left\langle \frac{b_j}{b_1} \right\rangle + 0.27207 \left\langle \left(\frac{b_j}{b_1}\right)^2 \right\rangle$$
$$+ 0.03044 \left\langle \frac{a_{1j}}{a_{11}} \right\rangle - 2.65661 \left\langle \left(\frac{a_{1j}}{a_{11}}\right)^2 \right\rangle$$
$$- 3.96793 \left\langle \frac{a_{1j}^2 b_j}{a_{11}^2 b_1} \right\rangle + 1.33421 \left\langle \frac{a_{1j} b_j^2}{a_{11} b_1^2} \right\rangle$$
$$\left.\left. + 0.08420 \left\langle \frac{a_{1j} b_j}{a_{11} b_1} \right\rangle \right] \right\}^{-1} \tag{15}$$

where the averaging process $\langle\ \rangle$ is defined by Eqs. 12 and 13. Details of the derivation are given in the Appendix B. Note that these expressions remain unchanged when the SRK constants of each of the pure fluids are calculated on a molar basis as follows:

$$a_{ii} = 0.42748 \frac{R^2 (T_{ci})^2}{P_{ci}} \alpha_i(T) \tag{16}$$

$$b_i = 0.08664 \frac{RT_{ci}}{P_{ci}} \tag{17}$$

Equations 14 and 15 for T_c and v_c satisfy two constraints:

1. When there is no impurity ($\epsilon = 0$), the critical temperature and number density of the mixture are the same as those of the solvent (i.e., $T_c = T_{c1}$ and $v_c = v_{c1}$).

2. When the solvent itself is added as an impurity $[(b_j/b_1) = (a_{1j}/a_{11}) = 1]$, the critical properties of the mixture remain unchanged.

It should also be noted that Eqs. 14 and 15 do not contain any terms that correct for interactions between the impurities (a_{ij}). Only solvent-impurity interactions (a_{1j}) are considered. This is a result of the first-order Taylor series expansion about the critical point of the solvent that was used in the derivation of the equations (see Appendix A). Another consequence of the first-order development is that, for an impurity of given constitution, Eqs. 14 and 15 predict shifts in the critical temperature and number density of solvent that are proportional to the total mole fraction of the impurity. This is an important result, especially for multicomponent systems. It means that, in the limit of infinite dilution, the effect of a complex impurity on the critical point of the solvent is directly proportional to the total amount of the impurity.

Equations 14 and 15 allow the calculation of T_c and v_c of a dilute multicomponent mixture from a knowledge of the critical properties of all components, and binary interaction parameters for the interactions between the solvent and the impurities, if available. The critical pressure of the mixture can then be calculated using the SRK equation of state. However, because the critical compressibility of real fluids is not predicted accurately by a cubic equation of state such as the SRK equation, the procedure must be modified to give good predictions of all three critical constants of a dilute mixture. The procedure adopted in the present work was as follows:

1. Given T_{c1} and P_{c1} of the solvent, v'_{c1} is calculated using the SRK compressibility of $1/3$
2. This value of v'_{c1} is used in Eq. 14 to obtain v'_c of the dilute multicomponent mixture
3. P_c of the dilute system is then calculated from the SRK equation using the above value of v'_c , and the value of T_c calculated from Eq. 15
4. The experimental value of v_{c1} is then used in Eq. 14 to obtain v_c

Extension to dilute polydisperse mixtures

In a dilute mixture containing impurities, the compositon is commonly represented by the mole fraction x_i of each species i. If the number of impurity species is large, it may be more convenient to adopt a continuous description of the mole fractions. The composition of the impurity is then determined by a continuous mole fraction distribution function $D(k)$ or the mole fraction density function $F(k)$ where F is defined as

$$F(k) = \frac{1}{\epsilon}\frac{dD(k)}{dk} \tag{18}$$

so that

$$\int_a^b F(k)\,dk = 1 \tag{19}$$

The identity variable k may be a property such as the molecular weight or the boiling point, and its range may be finite or infinite.

With this notation, the averaging process for the two generic functions $h(1, i)$ and $g(i)$ already defined with the discrete index, becomes:

$$\langle h_{1,i}\rangle \equiv \frac{1}{\epsilon}\sum_{j=2}^{c} x_j h_{1j} \equiv \int_a^b F(k)h(1,k)\,dk \tag{20}$$

$$\langle g_j\rangle \equiv \frac{1}{\epsilon}\sum_{j=2}^{c} x_j g_j \equiv \int_a^b F(k)g(k)\,dk \tag{21}$$

Equations 10 and 11 can be combined with Eqs. 20 and 21 to predict shifts in the critical temperature and number density of solvent that are proportional to give the critical point of a solvent

Table 1. Compositions of Dilute Mixtures Studied

Mix. No.	Components (mol %)	Ref.*
1	$nC_1(91)$, $nC_2(5.6)$, $nC_3(0.12)$, $N_2(3.3)$	a
2	$nC_1(95.9)$, $nC_2(2.6)$, $nC_3(0.01)$, $N_2(1.5)$	a
3	$nC_1(95)$, $nC_2(2.6)$, $nC_3(0.78)$, $N_2(1.6)$	a
4	$nC_1(94.5)$, $nC_2(2.6)$, $nC_3(0.81)$, $nC_4(0.52)$, $N_2(1.6)$	a
5	$nC_1(94.3)$, $nC_2(2.7)$, $nC_3(0.74)$, $nC_4(0.49)$, $nC_5(0.01)$, $nC_6(0.27)$, $N_2(1.4)$	a
6	$CO_2(97.39)$, $nC_2(2.61)$	b
7	$CO_2(90.25)$, $nC_2(9.75)$	b
8	$CO_2(98.95)$, $nC_2(1.05)$	b
9	$CO_2(98.57)$, $nC_2(1.43)$	b
10	$CO_2(97.39)$, $nC_2(2.61)$	b
11	$CO_2(97.34)$, $nC_2(2.66)$	b
12	$CO_2(97.18)$, $nC_2(2.82)$	b
13	$CO_2(96.67)$, $nC_2(3.33)$	b
14	$CO_2(96.59)$, $nC_2(3.41)$	b
15	$CO_2(96.09)$, $nC_2(3.91)$	b
16	$CO_2(95.04)$, $nC_2(4.96)$	b
17	$CO_2(90.15)$, $nC_2(9.85)$	b
18	$CO_2(97.48)$, $nC_2(2.52)$	b
19	$CO_2(91.44)$, $nC_2(8.56)$	b
20	$CO_2(97.51)$, $nC_2(1.23)$, $nC_3(1.26)$	b
21	$CO_2(97.44)$, $nC_2(1.93)$, $nC_3(0.63)$	b
22	$CO_2(97.51)$, $nC_2(0.63)$, $nC_3(1.86)$	b
23	$CO_2(97.46)$, $nC_2(1.27)$, $nC_4(1.27)$	b
24	$CO_2(97.39)$, $nC_3(1.32)$, $nC_4(1.29)$	b
25	$CO_2(97.50)$, $nC_2(0.81)$, $nC_3(0.84)$, $nC_4(0.85)$	b
26	$CO_2(90.73)$, $nC_2(4.82)$, $nC_3(4.43)$	b
27	$CO_2(91.15)$, $nC_2(4.45)$, $nC_3(4.40)$	b
28	$CO_2(91.16)$, $nC_2(4.43)$, $nC_3(4.41)$	b
29	$CO_2(93.62)$, $nC_2(2.82)$, $nC_3(3.56)$, $nC_4(3.23)$	b
30	$nC_4(89.8)$, $nC_6(10.2)$	c
31	$nC_6(89.65)$, $nC_4(10.35)$	c
32	$nC_4(87.45)$, $nC_5(12.5)$	c
33	$nC_5(86.01)$, $nC_4(13.99)$	c
34	$nC_3(92.6)$, $nC_4(7.4)$	d
35	$nC_3(91.8)$, $nC_6(8.2)$	d
36	$nC_3(90.9)$, $nC_7(9.1)$	d
37	$nC_{10}(90.0)$, $nC_{12}(10.0)$	e
38	$nC_{12}(90.0)$, $nC_{10}(10.0)$	e
39	$nC_9(90.0)$, $nC_{13}(10.0)$	e
40	$nC_{13}(90.0)$, $nC_9(10.0)$	e
41	$nC_6(90.0)$, $nC_{13}(10.0)$	e
42	$nC_{13}(90.0)$, $nC_6(10.0)$	e
43	$nC_{10}(90.0)$, $nC_6(10.0)$	e
44	$nC_4(94.61)$, $nC_8(5.39)$	f
45	$nC_3(95.9)$, $nC_8(4.19)$	f
46	$nC_{14}(90.0)$, $nC_6(10.0)$	e
47	$nC_6(90.0)$, $nC_{14}(10.0)$	e

*a: Peng & Robinson (1977); b: Morrison & Kincaid (1984); c: Kay et al. (1975); d: Kay (1970); e: Pak & Kay (1972); f: Kay et al. (1974)

containing a polydispersed impurity. Equations 14 and 15 are again obtained, but with the averaging process defined by Eqs. 20 and 21. The possible use of the dilute mixture-SRK (dilute-SRK) approach for dilute polydisperse mixtures could be of interest, for example, in the calculation of the properties of undefined mixtures.

Comparison with Literature Data

Experimental critical properties of 47 dilute mixtures were obtained from the literature, with dilute mixtures being arbitrarily defined as mixtures in which the solvent mole fraction is greater than 0.9. The only multicomponent systems for which data are available in the literature are mixtures containing hydrocarbons, with or without CO_2. The compositions of these mixtures are reported in Table 1. Some binary mixtures are included in Table 1 because of a lack of experimental data on ternary and higher mixtures in the literature. Mixtures 1–5 are multicomponent mixtures with methane as the solvent. Mixtures 6–28 are binary and multicomponent mixtures with CO_2 as the solvent and C_2H_6, C_3H_8, C_4H_{10} as the impurities.

Table 2. Comparison of Various Estimation Methods for T_c, P_c, and v_c of Dilute Mixtures

Mix.	T_c, K				P_c, kPa				v_c, mL/mol			
No.	Exp.	A	B	C	Exp.	A	B	C	Exp.	A	B	C
1	199.3	2.6	0.0	−0.9	5341	19	719	−387	—	—	—	—
2	193.9	1.7	0.6	0.3	4932	−1	298	−166	—	—	—	—
3	196.5	2.6	0.7	−0.2	5180	29	682	−327	—	—	—	—
4	199.5	4.0	0.8	−1.0	5456	246	1391	−496	—	—	—	—
5	201.1	9.4	2.5	−2.0	5578	1411	3068	−568	—	—	—	—
6	302.7	1.3	1.2	1.2	7250	24	307	26	95.1	0.2	−3.4	20.8
7	298.9	4.7	4.1	4.2	6935	37	1093	65	98.2	1.1	−12.1	22.5
8	304.2	−0.2	0.7	−1.0	7324	−42	517	−48	—	—	—	—
9	304.1	−0.1	1.0	−1.2	7243	3	764	−5	—	—	—	—
10	304.1	−0.3	1.8	−2.2	7229	−98	1294	−105	—	—	—	—
11	304.1	−0.3	1.8	−2.2	7230	−103	1315	−110	95.5	1.7	−13.9	22.3
12	304.1	−0.4	1.9	−2.3	7200	−89	1415	−95	—	—	—	—
13	304.1	−0.5	2.3	−2.7	7180	−118	1660	−122	—	—	—	—
14	304.2	−0.6	2.2	−2.9	7178	−124	1697	−127	—	—	—	—
15	304.2	−0.7	2.5	−3.2	7158	−152	1937	−151	—	—	—	—
16	304.3	−0.9	3.1	−4.0	7108	−203	2451	−190	—	—	—	—
17	305.3	−2.8	5.3	−7.0	6950	−515	4797	−382	100.4	6.8	−40.1	27.7
18	306.1	−1.2	1.9	−4.3	7336	−316	2986	−298	95.8	3.3	−27.7	24.1
19	315.2	−5.8	4.7	−12.2	7663	−1523	9987	−1156	101.1	12.8	−60.1	32.6
20	303.6	0.3	1.3	−0.7	7256	−46	758	−49	95.2	0.9	−8.4	21.5
21	303.2	0.8	1.2	0.2	7263	−22	523	−22	95.5	0.2	−6.3	20.8
22	303.9	0.0	1.4	−1.4	7251	−74	985	−79	95.4	1.2	−10.8	21.7
23	304.5	0.0	1.5	−1.8	7279	−132	1661	−127	95.8	1.4	−17.7	22.1
24	305.2	−0.8	1.8	−3.4	7278	−208	2183	−204	96.0	2.2	−22.0	22.9
25	304.4	−0.1	1.5	−1.9	7262	−116	1527	−116	95.7	1.4	−16.3	22.1
26	302.0	1.1	4.5	−1.3	6937	−185	2708	−127	98.9	3.5	−26.4	24.7
27	306.1	−0.9	4.2	−5.2	7212	−653	5639	−509	100.2	5.9	−45.1	27.2
28	309.1	−4.4	4.7	−10.2	7231	−913	7368	−700	100.6	9.4	−51.6	29.9
29	306.1	−1.8	5.0	−6.3	7128	−674	5828	−498	99.8	7.8	−45.0	28.2
30	437.6	0.3	−1.9	−3.3	3878	−86	739	−128	263.9	−1.0	−49	62.0
31	501.8	0.3	−1.0	−1.6	3187	−85	−239	−67	360.2	−4.8	12.9	89.9
32	432.0	0.1	−0.5	−1.1	3782	−19	368	−27	262.0	−0.5	−25.2	57.7
33	464.6	0.1	−0.3	−0.8	3472	−34	−207	−30	303.3	−8.5	6.8	72.2
34	375.0	−3.2	−0.3	−5.1	4285	−102	300	−117	200.2	7.1	−9.6	46.2
35	390.0	2.3	−3.5	−6.4	4690	−155	1889	−421	199.3	2.5	−62.4	58.9
36	400.6	7.4	−6.4	−13.0	5109	−79	3689	−848	—	—	—	—
37	621.8	1.1	0.2	0.2	2126	−47	89	−49	—	—	—	—
38	655.3	−0.3	−0.8	−0.8	1904	−52	−112	−51	—	—	—	—
39	605.5	2.3	−1.5	−1.7	2323	−55	334	−81	—	—	—	—
40	669.5	1.4	−0.3	−0.5	1822	−11	−93	−5	—	—	—	—
41	542.2	11.6	−12.9	−12.8	3442	−15	2409	−493	—	—	—	—
42	666.2	3.5	−1.2	−1.7	1991	−133	−223	−90	—	—	—	—
43	609.5	2.4	−0.1	−1.8	2306	−119	−227	−95	—	—	—	—
44	440.0	0.8	−4.0	−8.8	4049	−145	1196	−328	257.6	−0.5	−68.3	71.0
45	390.0	2.3	−6.8	−11.9	4930	−139	2470	−696	191.4	−0.4	−70.6	66.1
46	689.2	−2.5	−7.6	−8.2	1757	−225	−290	−168	—	—	—	—
47	548.2	13.5	−21.5	−18.6	3568	−191	4696	−707	—	—	—	—

A: Error when using dilute-SRK method (calc-exp)
B: Error when using dilute-vdW method (calc-exp)
C: Error when using discrete-SRK method (calc-exp)

Mixtures 30–47 are binary *n*-alkane mixtures, with C_4H_{10}, C_5H_{12}, C_6H_{14}, C_9H_{20}, $C_{10}H_{22}$, $C_{13}H_{28}$, $C_{14}H_{30}$ as the solvents. In the case of four of these mixtures (30, 31, 32, 33), the mole fraction of the solvent was slightly less than 0.9, but the data were nevertheless included in order to test as broad a range of components as possible. Experimental T_c and P_c were available for all 47 mixtures, but v_c was reported for only 24 mixtures. The experimental values are given in Table 2, together with the absolute deviations between experimental values and the values calculated using three different methods. The methods tested include the dilute mixture-SRK method developed in this work, the dilute mixture-vdW approach of Gualtieri et al., and a discrete-SRK method based on the SRK equation coupled with the rigorous solution of the Gibbs criteria. The rigorous method was based on the algorithm of Michelsen and Heideman (1981). It should be added here that in the discrete-SRK method the Gibbs criteria are solved directly for T_c and v_c of the mixture. On the other hand, in the dilute-SRK method only the shifts in the (experimental) critical properties of the solvent are calculated using the equation of state. Thus, the dilute-SRK method is not a limiting case of the discrete-SRK method, since the discrete-SRK method converges to the T_c and P_c (but not v_c) of the solvent as the impurity concentration goes to zero, whereas the dilute-SRK approach converges to T_c, P_c, and v_c of the solvent. Binary interaction parameters k_{ij} for use with both the SRK methods were obtained from the work of Galicia-Luna and Perez (1987), who used the discrete-SRK approach to fit the critical loci of 32 binary systems. The parameters of Galicia-Luna and Perez are given in Table 3. Note that these parameters are not optimized for the dilute concentration range of the mixtures studied, but were obtained by a fit of T_c, P_c data over the whole concentration range of the binary mixtures studied. The k_{ij} were set equal to zero when no values were available or when the dilute-vdW method was used. The overall average absolute deviations between theory and experiment were 0.66, 0.78, and 1.07 K, for critical temperatures calculated using the dilute-SRK, dilute-vdW, and the discrete-SRK methods, respectively. For the critical pressure, the corresponding absolute average deviations were 3.76, 31.3, and 4.85 kPa, respectively; whereas for the critical volume, they were 2.92, 22.73, and 25.38 mL/mol, respectively.

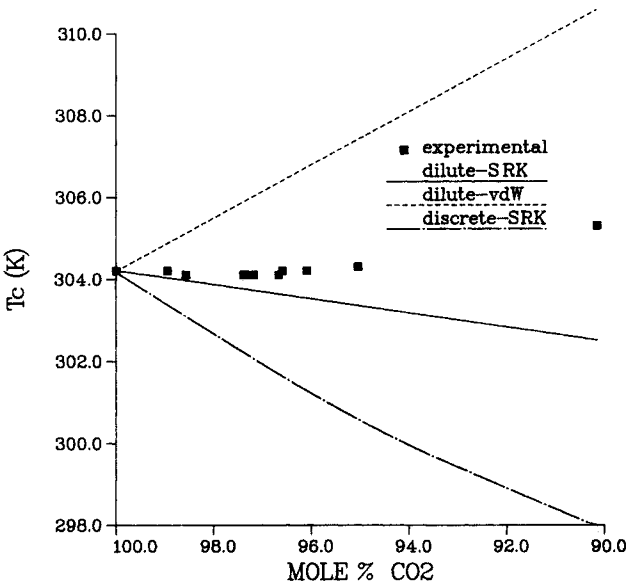

Figure 1. Experimental and predicted critical temperatures of CO_2-C_3H_8 mixtures.

Experimental data are those of Morrison and Kincaid

The T_c and P_c predictions of the dilute-SRK and discrete-SRK methods are comparable and probably within the accuracy of the experimental data. The dilute-vdW method of Gualtieri et al. gives surprisingly good predictions of T_c, but it is not as accurate in the case of P_c. The latter is not surprising, in view of the binary interaction parameters used with the two SRK methods. Finally, the v_c predictions are only acceptable in the case of the dilute-SRK method. As explained above, both the dilute-vdW and the dilute-SRK approaches calculate the shift in the critical volume of the solvent caused by the presence of the impurity. In the limit of zero impurity, they reduce to the experimental critical volume of the solvent. Thus the equation of state is only used to calculate the (small) shift in the critical properties. The dilute-vdW method gives poor predictions, partly due to the limitation of the vdW equation of state and partly to setting all k_{ij} to zero in the calculations. The dilute-SRK method, on the other hand, gives excellent predictions of v_c, even though the k_{ij} used in the calculations were not obtained specifically for the dilute concentration range. Finally, the discrete-SRK method also gives poor predictions of v_c, in spite of the use of k_{ij}. This is because conventional two-constant equation of state methods cannot accurately predict all three *PVT* properties, as is well known.Note that only T_c and P_c of the solvent are used (to obtain the equation of state constants) in the

Table 3. Binary Interaction Parameters of Galicia Luna and Perez (1987)

	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	N_2	CO_2
C_1	0.011	0.045	0.046	0.010	0.013	0.019	0.074	−0.055	0.0	*	*
C_2		−0.018	0.036	0.100	0.034	0.078	*	−0.044	0.0	0.018	0.0
C_3			0.068	0.021	0.019	0.038	0.051	*	0.0	−0.026	0.129
C_4				0.004	0.008	0.045	0.046	*	0.0	−0.027	0.150
C_5					*	0.016	0.029	0.007	0.025	*	0.090
C_6						−0.001	−0.001	0.0	0.026	0.012	*
C_7							−0.001	0.0	0.026	*	*
C_8								0.0	*	*	*
C_9									0.0	*	*
C_{10}										*	*
N_2											*

*Corresponding k_{ij} was not determined

Table 4. Composition of the Synthesized Mixtures

Mixture	Hexane	Heptane	Octane	Nonane	Decane
No. 1	97.82	0.55	0.55	0.54	0.55
No. 2	95.00	1.25	1.26	1.24	1.25
No. 3	90.47	2.39	2.40	2.37	2.39

discrete-SRK calculations, v_c of the solvent being fixed by the SRK critical compressibility of $1/3$. The largest errors in predictions of the two dilute-mixture methods generally occur when the components of the mixtures are very different (e.g., mixtures 4, 5). This is because of the curvature of the critical locus that is characteristic of such mixtures. Even for such mixtures, the dilute methods appear to work well over a smaller concentration range, say, less than 5% impurities.

The curvature of the critical locus is particularly important in the CO_2–C_3H_8 binary system, which was studied with great care by Morrison et al. (1984) (mixtures 8–17). Morrison et al. showed that the critical locus of this system exhibits a temperature minimum at approximately 97.3 mol % CO_2 (Figure 1). The new method predicts the correct trend in the critical locus when the amount of impurity is very small but, as expected, predicts the wrong trend when the slope of the experimental curve changes as the amount of impurity increases. This indicates that the new technique cannot predict correctly the properties of mixtures whose critical loci exhibit extrema in the dilute mixture range. Moreover, the error resulting from the poor CO_2–C_3H_8 prediction is propagated to all multicomponent mixtures containing these two substances (mixtures 20, 21, 22, 24, 25, 26, 28, 29). It should, however, be added that this type of behavior in the binary critical locus is not common.

Experimental Determination of Critical Properties of Dilute Mixtures

Since critical point data for dilute multicomponent mixtures are very scarce in the literature, three such mixtures were synthesized and their critical properties measured using a sealed ampoule method. Details of the experimental technique and apparatus have been described by Anselme and Teja (1988). Hexane was chosen as the solvent in the present work because it is thermally stable at its critical temperature and because it is a liquid at room temperature. The latter facilitates the loading of the sample in the experiments. Heptane, octane, nonane, and decane where chosen to constitute the impurity, because they too are liquids at room temperature and are all stable near the critical temperature of hexane. An approximately equimolar mixture of heptane, octane, nonane, and decane was prepared.

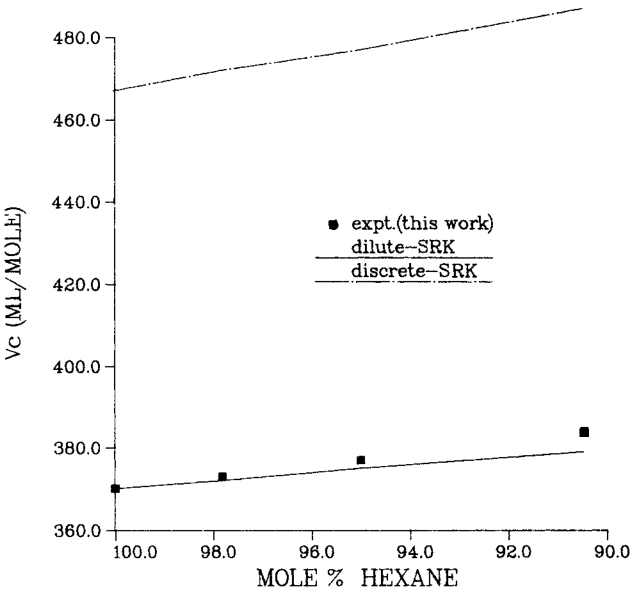

Figure 2. Experimental and predicted critical of $n\text{-C}_6\text{H}_{14}$ + $n\text{C}_7\text{H}_{16}$ + $n\text{C}_8\text{H}_{18}$ + $n\text{C}_9\text{H}_{20}$ + $n\text{C}_{10}\text{H}_{22}$ mixtures.

The composition of this mixture was determined by gravimetry as follows:

25.02% heptane
25.13% octane
24.83% nonane
25.02% decane

This mixture was then diluted with various quantities of hexane. Three dilute mixtures containing different amounts of an impurity of identical constitution were prepared in this manner. The purity of the alkanes used were: 99.5% for hexane, heptane, octane, and nonane, and 99.9% for decane. Heptane was supplied by Aldrich, octane by Fluka and the other alkanes were supplied by Wiley. The chemicals were used as received. The compositions of the three dilute mixtures studied are reported in Table 4. The critical temperatures, densities, and corresponding critical molar volumes of the mixtures and of pure hexane obtained in this study are reported in Table 5. The critical properties of hexane agree with values found in the literature. No literature values have been reported for the three mixtures studied in this work.

In Table 5, our experimental results are compared with the predictions of the dilute mixture-SRK approach and the discrete-SRK approach. The dilute-SRK method accurately predicts all critical properties (T_c, P_c, v_c) of the mixtures studied. Figures 2

Table 5. Measured and Predicted Critical Temperature and Volume for the Synthesized Mixtures

		T_c			v_c	
Fluid	$T_{c\,\text{exp}}$, K	A	B	$v_{c\,\text{exp}}$ mL/mol	A	B
Pure Hexane	507.3 ± 0.3	507.3	507.3	370 ± 7	370	467
Mixture No. 1	509.9 ± 0.3	510.0	509.4	373 ± 7	372	472
Mixture No. 2	512.8 ± 0.3	513.4	511.8	377 ± 7	375	477
Mixture No. 3	517.4 ± 0.3	518.9	515.7	384 ± 7	379	487

A: Calculated with the dilute-SRK method
B: Calculated using the discrete-SRK method

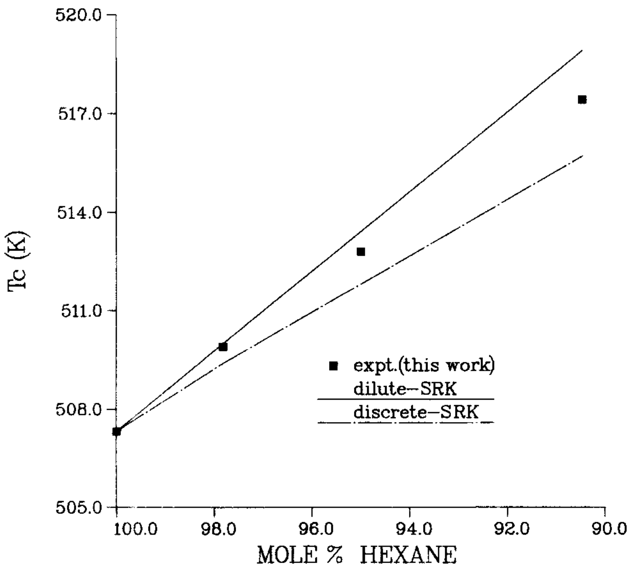

Figure 3. Experimental and predicted critical temperatures of n-C_6H_{14} + nC_7H_{16} + nC_8H_{18} + nC_9H_{20} + $nC_{10}H_{22}$ mixtures.

and 3 show that the predicted critical locus is linear with the amount of impurity for these multicomponent mixtures. The dilute mixture approach is therefore only limited by the curvature of the critical locus of the mixture. In the case of dilute mixtures of alkanes, the curvature of the critical locus is not very pronounced and this results in good predictions even when the concentration of the impurity approaches 10 mole %.

Conclusions

The dilute mixture approach of Gualtieri et al. (1982) was combined with the Soave-Redlich-Kwong equation of state to obtain expressions for the critical volume and temperature of multicomponent mixtures. When combined with a pressure-explicit equation of state, these equations allow the computation of T_c, P_c, and v_c of a dilute mixture from a knowledge of its composition and the critical properties of the components. No iterations are required in the calculations. The dilute-SRK method was tested using 47 dilute mixtures from the literature and three synthetic mixtures whose critical properties were measured in this work. Predictions using the method were generally excellent for all three critical properties. Only mixtures in which the critical locus exhibited an appreciable change in curvature in the dilute region (such as CO_2–C_3H_8) were not well predicted. Even for such mixtures, however, the method gave good predictions when the mole fraction of the impurities was less than about 5 mol %. Finally, it is believed that the method will also work well for mixtures containing nonhydrocarbon components, since only the shifts in the critical properties of the solvent are calculated in this approach.

Notation

A = Helmholtz energy
a, b = constants in SRK equation
D = mole fraction distribution function
D, D^* = determinants
F = mole fraction density function
g, h = generic quantities
k = Boltzmann constant
k_{ij} = binary interaction parameter
M = constant in SRK equation
P = pressure
R = gas constant
T = temperature
V = volume
$\tilde{v}$ = volume per molecule
x = mole fraction

Greek letters

α = vapor pressure function in SRK equation
$\beta = 1/kT$
δ = Kroenecker delta
ϵ = mole fraction of impurities
η = number density of impurities
Λ = de Broglie wavelength
ω = acentric factor
π = nonideal mixing term
ρ = number density

Subscripts

c = critical
i, j = component i, j
r = reduced value

Other

$\langle\ \rangle$ = average value

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Appendix A: Effect of a Multicomponent Impurity on the Properties of a Dilute Mixture

The dilute mixture approach of Gualtieri et al. (1982) is outlined in this section. More details can be found in the original reference. For a c component mixture, the critical point conditions can be written:

$$D = \det \left| \frac{\partial^2 \tilde{A}}{\partial \rho_i \partial \rho_j} \right| = 0 \text{ for } i, j = 1, \ldots, c \qquad \text{(A1)}$$

$$D' = \det \left| (1 - \delta_{kj}) \frac{\partial^2 \tilde{A}}{\partial \rho_i \partial \rho_j} + \delta_{kj} \frac{\partial D}{\partial \rho_i} \right| = 0 \text{ for } i, j = 1, \ldots, c \qquad \text{(A2)}$$

where $\tilde{A}$ is the Helmholtz energy density function given by:

$$\beta \tilde{A}(T, \{\rho_i\}) = \sum_i \rho_i \ln \rho_i - \rho + \sum_i \rho_i \ln \Lambda_i^3 + \pi \qquad \text{(A3)}$$

If we define

$$\pi_{ij} = \frac{\partial^2 \pi}{\partial \rho_i \partial \rho_j} \qquad \text{(A4)}$$

then the first condition for criticality $D = 0$ can be expressed as

$$D = \det \left| \frac{\delta_{ij}}{\rho_i} + \pi_{ij} \right| \qquad \text{(A5)}$$

When this determinant is expanded using an identity given by Muir (1960), it becomes:

$$D = \left(\prod_i \frac{1}{\rho_i} \right) \left[1 + \rho_1 \pi_{11} + \sum_{j>1} \rho_j \pi_{jj} + \rho_1 \sum_{j>1} \rho_j \begin{vmatrix} \pi_{11} & \pi_{1j} \\ \pi_{j1} & \pi_{jj} \end{vmatrix} + O\left(\rho_1 \sum_{k>j>1} \rho_j \rho_k \right) \right] \qquad \text{(A6)}$$

so that the critical condition $D = 0$ becomes:

$$D^* = D \Big/ \prod_i (1/\rho_i) = 1 + \rho_1 \pi_{11} + \eta \{ \langle \pi_{jj} + \rho_1 [\pi_{11} \pi_{jj} - \pi_{1j}^2] \rangle \} + o(\eta^2) + \cdots = 0 \qquad \text{(A7)}$$

The effect of adding a multicomponent impurity to pure 1 can be found by expanding D^* around the critical point of pure component 1 (denoted below by $c1$):

$$D^*(\rho_l, \eta, T) = 0 = D^*(\rho_{c11}, 0, T_{c1}) + \left(\frac{dD^*}{d\eta} \right)_{c1} \eta + \cdots \qquad \text{(A8)}$$

where second- and higher order terms have been neglected and the expansion is carried out along the critical locus. The term $D^*(\rho_{c11}, 0, T_{c1})$ is equal to zero because of Eq. A1 applied to pure component 1. The first-order term is then given by:

$$\left. \frac{dD^*}{d\eta} \right|_{c1} = \left. \frac{\partial(\rho_1 \pi_{11})}{\partial \rho_1} \right|_{c1} \left. \frac{d\rho_1}{d\eta} \right|_{c1} + \left. \frac{\partial(\rho_1 \pi_{11})}{\partial \eta} \right|_{c1} + \left. \frac{\partial(\rho_1 \pi_{11})}{\partial T} \right|_{c1} \left. \frac{dT_c}{d\eta} \right|_{c1} + \{ \langle \pi_{jj}(1 + \rho_1 \pi_{11}) - \rho_{11} \pi_{1j}^2 \rangle \} \qquad \text{(A9)}$$

Also

$$\left. \frac{\partial(\rho_1 \pi_{11})}{\partial \rho_1} \right|_{c1} = 0 \qquad \text{(A10)}$$

since this is simply Eq. A2 for pure component 1. Also note that the term $(1 + \rho_1 \pi_{11})$ in Eq. A9 equals zero because of Eq. A1 for pure 1.

When the first-order term is set equal to zero, the effect of the impurity on the critical termperature can be obtained. It is given by:

$$\left. \frac{dT_c}{d\eta} \right|_{c1} = \left. \frac{\langle \rho_1 (\pi_{1j})^2 \rangle - \dfrac{\partial(\rho_1 \pi_{11})}{\partial \eta}}{\dfrac{\partial(\rho_1 \pi_{11})}{\partial T}} \right|_{c1} \qquad \text{(A11)}$$

Gualtieri et al. manipulated the second critical point condition, $D' = 0$, in a similar fashion (Muir identity and first-order Taylor series expansion) to obtain an expression for the effect of a multicomponent impurity on the critical number density given by:

$$\left. \frac{d\rho_1}{d\eta} \right|_{c1} = \left\{ 3 \left\langle \rho_1 \pi_{1j} \frac{\partial \pi_{1j}}{\partial \rho_1} \right\rangle - \langle \rho_1 \pi_{1j}^3 \rangle - \rho_1 \left. \frac{\partial^2 \pi_{11}}{\partial \rho_1 \partial T} \frac{dT_c}{d\eta} \right|_{c1} - \rho_1 \left. \frac{\partial^2 \pi_{11}}{\partial \rho_1 \partial \eta} \right|_{c1} \right\} \times \left\{ \frac{\partial^2 [\rho_1 \pi_{11}]}{\partial \rho_1^2} \right\}^{-1} \qquad \text{(A12)}$$

Note that the last expression includes the term $dT_c/d\eta|_{c1}$, which is the corresponding temperature shift and that Eqs. A11 and A12 are valid for any equation of state. The equation of state contribution appears in the π terms, which increase rapidly in number and complexity as the equation of state becomes more complex.

Appendix B: The Dilute Mixture-SRK Approach

In this section, the dilute mixture approach of Gualtieri et al. (1982) is combined with the SRK equation of state. To apply Eqs. A11 and A12 to SRK fluids, we must first derive an equation for π_{ij}. The three terms in the equation for $dT_c/d\eta|_{c1}$, Eq. A11, can then be obtained, leading to an equation for T_c of dilute mixtures. Finally, each of the five terms in Eq. A12 for $d\rho_1/d\eta|_{c1}$ are obtained, leading to an equation for v_c of the mixture.

Equation 9 gives the expression for π of an SRK fluid. This expression can be extended to mixtures as follows:

$$\pi = -\sum_{i=1}^{c} \rho_i \ln (1 - \rho_i b_i) - \beta \frac{\sum_i \sum_j \rho_i \rho_j a_{ij}}{\sum_i \rho_i b_i} \ln (1 + \rho_i b_i) \qquad \text{(B1)}$$

Equation B1 can be differentiated twice to give:

$$\pi_{ij} = \frac{b_i + b_j}{1 - b} + \frac{\rho b_i b_j}{(1 - b)^2} + 2\beta \frac{\ln(1 + b)}{b^3}\left[- b^2 a_{ij} + b b_j \sum_k \rho_k a_{ik} + b b_i \sum_k \rho_k a_{kj} - b_i b_j a\right] + \beta\left[\frac{- 2b_i \sum_k \rho_k a_{kj}}{b(1 + b)} + \frac{a b_i b_j (3b + 2)}{b^2(1 + b)^2} - \frac{2b_j \sum_k \rho_k a_{ik}}{b(1 + b)}\right] \quad \text{(B2)}$$

For the pure solvent,

$$a_{11} = 0.42748 \frac{k^2 (T_{c1})^2}{P_{c1}} \alpha_1(T) \quad \text{(B3)}$$

$$b_1 = 0.08664 \frac{k T_{c1}}{P_{c1}} \quad \text{(B4)}$$

where

$$\sqrt{\alpha_1(T)} = 1 + M_1 \left(1 - \sqrt{\frac{T}{T_{c1}}}\right) \quad \text{(B5)}$$

Equations B3 and B4 can be combined to give:

$$\beta = 4.93398 \frac{b_1}{a_{11} \alpha(T)} \quad \text{(B6)}$$

so that at T_{c1}

$$\beta = 4.93398 \frac{b_1}{a_{11}} \quad \text{(B7)}$$

This can be used in the expression of π_{ij} to obtain

$$\pi_{1j}|_{c1}\, b_1 \left[1.35121 + 2.63364 \frac{b_j}{b_1} - 7.83221 \frac{a_{1j}}{a_{11}}\right] \quad \text{(B8)}$$

Critical temperature of a dilute SRK mixture

The three terms needed to express T_c of a dilute mixture are $\langle \rho_1 \pi_{1j}^2 \rangle |_{c1}$, $\partial \rho_1 \pi_{11} / \partial \eta |_{c1}$ and $d\rho_1 \pi_{11}/dT |_{c1}$. Applying the averaging process of Eq. B2 to π_{1j}

$$\langle \rho_1 \pi_{1j}^2 \rangle |_{c1} = b_1 \left\{0.47455 + 1.80283 \left\langle \left(\frac{b_j}{b_1}\right)^2 \right\rangle + 15.94441 \left\langle \left(\frac{a_{1j}}{a_{11}}\right)^2 \right\rangle + 1.84990 \left\langle \frac{b_j}{b_1} \right\rangle - 5.50142 \left\langle \frac{a_{1j}}{a_{11}} \right\rangle - 10.72287 \left\langle \frac{a_{1j} b_j}{a_{11} b_1} \right\rangle \right\} \quad \text{(B9)}$$

Then, since

$$\eta = \rho_2 + \rho_3 + \cdots + \rho_c \quad \text{(B10)}$$

a first-order Taylor series expansion in η can be carried out for $\pi_{11}\rho_1$ as follows:

$$\rho_1 \pi_{11} = \frac{2b_1\rho_1}{1 - b_1\rho_1} + \left(\frac{b_1\rho_1}{1 - b_1\rho_1}\right)^2 + \beta \rho_1 a_{11} \left[\frac{-4}{1 + b_1\rho_1} + \frac{3b_1\rho_1 + 2}{(1 + b_1\rho_1)^2}\right] + \eta b_1 \left\{0.47455 + 1.75699 \left\langle \frac{b_k}{b_1} \right\rangle + 1.61578 \left\langle \frac{a_{1k}}{a_{11}} \right\rangle \right\} + O(\eta^2) \quad \text{(B11)}$$

This expression can be differentiated with respect to η to obtain:

$$\left.\frac{\partial \rho_1 \pi_{11}}{\partial \eta}\right|_{c1} = b_1 \left\{0.47455 + 1.75699 \left\langle \frac{b_k}{b_1} \right\rangle + 1.61578 \left\langle \frac{a_{1k}}{a_{11}} \right\rangle \right\} \quad \text{(B12)}$$

Finally, to derive $d\rho_1\pi_{11}/dT |_{c1}$, we start from

$$\frac{d\beta}{dT} = - \frac{1}{kT^2} = - \frac{1}{T}\beta \quad \text{(B13)}$$

Substituting Eq. B6, we obtain:

$$\left.\frac{d\beta}{dT}\right|_{c1} = - \frac{1}{T_{c1}} \left(\frac{b_1}{a_{11}} 4.93398\right) \quad \text{(B14)}$$

Also, by differentiating Eq. B7, we have

$$\left.\frac{d\alpha_1}{dT}\right|_{c1} = - \frac{M_1}{T_{c1}} \quad \text{(B15)}$$

Therefore, differentiation of Eq. B3 leads to

$$\left.\frac{da_{11}}{dT}\right|_{c1} = a_{11}|_{c1} \left.\frac{d\alpha}{dT}\right|_{c1} = - a_{11}|_{c1} \frac{M}{T_{c1}} \quad \text{(B16)}$$

Hence, from Eq. B11

$$\rho_1 \pi_{11}|_{c1} = \frac{2b_1\rho_1}{1 - b_1\rho_1} + \left(\frac{b_1\rho_1}{1 - b_1\rho_1}\right)^2 + \beta \rho_1 a_{11} \left[\frac{-4}{1 + b_1\rho_1} + \frac{3b_1\rho_1 + 2}{(1 + b_1\rho_1)^2}\right] \quad \text{(B17)}$$

which can be differentiated to give:

$$\left.\frac{d\rho_1 \pi_{11}}{dT}\right|_{c1} = 1.82576 \frac{M + 1}{T_{c1}} \quad \text{(B18)}$$

The shift of the critical temperature can now be obtained as follows:

$$\left.\frac{dT_c}{d\eta}\right|_{c1} = \frac{T_{c1}}{\rho_{c1}(1 + M_1)}\left\{0.25666\left\langle\left(\frac{b_j}{b_1}\right)^2\right\rangle + 2.26989\left\langle\left(\frac{a_{1j}}{a_{11}}\right)^2\right\rangle - 1.52654\left\langle\frac{a_{1j}b_j}{a_{11}b_1}\right\rangle + 0.01323\left\langle\frac{b_j}{b_1}\right\rangle - 1.01322\left\langle\frac{a_{1j}}{a_{11}}\right\rangle\right\} \quad \text{(B19)}$$

This critical temperature shift can be expressed in terms of a more familiar set of variables since

$$\frac{dT_c}{d\epsilon} = \frac{dT_c}{d\eta}\frac{d\eta}{d\epsilon} = \frac{dT_c}{d\eta}\rho_{c1} \quad \text{(B20)}$$

Therefore, for a dilute mixture containing an impurity of mole fraction ϵ, the critical temperature is given by:

$$T_c = T_{c1}\left\{1 + \frac{\epsilon}{1 + M}\left[0.25666 - \left\langle\left(\frac{b_j}{b_1}\right)^2\right\rangle + 2.26989\left\langle\left(\frac{a_{1j}}{a_{11}}\right)^2\right\rangle - 1.52654\left\langle\frac{a_{1j}b_j}{a_{11}b_1}\right\rangle + 0.01323\left\langle\frac{b_j}{b_1}\right\rangle - 1.01322\left\langle\frac{a_{1j}}{a_{11}}\right\rangle\right]\right\} \quad \text{(B21)}$$

Critical number density of a dilute SRK mixture

The derivations of the five terms needed to compute the number density shift for a dilute mixture, Eq. A12 are analogous to those for the critical temperature shift. For the sake of brevity, only the final expressions are shown below.

$$\left\langle\rho_1\pi_{1j}\frac{\partial\pi_{1j}}{\partial\rho_1}\right\rangle = b_1^2\left\{0.64123 + 3.62388\left\langle\frac{b_j}{b_1}\right\rangle - 1.53352\left\langle\frac{a_{1j}}{a_{11}}\right\rangle + 4.62730\left\langle\left(\frac{b_j}{b_1}\right)^2\right\rangle - 12.65512\left\langle\left(\frac{a_{1j}}{a_{11}}\right)^2\right\rangle - 9.50570\left\langle\frac{a_{1j}b_j}{a_{11}b_1}\right\rangle\right\} \quad \text{(B22)}$$

$$\left\langle\rho_1\pi_{1j}^3\right) = b_1^2\left\{0.64124 + 4.74807\left\langle\left(\frac{b_j}{b_1}\right)^3\right\rangle - 124.88030\left\langle\left(\frac{a_{1j}}{a_{11}}\right)^3\right\rangle + 3.74951\left\langle\frac{b_j}{b_1}\right\rangle + 7.30813\left\langle\left(\frac{b_j}{b_1}\right)^2\right\rangle - 11.15065\left\langle\frac{a_{1j}}{a_{11}}\right\rangle + 64.63349\left\langle\left(\frac{a_{1j}}{a_{11}}\right)^2\right\rangle + 125.97651\left\langle\left(\frac{a_{1j}}{a_{11}}\right)^2\frac{b_j}{b_1}\right\rangle - 42.36078\left\langle\left(\frac{b_j}{b_1}\right)^2\frac{a_{1j}}{a_{11}}\right\rangle - 43.46723\left\langle\frac{a_{1j}b_j}{a_{11}b_1}\right\rangle\right\} \quad \text{(B23)}$$

$$\left.\rho_1\frac{\partial^2\pi_{11}}{\partial T\partial\rho_1}\frac{\partial T_c}{\partial\eta}\right|_{c1} = b_2^1\left\{-2.06411\left\langle\left(\frac{b_j}{b_1}\right)^2\right\rangle - 18.25493\left\langle\left(\frac{a_{1j}}{a_{11}}\right)^2\right\rangle + 12.27676\left\langle\frac{a_{1j}b_j}{a_{11}b_1}\right\rangle - 0.10640\left\langle\frac{b_j}{b_1}\right\rangle + 8.14853\left\langle\frac{a_{1j}}{a_{11}}\right\rangle\right\} \quad \text{(B24)}$$

$$\left.\rho_1\frac{\partial^2\pi_{11}}{\partial\rho_1\partial\eta}\right|_{c1} = b_1^2\left\{1.28243 + 3.42729\left\langle\frac{b_j}{b_1}\right\rangle - 2.56489\left\langle\frac{a_{1j}}{a_{11}}\right\rangle\right\} \quad \text{(B25)}$$

and finally

$$\frac{\partial^2(\rho_1\pi_{11})}{\partial\rho_1^2} = 31.74865b_1^2 \quad \text{(B26)}$$

These expressions are used in Eq. A12 and lead to

$$\frac{d\rho_c}{d\eta} = -0.14952\left\langle\left(\frac{b_j}{b_1}\right)^3\right\rangle + 3.93341\left\langle\left(\frac{a_{1j}}{a_{11}}\right)^3\right\rangle + 0.11973\left\langle\frac{b_j}{b_1}\right\rangle + 0.27207\left\langle\left(\frac{b_j}{b_1}\right)^2\right\rangle + 0.03044\left\langle\frac{a_{1j}}{a_{11}}\right\rangle - 2.65661\left\langle\left(\frac{a_{1j}}{a_{11}}\right)^2\right\rangle - 3.96793\left\langle\left(\frac{a_{1j}}{a_{11}}\right)^2\frac{b_j}{b_1}\right\rangle + 1.33421\left\langle\left(\frac{b_j}{b_1}\right)^2\frac{a_{1j}}{a_{11}}\right\rangle + 0.08420\left\langle\frac{a_{1j}b_j}{a_{11}b_1}\right\rangle \quad \text{(B27)}$$

This can be expressed in more familiar terms. For a dilute mixture containing an impurity of mole fraction ϵ, the critical number density is given by

$$\rho_c = \rho_{c1} + \epsilon\frac{d\rho_c}{d\epsilon} \quad \text{(B28)}$$

where

$$\frac{d\rho_c}{d\epsilon} = \frac{d\rho_c}{d\eta}\frac{d\eta}{d\epsilon} = \frac{d\rho_c}{d\eta}\frac{d[(1 - x_1)\rho_c]}{d\epsilon} = \frac{d\rho_c}{d\eta}\rho_{c1} \quad \text{(B29)}$$

Therefore,

$$\frac{1}{v_c} = \frac{1}{v_{c1}}\left\{1 + \epsilon\left[1 - 0.14952\left\langle\left(\frac{b_j}{b_1}\right)^3\right\rangle + 3.93341\left\langle\left(\frac{a_{1j}}{a_{11}}\right)^3\right\rangle + 0.11973\left\langle\frac{b_j}{b_1}\right\rangle + 0.27207\left\langle\left(\frac{b_j}{b_1}\right)^2\right\rangle + 0.03044\left\langle\frac{a_{1j}}{a_{11}}\right\rangle - 2.65661\left\langle\left(\frac{a_{1j}}{a_{11}}\right)^2\right\rangle - 3.96793\left\langle\left(\frac{a_{1j}}{a_{11}}\right)^2\frac{b_j}{b_1}\right\rangle + 1.33421\left\langle\left(\frac{b_j}{b_1}\right)^2\frac{a_{1j}}{a_{11}}\right\rangle + 0.08420\left\langle\frac{a_{1j}b_j}{a_{11}b_1}\right\rangle\right]\right\} \quad \text{(B30)}$$

where v_c and v_{c1} are the molar critical volumes of the dilute mixture and of the solvent, respectively.

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