On Density Microheterogeneities in Dilute Supercritical Solutions

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The dilute supercritical mixtures were examined in the framework of the Kirkwood−Buff theory of solutions. Various expressions were employed for the excess number of aggregated molecules of solvent around individual solute molecules to conclude that at infinite dilution the above mentioned excess is zero. This suggested that the density enhancement observed when small amounts of a solute were added to a solvent near the critical point of the latter may not be caused by the aggregation of the solvent molecules around individual solute molecules as usually considered. Further, comparing experimental results, it was shown that the density enhancement caused by the near critical fluctuations in a pure solvent are almost the same, in a wide range of pressures, as those in dilute supercritical mixtures near the critical point of the solvent.

Introduction

During the last three decades the use of supercritical fluids (SCF) has dramatically increased because of their applications to extraction, chromatography, and as media for chemical reactions.[1−6] The most interesting applications of SCFs occur in the following ranges of pressure and temperature:[3,7] $1 < P/P_c < 2$ and $1 < T/T_c < 1.1$, where P and T are the pressure and temperature and P_c and T_c are their critical values. Under these conditions, SCFs (such as CO_2, C_2H_4, CHF_3, etc.) are typically less dense than the liquids by factors of $1.5−3$.[3] Since these intervals of pressure and temperature are close to the critical point, the compressibility of SCFs is high (at the critical point it becomes infinite).[3] Experiment also shows that for a SCF near the critical point of the solvent, the partial molar volume of the solute at infinite dilution becomes usually negative and large in magnitude;[8] this behavior is not, however, typical for a nonelectrolyte solution far from the critical region. Because of the high compressibility of fluids near the critical point, their density and dissolving power can be tuned through small changes in pressure.[3] The high dissolving power of the SCF leads to unusually high solubilities of solids in the SCFs. Compared to that of a dilute gas, the solubility enhancement can be as large as 10^{12} (ref 7). A large body of research was aimed at understanding the unusual properties of SCFs at the molecular level, and comprehensive reviews were recently published.[3−6] One of the key problems regarding intermolecular interactions in a dilute solution involving a SCF as solvent (such a solution will be called SCR mixture) is the so-called local density enhancement induced by the addition of a small amount of solute into the solvent near the critical point of the latter.[3−6] There have been many attempts to explain this effect.[3−6] The large negative infinite dilution partial molar volume of the solute suggested that the aggregation of solvent molecules around individual molecules of solute is responsible for the enhancement.[7,9] This explanation was challenged with the argument that because of the high compressibility near the critical point of the solvent, the addition of a small amount of solute causes a large change in volume, which is responsible for the negative partial molar volume of the solute at high dilution.[10]

In this paper, some recent experimental results regarding the density fluctuations in pure SCF[11−15] are used to show that the local density enhancement in dilute SCR mixtures is mainly due to the near critical fluctuations in the solvent and an explanation is suggested for the negative partial molar volume of the solute. This conclusion was also strengthened by a discussion, presented in the following section, based on the Kirkwood−Buff (KB) theory of solution.[16] First, the problem will be examined in the framework of the Kirkwood−Buff theory of solution. Second, using experimental results about the near critical fluctuations in pure SCF, it will be shown that the density enhancement in dilute SCR mixtures is mainly caused by the near critical density fluctuations in pure SCF.

Theory and Formulas

1. The Kirkwood−Buff Integrals. The Kirkwood−Buff theory of solution relates the so-called Kirkwood−Buff integral (defined below) to macroscopic quantities, such as the compressibility, partial molar volumes, and the composition derivative of the activity coefficient.

The Kirkwood−Buff integrals (KBIs) are given by the expressions

$$G_{ij} = \int_0^\infty (g_{ij} - 1)\, 4\pi r^2\, dr \quad i,j = 1,2 \qquad (1)$$

where g_{ij} is the radial distribution function between species i and j and r is the distance between the centers of molecules i and j. The KBIs in binary mixtures can be calculated using the expressions:[17]

$$G_{12} = G_{21} = RTk_T - \frac{V_1 V_2}{VD} \qquad (2)$$

and

$$G_{ii} = G_{12} + \frac{1}{x_i}\left(\frac{V_j}{D} - V\right) \quad i \neq j \qquad (3)$$

where

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$$D = \left(\frac{\partial \ln \gamma_i}{\partial x_i}\right)_{P,T} x_i + 1 \qquad (4)$$

In eqs 2−4, T is the absolute temperature, P is the pressure, k_T is the isothermal compressibility, V_i is the partial molar volume of component i, x_i is the molar fraction of component i, V is the molar volume of the mixture, R is the universal gas constant, and γ_i is the activity coefficient of component i. In the following considerations, expressions for the KBIs at the extreme concentrations ($x_1 \to 0$ and $x_2 \to 0$), as well as expressions for KBIs for ideal systems, will be needed. All these expressions are provided in Appendix 1.

2. Excess Number of Molecules Near a Central One. Ben-Naim[20] suggested to calculate the excess (the BN excess) number of j molecules around a central molecule i as

$$\Delta n_{ji} = c_j G_{ji} \qquad (5)$$

and Debenedetti[21] considered this excess as a measure of aggregation. Matteoli and Lepori[18,22] noted that the $c_j G_{ji}$ are nonzero for ideal mixtures, which should be considered non-aggregated and suggested that the effects due to aggregation are better reflected in excesses (the ML excesses) defined as

$$\Delta n'_{ji} = c_j (G_{ji} - G^{id}_{ji}) \qquad (6)$$

where G^{id}_{ji} are the KBs integrals for ideal systems (see Appendix 1 for the expressions of G^{id}_{ij}). In other words, the ideal mixture was considered as a reference system.

However, $\Delta n'_{ii}$ and $\Delta n'_{ji}$ are not independent quantities, because the volume occupied by the excess i molecules aggregated around an i molecule should be equal to the volume left free by the j molecules around the same i molecule.[22] This leads to the following relation:

$$V_j \Delta n'_{ji} = -V_i \Delta n'_{ii} \qquad (7)$$

It was, however, noted that if the number of molecules clustered around a central one is calculated as $c_j (G_{ji} - G^{id}_{ji})$, eq 7 can not be satisfied identically.[19,23] Equation 7 can be satisfied only if G^{id}_{ij} is replaced by another reference state G^V_{ij}, which for ideal mixtures reduces to G^{id}_{ij} (see Appendix 1 for the expressions of G^V_{ij}). Hence, the excess (the SR excess) which satisfies eq 7 is given by

$$\Delta n''_{ji} = c_j (G_{ji} - G^V_{ji}) \qquad (8)$$

In the next section, the density enhancement provided by the BN, ML, and SR excesses will be examined in more detail at low dilution.

3. Density Enhancement in SCR Mixtures through the KB Theory of Solutions. Usually, the local densities in SCR mixtures were determined in very dilute solutions (molar fractions of solute between 10^{-4} and 10^{-8}), in order to avoid the experimental and computational complications caused by solute−solute interactions.[24,25] The experimental data are provided in refs 24 and 25 as either the density augmentation $\Delta \rho^{(2)}$ around a solute molecule[25] (the solvent is denoted as component 1 and the solute as component 2), or the local density $\rho^{(2)}$ around a solute molecule.[25]

The density augmentation is provided by the expression

$$\Delta \rho^{(2)} = \frac{\Delta n_{12} + \Delta n_{22}}{V^{(2)}_{cor}} \qquad (9)$$

for the BN excesses and similar expressions in which Δn_{ji} are replaced by $\Delta n'_{ji}$ and $\Delta n''_{ji}$ for the ML and SR excesses, respectively. In eq 9, $V^{(2)}_{cor}$ is the correlation volume, i.e., the volume around a solute molecule where the density differs from that in the bulk. Usually, the density augmentation $\Delta \rho^{(2)}$ or the local density $\rho^{(2)}$ is compared with $\rho^{(2)}_{bulk}$, the bulk density around a solute molecule (which can be taken as the density of the pure SCF).

Now expressions for $\Delta \rho^{(2)}$ will be derived when the molar fraction of the solute is very small ($x_2 \approx 10^{-4}-10^{-8}$) for the three expressions written above for the aggregated excesses. For small x_2 one can suppose that $V_1 = V^0_1$, $V_2 = V^\infty_2$, $k_T = k^0_{T,1}$, where the superscripts (0) and (∞) refer to the pure component and infinite dilution, respectively, and $D = (\partial \ln \gamma_2/\partial x_2)_{P,T} x_2 + 1 \equiv K_2 x_2 + 1$, where K_2 is independent of composition.[26]

For the BN excess one thus obtains

$$\Delta n_{12} = c_1 G_{12} = c_1 (RTk^0_{T,1} - V^\infty_2) \qquad (10a)$$

$$\Delta n_{22} = c_2 G_{22} = c_2 (RTk^0_{T,1} + V^0_1 - 2V^\infty_2 - K_2 V^0_1) \qquad (10b)$$

which for infinite solute dilution become

$$\lim_{x_2 \to 0} \Delta n_{12} = \lim_{x_2 \to 0} c_1 G_{12} = c^0_1 (RTk^0_{T,1} - V^\infty_2) \qquad (10c)$$

and

$$\lim_{x_2 \to 0} \Delta n_{22} = \lim_{x_2 \to 0} c_2 G_{22} = 0 \qquad (10d)$$

The ML excesses are given by

$$\Delta n'_{12} = c_1 (G_{12} - G^{id}_{12}) = c_1 (V^0_2 - V^\infty_2) \qquad (11a)$$

$$\Delta n'_{22} = c_2 (G_{22} - G^{id}_{22}) = c_2 (2V^0_2 - 2V^\infty_2 - K_2 V^0_1) \qquad (11b)$$

At infinite dilution they become

$$\lim_{x_2 \to 0} \Delta n'_{12} = \lim_{x_2 \to 0} c_1 (G_{12} - G^{id}_{12}) = c^0_1 (V^0_2 - V^\infty_2) \qquad (11c)$$

$$\lim_{x_2 \to 0} \Delta n'_{22} = \lim_{x_2 \to 0} c_2 (G_{22} - G^{id}_{22}) = 0 \qquad (11d)$$

The SR excesses have the form

$$\Delta n''_{12} = c_1 (G_{12} - G^V_{12}) = c_1 V^\infty_2 K_2 x_2 \qquad (12a)$$

$$\Delta n''_{22} = c_2 (G_{22} - G^V_{22}) = -c_2 V^0_1 K_2 \qquad (12b)$$

and for infinite solute dilution

$$\lim_{x_2 \to 0} \Delta n''_{12} = \lim_{x_2 \to 0} c_1 (G_{12} - G^V_{12}) = 0 \qquad (12c)$$

$$\lim_{x_2 \to 0} \Delta n''_{22} = \lim_{x_2 \to 0} c_2 (G_{22} - G^V_{22}) = 0 \qquad (12d)$$

The local density enhancement for the BN excesses (eqs 10a and 10b) is given by

$$\Delta \rho^{(2)} = \frac{c_1 (RTk^0_{T,1} - V^\infty_2) + c_2 (RTk^0_{T,1} + V^0_1 - 2V^\infty_2 - K_2 V^0_1)}{V^{(2)}_{cor}} \qquad (13)$$

for the ML excesses (eqs 11a−11b) by

$$\Delta\rho^{(2)} = \frac{c_1(V_2^0 - V_2^\infty) + c_2(2V_2^0 - 2V_2^\infty - K_2V_1^0)}{V_{cor}^{(2)}} \quad (14)$$

and for the SR excesses (eqs 12a and 12b) by

$$\Delta\rho^{(2)} = \frac{c_1V_2^\infty K_2x_2 - c_2V_1^0K_2}{V_{cor}^{(2)}} \quad (15)$$

The above three equations (eqs 13−15) will be further used to evaluate the correlation volume.

Calculations

1. Source of Data. There are only a few local density data, and partial molar volumes of solutes at infinite dilution are scarce as well. Only two systems could be identified for which data for the calculation of the correlation volume are available: CO_2 + naphthalene and CO_2 + pyrene. The augmented local density data in these systems were taken from ref 24 and the partial molar volume of the solute at infinite dilution in CO_2 + naphthalene system from ref 8. Because the partial molar volume of the solute at infinite dilution for the CO_2 + pyrene system was not available, it was taken equal to that for the CO_2 + phenanthrene.[27] The density and compressibility of the pure SCR CO_2 were taken from refs 1 and 24, respectively, and the solubilities of naphthalene and pyrene in SCR CO_2 from refs 28 and 29, respectively.

2. Calculation of K_2. K_2 is defined as

$$K_2 = \left(\frac{\partial \ln \gamma_2}{\partial x_2}\right)_{P,T,x_2\to 0} \quad (16)$$

and was calculated through the fugacity coefficient of solute $\hat{\phi}_2$, which in the dilute region is given by[26]

$$\ln \hat{\phi}_2 = \ln \hat{\phi}_2^\infty + K_2x_2 \quad (17)$$

where $\hat{\phi}_2^\infty$ is the infinite dilution fugacity coefficient. Solubility data were first used to calculate the fugacity coefficient at saturation, using the expression[30]

$$x_{2,S} = \frac{P_2^0}{P\hat{\phi}_2}\exp\left(\frac{(P - P_2^0)V_2^0}{RT}\right) \quad (18)$$

where $x_{2,S}$ is the molar fraction at saturation of the solute, and P_2^0 and V_2^0 are the saturation vapor pressure and molar volume of the solid solute, respectively. The values of P_2^0 and V_2^0 for naphthalene and pyrene were taken from ref 31. The equation for the fugacity coefficient based on the Soave−Redlich−Kwong equation of state was then employed to calculate the binary interaction parameter k_{12}, which appears in one of the mixing rules (see Appendix 2).

Further, the fugacity coefficient was calculated as a function of x_2, and the value of K_2 was obtained from the slope of the curve $\ln \hat{\phi}_2$ against x_2 (for additional details see Appendix 2). The calculated values of K_2 for the CO_2 + naphthalene and CO_2 + pyrene systems are plotted in Figure 1. Similar calculations were carried out using the Peng−Robinson (PR) EOS.[33] Good agreement was found between the values of K_2 obtained from the two equations of state.
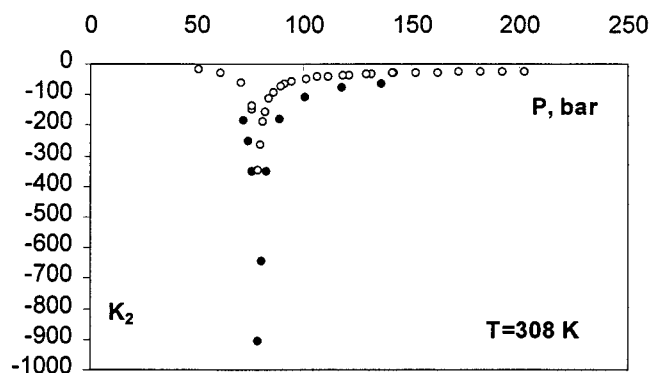

Figure 1. K_2 values calculated with the SRK EOS; (○) CO_2 + naphthalene, (●) CO_2 + pyrene.

TABLE 1: The Correlation Volume and Excess Number of Molecules around a Solute Molecule in Mixtures of Naphthalene and CO_2 Based on BN Excesses

P, bar	$V_{cor}^{(2)}$, cm^3	$r_{cor}^{(2)}$, Å	$n_1 = c_1V_{cor}^{(2)}$, number of bulk molecules	Δn_{12}, molecules
System CO_2 + Naphthalene, $x_2 = 3.5 \times 10^{-5}$, T = 308 K				
141.1	760	6.7	13.9	0.4
129.6	1930	9.1	34.5	1.0
106.8	2020	9.3	34.5	3.6
94.7	6910	14.0	111.3	6.9
89.2	10590	16.1	157.8	9.5
83.9	18000	19.3	250.7	45.0
81.9	34090	23.8	397.8	75.0
79.9	33860	23.8	329.0	115.1
78.7	19510	19.8	169.0	70.2
75.8	8790	15.2	58.6	24.6
System CO_2 + Pyrene, $x_2 = 3.0 \times 10^{-8}$, T = 308 K				
136.3	17	19	0.3	0.7
118.1	700	6.5	12.3	2.2
100.7	1950	9.2	32.8	6.4
89.0	5390	12.9	81.4	14.0
82.9	14180	17.8	181.4	69.5
80.4	16320	18.6	148.4	104.5
78.7	10020	15.8	77.4	61.1
75.6	4800	12.4	30.0	23.1
73.9	4040	11.7	23.0	18.2
71.6	4430	12.1	23.7	14.2

The correlation volume ($V_{cor}^{(2)}$) and correlation radius ($r_{cor}^{(2)} = (3V_{cor}^{(2)}/4\pi)^{1/3}$) were calculated using eqs 13−15. The results are summarized in Tables 1−3.

The calculations based on eqs 13 and 14 indicated that in the dilute region (molar fraction of solute between 10^{-4} and 10^{-8}), the second term in the numerator ($c_2(RTk_{T,1}^0 + V_1^0 - 2V_2^\infty - K_2V_1^0)$ in eq 13 and $c_2(2V_2^0 - 2V_2^\infty - K_2V_1^0)$ in eq 14) is negligible and that the relations valid at infinite dilution (eqs 10c and 11c) can be used. Equation 13, whose numerator at infinite dilution becomes $c_1^0(RTk_{T,1}^0 - V_2^\infty)$, was used to calculate the solvent cluster size around a solute molecule at infinite dilution.[21] The cluster size for a solution of naphthalene in SCF CO_2 at 308.39 K was thus found to vary between 20 and 100 molecules of CO_2 per molecule of solute in the pressure range 75−90 bars. The terms $RTk_{T,1}^0$ and V_2^∞ provided comparable contributions to the cluster size, because not too far from the critical point of the solvent, the compressibility $k_{T,1}^0$ has large positive values and the partial molar volume at infinite dilution of the solute is negative and large in absolute value. The above values are in agreement with the solvent cluster sizes around a solute molecule evaluated from the experimental partial molar volume of the solute at infinite dilution.[9] However, eq 10c and the equation for $\lim_{x_2\to 0} \Delta n_{11}$ ($\lim_{x_2\to 0} \Delta n_{11} = \lim_{x_2\to 0} c_1G_{11} = c_1^0(RTk_{T,1}^0 - V_1^0)$) should be valid not only for SCR mixtures, but also for

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TABLE 2: The Correlation Volume and Excess Number of Molecules around a Solute Molecule in Mixtures of Naphthalene and CO_2 based on ML Excesses
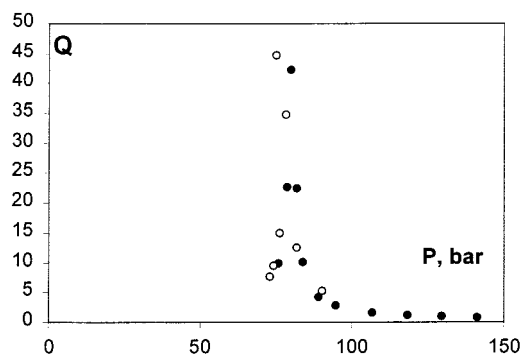
P, bar	$V_{cor}^{(2)}$, cm^3	$r_{cor}^{(2)}$, Å	$n_1 = c_1 V_{cor}^{(2)}$, number of bulk molecules	$\Delta n'_{12}$, molecules
System CO_2 + Naphthalene, $x_2 = 3.5 \times 10^{-5}$, T = 308 K			
141.1	2700	10.2	49.2	1.6
129.6	3940	11.6	70.5	2.0
106.8	2140	9.5	36.6	3.8
94.7	5800	13.2	93.4	5.8
89.2	7620	14.4	113.5	6.9
83.9	14540	17.9	202.6	36.4
81.9	24450	21.3	285.3	53.8
79.9	21750	20.5	211.3	73.9
78.7	13500	17.5	116.9	48.6
75.8	5500	13.0	36.7	15.4
System CO_2 + Pyrene, $x_2 = 3.0 \times 10^{-8}$, T = 308 K			
136.3	45	2.6	0.8	1.8
118.1	910	7.1	16.2	2.8
100.7	1830	9.0	30.8	6.0
89.0	4120	11.8	62.3	10.7
82.9	11000	16.4	140.8	53.9
80.4	10810	16.2	98.2	69.2
78.7	6980	14.0	53.9	42.6
75.6	3120	10.7	19.5	15.0
73.9	2660	10.2	15.1	12.0
71.6	2850	10.4	15.2	9.2

TABLE 3: The Correlation Volume and Excess Number of Molecules around a Solute Molecule in Mixtures of Naphthalene and CO_2 based on SR excesses

P, bar	$V_{cor}^{(2)}$, cm^3	$r_{cor}^{(2)}$, Å	$n_1 = c_1 V_{cor}^{(2)}$, number of bulk molecules	$\Delta n''_{12}$, molecules
System CO_2 + Naphthalene, $x_2 = 3.5 \times 10^{-5}$, T = 308 K			
141.1	1.0	0.7	0.02	0
129.6	2.2	1.0	0.04	0
106.8	2.4	1.0	0.04	0
94.7	9.9	1.6	0.2	0
89.2	17.4	1.9	0.3	0.02
83.9	56.5	2.9	0.8	0.2
81.9	131.6	3.7	1.5	0.3
79.9	199.3	4.3	1.9	0.7
78.7	162.6	4.0	1.4	0.6
75.8	26.8	2.2	0.2	0.1
System CO_2 + Pyrene, $x_2 = 3.0 \times 10^{-8}$, T = 308 K			
136.3	4×10^{-5}	0.02	7×10^{-7}	13×10^{-8}
118.1	0.001	0.08	2×10^{-5}	10^{-5}
100.7	0.005	0.12	9×10^{-5}	10^{-5}
89.0	0.02	0.20	0.0003	0.0001
82.9	0.1	0.4	0.001	0.001
80.4	0.2	0.4	0.002	0.001
78.7	0.2	0.4	0.001	0.002
75.6	0.03	0.2	0.0002	0.0002
73.9	0.02	0.2	0.0001	0.0001
71.6	0.02	0.2	9×10^{-5}	10^{-5}

Figure 2. $Q = \langle (\Delta N_1)^2 \rangle / \langle N_1 \rangle$ in SCF CO_2 at 308 K: (○) experimental data[13] ($T = 307.1-307.2$ K), (●) calculated with eq 19.

critical point at infinite dilution. While the ML excesses provide reasonable values, they do not satisfy the volume conservation condition. The SR excesses do satisfy the volume conservation condition and lead at infinite dilution to zero excess solvent molecules aggregated around individual solute molecules. The latter result stimulated us to look for a different interpretation of the density enhancement. The comparison between the experimental results regarding the near critical density enhancement in the pure SCF and the density enhancement caused by the addition of extremely small amounts of solute appears to show that the former constitute the main effect. Details are provided in the next section.

Density Enhancement as a Result of the Near Critical Fluctuations in the Pure SCF

A number of experimental results are available regarding the quantity $Q = \langle (\Delta N_1)^2 \rangle / \langle N_1 \rangle$ (which involves the average of the square of the fluctuation ΔN_1 of the number of molecules N_1 and the average of the number of molecules N_1) and the correlation length in pure SCF.[11-15] This information was obtained via the small-angle X-ray scattering (SAXS) and refs 13−14 provide details about the pressure and temperature dependencies of $Q = \langle (\Delta N_1)^2 \rangle / \langle N_1 \rangle$ and correlation length in pure SCF CO_2. It is worth noting that $\langle (\Delta N_1)^2 \rangle / \langle N_1 \rangle$ can be also calculated using the expression[34]

$$\frac{\langle (\Delta N_1)^2 \rangle}{\langle N_1 \rangle} = c_1^0 RT k_{T,1}^0 \qquad (19)$$

and Figure 2 shows that there is agreement between the calculated and experimental values of $Q = \langle (\Delta N_1)^2 \rangle / \langle N_1 \rangle$.

Let us compare the density enhancements generated by the near critical density fluctuations in a pure solvent to those observed when small amounts of solute were added to the solvent. The density enhancements in pure CO_2 and pure CHF_3 were calculated from the experimental data provided by refs 13−15 regarding the correlation lengths and the fluctuations of the number of molecules given by $Q = \langle (\Delta N_1)^2 \rangle / \langle N_1 \rangle$. The calculations are compared with the experimental results obtained for CO_2 + naphthalene and CO_2 + pyrene[24] in Figure 3 and for CHF_3 + pyrene[24] in Figure 4. Figures 3 and 4 clearly reveal that the density enhancements in these mixtures are almost identical to those in the pure solvent. We are therefore tempted to conclude that the density enhancement in dilute SCR mixtures is mainly caused by the near critical density fluctuations in the pure SCF. An explanation for the negative partial molar volume of the solute at infinite dilution, which differs from that which involves the aggregation of the solvent about the solute,[9] was provided by Economou and Donohue.[10] Because of the high
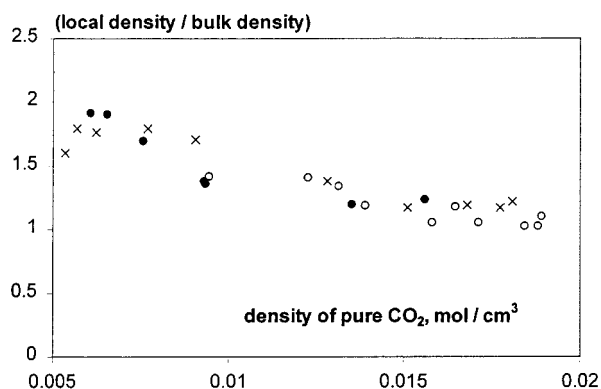
any binary mixture such as alcohol/water far from the critical point. In the latter cases $RT k_{T,1}^0$ is negligible compared to V_2^∞ (which is positive) and V_1^0. This means that at infinite dilution ($x_2 \to 0$) and far from the critical point, $\lim_{x_2 \to 0} c_1 G_{12}$ and $\lim_{x_2 \to 0} c_1 G_{11}$ for all "normal" binary mixtures are negative and hence that there are deficits of molecules 1 in the aggregates around both 1 and 2 molecules compared to the bulk numbers, regardless of the nature of the interactions between molecules.

The results listed in Tables 1 and 2 also indicate that the sizes of the solvent aggregates predicted from the BN and ML excesses are in agreement with those evaluated from the large negative partial molar volume of the solute at infinite dilution.[9] However, as already noted the BN excesses provide unreasonable results for the aggregate sizes in mixtures far from the

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Figure 3. Comparison between the experimental density enhancement in pure SCF CO_2 and density enhancement in the SCR mixtures CO_2 + naphthalene and CO_2 + pyrene: (●) calculated from experimental data[13,14] ($T = 307.1-307.2$ K) for pure CO_2, (○) experimental data[24] for the system CO_2 + naphthalene ($T = 308$ K and $x_2 = 3.5 \times 10^{-5}$), (×) experimental data[24] for the system CO_2 + pyrene ($T = 308$ K and $x_2 = 3.0 \times 10^{-8}$).
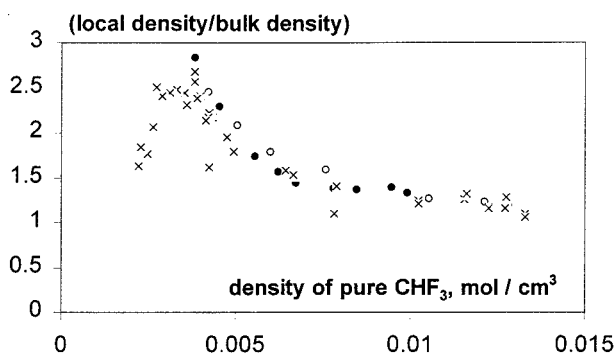

Figure 4. Comparison between the density enhancement in pure SCF CHF_3 and density enhancement in SCR mixtures CHF_3 + pyrene: (●) calculated from experimental data[15] ($T = 310.8-311.5$ K) for pure CHF_3, (○) experimental data[24] for the system CHF_3 + pyrene ($T = 303$ K and $x_2 = 5 \times 10^{-6}$), (×) experimental data[24] for the system CHF_3 + pyrene ($T = 303$ K and $x_2 = 3 \times 10^{-7}$). For this solvent (CHF_3) there are no data for densities lower than ≈ 0.004. However, the experimental data for pure SCF Ar indicate[35] a shape of the curve very similar to the experimental curves for the mixture CHF_3 + pyrene over the entire range of densities.

compressibility near the critical point of the solvent the addition of a small amount of solute causes a large decrease in the volume of the system.

Conclusion

One first demonstrates that in a dilute supercritical mixture the aggregation number of the solvent around individual solute molecules tends to zero at infinite solute dilution. These theoretical considerations suggested that it is necessary to revise the conventional explanation, which considers that the clustering of solvent molecules around individual solute molecules is responsible for the density augmentation observed when small amounts of solute were added to a solvent near the critical point of the latter. By comparing the density fluctuations determined by small-angle X-ray scattering for pure supercritical solvents and the density augmentation determined experimentally for dilute supercritical mixtures we noted that they almost coincide. In conclusion, it is likely that the near critical fluctuations are mainly responsible for the local density augmentation in dilute supercritical mixtures.

Appendixes

Appendix 1. (1) The KBIs for ideal systems are given by the expressions[18]

$$G_{12}^{id} = RTk_T^{id} - \frac{V_1^0 V_2^0}{V^{id}} \tag{A1-1}$$

$$G_{11}^{id} = G_{12}^{id} + V_2^0 - V_1^0 \tag{A1-2}$$

$$G_{22}^{id} = G_{12}^{id} - (V_2^0 - V_1^0) \tag{A1-3}$$

where k_T^{id} and V^{id} are the isothermal compressibility and the molar volume of an ideal mixture and V_i^0 is the molar volume of the pure component i.

(2) The KBIs at infinite dilution have the forms[17]

$$\lim_{x_i \to 0} G_{12} = RTk_{T,j}^0 - V_i^\infty \tag{A1-4}$$

$$\lim_{x_i \to 1} G_{12} = RTk_{T,i}^0 - V_j^\infty \tag{A1-5}$$

$$\lim_{x_i \to 0} G_{ii} = RTk_{T,j}^0 + V_j^0 - 2V_i^\infty - V_j^0 \left(\frac{\partial \ln \gamma_i}{\partial x_i}\right)_{P,T,x_i=0} \tag{A1-6}$$

$$\lim_{x_i \to 1} G_{ii} = RTk_{T,i}^0 - V_i^0 \tag{A1-7}$$

where V_i^∞ is the partial molar volume of component i at infinite dilution, $k_{T,i}^0$ is the isothermal compressibility of the pure component i.

(3) The expressions for G_{ij}^V are[19]

$$G_{12}^V = G_{21}^V = RTk_T - \frac{V_1 V_2}{V} \tag{A1-8}$$

$$G_{ii}^V = G_{12}^V + V_j - V_i \quad i \neq j \tag{A1-9}$$

Appendix 2. The Soave−Redlich−Kwong (SRK) EOS[32]

$$P = \frac{RT}{V - b} - \frac{a(T)}{V(V + b)} \tag{A2-1}$$

was selected to calculate the fugacity coefficient. In eq A2-1, V is the molar volume of the mixture and a and b are the EOS mixture parameters. The latter quantities are provided by the usual mixing rules:

$$a = x_1^2 a_1 + x_2^2 a_2 + 2x_1 x_2 (a_1 a_2)^{0.5}(1 - k_{12}) \tag{A2-2}$$

and

$$b = x_1 b_1 + x_2 b_2 \tag{A2-3}$$

where a_i, b_i are the EOS parameters for the pure component i, and k_{12} is the binary interaction parameter, which was determined by fitting the experimental solubility data.

For the fugacity coefficient of the solute $\hat{\phi}_2$ the following expressions was used:

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$$RT \ln \hat{\phi}_2 = \frac{b_2}{b}(Z - 1) - \ln(Z - B) +$$

$$\frac{A}{B}\left(\frac{2(x_2 a_2 + x_1(a_1 a_2)^{0.5}(1 - k_{12}))}{a} - \frac{b_2}{b}\right) \times \ln\left(\frac{Z}{Z + B}\right) \quad \text{(A2-4)}$$

where $A = aP/(RT)^2$, $B = bP/RT$, and Z is the compressibility factor.

By fitting the experimental solubility data with the help of eqs 18 and A2-4, the binary interaction parameters k_{12} were determined (at 308 K, $k_{12} = 0.09803$ for CO_2 + naphthalene and $k_{12} = 0.07619$ for CO_2 + pyrene). These values of k_{12} were used to calculate K_2 at different pressures using eqs 17 and A2-4.

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